# SUPPORTING INFORMATION

## A DFT Study of the Solvent Effects on Systematically Substituted Dihydroazulene/Vinylheptafulvene Systems

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# Contents

# 1 Introduction

The following results support the article: *"A DFT Study of the Solvent Effects on Systematically Substituted Dihydroazulene/Vinylheptafulvene Systems: Improving the Capability of Molecular Energy Storage"*. It includes a functional and basis set investigation, extensional martial for the energy storage capacities, the activation energies for the thermal back-reaction and the UV-Vis spectra as well as information of the Gibbs free energies for all the investigated structures.

The results of the energy storage capacities have superscripts describing the utilized DHA and VHF structures:

- The monocyano structures:

  a: anti-DHA, b: syn-DHA, i: s-*trans*-*E*-VHF, j: s-*trans*-*Z*-VHF, k: s-*cis*-*E*-VHF, l: s-*cis*-*Z*-VHF.

- The dicyano structures:

  i: s-*trans*-VHF, k: s-*cis*-VHF.

# 2 Functional and Basis Set Investigation

Different functionals were investigated using Gaussian 09[1] in order to examine the effects of dispersion corrected functionals. Furthermore, different basis sets were investigated for comparison of computational cost and accuracy.

The investigated functionals were CAM-B3LYP[2] and PBE0[3,4] both with and without the D3 version of Grimme's dispersion with Becke-Johnson damping[5,6] and the original D3 damping function. As well as the functional M06-2X[7] with and without the D3 version of Grimme's dispersion with the original D3 damping function. All in conjunction with the 6-311+G(d) basis set[8–10].

The investigated basis sets were from the Pople series[8–10] as well as a correlation consistent basis set by Dunning[11]. All in conjunction with the Minnesota functional M06-2X.

**Table 1: A comparison of storage energies and thermal back-reaction barriers for different functionals.**

| **Storage Energies - Monocyano $NO_2$ on position 4** | | | | |
|---|---|---|---|---|
| | **Vacuum** | **Cyclohexane** | **Dichloromethane** | **Acetonitrile** |
| CAM-B3LYP | $65.89^{bk}$ | $67.49^{bk}$ | $68.45^{bl}$ | $68.41^{bl}$ |
| CAM-B3LYP-D3 | $61.48^{abk}$ | $66.31^{bk}$ | $67.32^{bk}$ | $67.14^{bj}$ |
| CAM-B3LYP-D3BJ | $64.03^{bk}$ | $65.42^{bk}$ | $66.80^{bj}$ | $66.52^{bj}$ |
| M06-2X | $65.43^{bk}$ | $67.04^{ak}$ | $69.09^{aj}$ | $69.08^{bj}$ |
| M06-2X-D3 | $65.20^{bk}$ | $66.80^{ak}$ | $68.69^{aj}$ | $68.26^{bi}$ |
| PBE0 | $78.86^{bk}$ | $79.83^{bk}$ | $79.17^{bi}$ | $79.79^{bj}$ |
| PBE0-D3 | $77.28^{bk}$ | $77.44^{bj}$ | $76.89^{bj}$ | $77.54^{bj}$ |
| PBE0-D3BJ | $77.91^{bk}$ | $78.51^{bj}$ | $77.16^{bj}$ | $77.19^{bj}$ |
| **Thermal Back-Reation Barrier - Monocyano $NO_2$ on position 4** | | | | |
| CAM-B3LYP | 140.82 | 138.66 | 123.39 | 124.13 |
| CAM-B3LYP-D3 | 142.11 | 140.34 | 136.31 | 122.36 |
| CAM-B3LYP-D3BJ | 141.27 | 139.41 | 134.06 | 131.76 |
| M06-2X | 140.77 | 137.87 | 135.40 | 134.90 |
| M06-2X-D3 | 140.56 | 137.78 | 135.33 | 134.70 |
| PBE0 | 110.60 | 108.53 | 95.45 | 95.57 |
| PBE0-D3 | 111.97 | 110.08 | 106.29 | 104.51 |
| PBE0-D3BJ | 110.52 | 108.45 | 104.64 | 102.98 |

The functional investigation showed that adding a dispersion correction to the M06-2X functional had almost no effect. This is due to the incorporation of dispersion corrections in the M06-2X functional itself. However, the most stable VHF structure changed from s-*trans*-*Z*-VHF to s-*trans*-*E*-VHF in acetonitrile when adding Grimme's dispersion correction.

For the other functionals, the dispersion corrections changed the results with about 2 kJ/mol in average and caused a few variations to the most stable structures. Only significant changes were seen in the TBR barrier of the PBE0 functional for dichloromethane and acetonitrile.

The results also showed some correlation between the results of the M06-2X derivations and the CAM-B3LYP derivations. However, the most stable structures were not identical. Furthermore, the PBE0 derivations were compared to the other functionals, more than 10 kJ/mol higher for the energy storage capacities and more than 30 kJ/mol for the TBR barriers.

**Table 2: A comparison of storage energies and thermal back-reaction barriers for different basis sets in vacuum.**

| **Storage Energies - Monocyano $NO_2$ on position 4** | | | | | |
|---|---|---|---|---|---|
| | 6-31+G* | 6-311+G* | 6-311++G* | 6-311++G** | cc-pVTZ |
| M06-2X | 66.65[bk] | 65.43[bk] | 65.71[bk] | 65.71[bk] | 62.26[bk] |
| **Thermal Back-Reation Barrier - Monocyano $NO_2$ on position 4** | | | | | |
| M06-2X | 139.72 | 140.77 | 140.81 | 140.80 | 142.31 |

The basis set investigation showed that the energy storage capacity was slightly decreased when using a larger basis set within the Pople series. On the other hand, the cc-pVTZ result showed a fairly lower energy storage of 3.45 kJ/mol compared to the 6-311++G(d,p) basis set. However, the most stable structures were not changes. The TBR barriers were slightly increased when using a larger basis set within the Pople series and the cc-pVTZ result was only 1.51 kJ/mol higher than for the 6-311++G(d,p) basis set.

# 3 Parent system properties

**Table 3: The storage energy capacities and thermal back-reaction barriers for the parent system in different solvents.**

| | **Parent Monocyano System** | | | **Parent Dicyano System** | | |
|---|---|---|---|---|---|---|
| **Storage Energies** | CAM-B3LYP | M06-2X | PBE0 | CAM-B3LYP | M06-2X | PBE0 |
| Vacuum | 52.24[ai] | 57.70[ai] | 58.63[ai] | 15.87[i] | 27.67[i] | 17.12[i] |
| Cyclohexane | 52.07[ai] | 57.19[ai] | 77.59[ai] | 10.39[i] | 22.68[i] | 10.55[i] |
| Acetonitrile | 52.45[ai] | 58.45[ai] | 57.19[ai] | -0.04[i] | 15.72[i] | -0.75[i] |
| **TBR Barrier** | CAM-B3LYP | M06-2X | PBE0 | CAM-B3LYP | M06-2X | PBE0 |
| Vacuum | 136.13 | 133.02 | 112.10 | 107.86 | 106.13 | 91.82 |
| Cyclohexane | 134.22 | 128.59 | 110.86 | 100.19 | 98.99 | 87.29 |
| Acetonitrile | 131.67 | 128.84 | 109.72 | 91.77 | 90.89 | 82.34 |

# 4 Thermochemical Properties

This section includes energy storage capacities and activation energies of the TBR.

## 4.1 Storage Energies

**Table 4: The $NH_2$ monocyano structures with energy storage capacities in units of kJ/mol. The storage capacities of the parent monocyano system in vacuum[12]; CAM-B3LYP: 52.24kJ/mol, M06-2X: 57.70kJ/mol, PBE0: 58.63kJ/mol.**

| **Vacuum** | | | | **Dichloromethane** | | | |
|---|---|---|---|---|---|---|---|
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | $25.96^{aj}$ | $35.60^{aj}$ | $29.80^{aj}$ | 1 | $25.63^{ai}$ | $34.94^{ai}$ | $28.79^{ai}$ |
| 3 | $70.46^{bk}$ | $70.27^{bj}$ | $79.76^{bj}$ | 3 | $66.33^{bl}$ | $66.83^{bi}$ | $79.35^{bl}$ |
| 4 | $35.92^{bi}$ | $35.10^{ai}$ | $39.57^{bi}$ | 4 | $39.80^{bi}$ | $38.63^{bi}$ | $41.02^{bi}$ |
| 5 | $50.01^{bi}$ | $53.82^{ai}$ | $54.73^{bi}$ | 5 | $47.80^{bi}$ | $50.33^{ai}$ | $50.07^{bi}$ |
| 6 | $45.20^{bi}$ | $49.90^{bi}$ | $50.08^{bi}$ | 6 | $42.60^{bi}$ | $48.89^{bi}$ | $43.99^{bi}$ |
| 7 | $39.82^{bi}$ | $46.16^{ai}$ | $42.10^{bi}$ | 7 | $35.75^{bi}$ | $41.02^{bi}$ | $32.35^{bi}$ |
| 8 | $47.60^{bi}$ | $56.50^{bi}$ | $54.74^{bi}$ | 8 | $43.21^{bi}$ | $48.56^{bi}$ | $49.71^{bi}$ |
| 9 | $47.93^{bi}$ | $50.13^{bi}$ | $53.25^{bi}$ | 9 | $48.03^{bi}$ | $51.74^{bj}$ | $53.15^{bi}$ |
| 10 | $51.46^{bi}$ | $54.43^{ai}$ | $57.83^{bi}$ | 10 | $51.53^{bi}$ | $52.85^{ai}$ | $55.72^{bi}$ |
| 11 | $52.91^{bi}$ | $57.61^{bi}$ | $60.22^{bi}$ | 11 | $51.07^{bi}$ | $56.16^{bi}$ | $59.03^{bi}$ |
| **Cyclohexane** | | | | **Ethanol** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | $26.11^{ak}$ | $35.30^{aj}$ | $29.31^{aj}$ | 1 | $25.27^{ai}$ | $34.48^{ai}$ | $28.40^{ai}$ |
| 3 | $69.85^{bk}$ | $69.49^{bi}$ | $79.86^{bj}$ | 3 | $66.12^{bl}$ | $66.74^{bi}$ | $78.43^{bl}$ |
| 4 | $37.03^{bi}$ | $36.51^{bi}$ | $39.95^{bi}$ | 4 | $40.36^{bi}$ | $40.08^{bi}$ | $42.04^{bi}$ |
| 5 | $48.97^{bi}$ | $52.14^{ai}$ | $53.02^{bi}$ | 5 | $47.54^{bi}$ | $49.13^{ai}$ | $49.34^{bi}$ |
| 6 | $43.54^{bi}$ | $49.20^{bi}$ | $47.08^{bi}$ | 6 | $42.32^{bi}$ | $49.00^{bi}$ | $42.64^{bi}$ |
| 7 | $37.84^{bi}$ | $43.06^{ai}$ | $38.35^{bi}$ | 7 | $35.32^{bi}$ | $41.14^{bi}$ | $33.15^{bi}$ |
| 8 | $43.39^{bi}$ | $54.22^{bi}$ | $51.89^{bi}$ | 8 | $42.89^{bi}$ | $49.36^{bi}$ | $49.87^{bi}$ |
| 9 | $47.59^{bi}$ | $50.98^{bi}$ | $52.96^{bi}$ | 9 | $48.16^{bj}$ | $51.05^{bj}$ | $52.75^{bj}$ |
| 10 | $50.61^{bi}$ | $53.59^{ai}$ | $56.74^{bi}$ | 10 | $52.02^{bi}$ | $53.72^{bi}$ | $55.79^{bi}$ |
| 11 | $51.70^{bi}$ | $56.08^{bi}$ | $59.24^{bi}$ | 11 | $51.58^{bi}$ | $56.37^{bi}$ | $59.04^{bi}$ |
| **Toluene** | | | | **Acetonitrile** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | $26.07^{ak}$ | $35.36^{aj}$ | $29.35^{aj}$ | 1 | $25.23^{ai}$ | $34.38^{ai}$ | $28.34^{ai}$ |
| 3 | $69.93^{bk}$ | $69.09^{bi}$ | $80.13^{bj}$ | 3 | $65.60^{bl}$ | $66.41^{bk}$ | $78.31^{bl}$ |
| 4 | $37.46^{bi}$ | $36.53^{bi}$ | $40.01^{bi}$ | 4 | $40.48^{bi}$ | $40.31^{bi}$ | $42.25^{bi}$ |
| 5 | $48.69^{bi}$ | $51.95^{ai}$ | $52.65^{bi}$ | 5 | $47.50^{bi}$ | $48.92^{ai}$ | $49.24^{bi}$ |
| 6 | $43.32^{bi}$ | $49.12^{bi}$ | $46.55^{bi}$ | 6 | $42.25^{bi}$ | $49.04^{bi}$ | $42.14^{bi}$ |
| 7 | $37.56^{bi}$ | $42.44^{ai}$ | $37.74^{bi}$ | 7 | $35.17^{bi}$ | $41.21^{bi}$ | $32.84^{bi}$ |
| 8 | $44.64^{bi}$ | $52.69^{bi}$ | $51.38^{bi}$ | 8 | $42.83^{bi}$ | $49.67^{bi}$ | $49.96^{bi}$ |
| 9 | $47.63^{bi}$ | $51.19^{bi}$ | $52.98^{bi}$ | 9 | $48.06^{bj}$ | $50.88^{bj}$ | $52.52^{bj}$ |
| 10 | $50.57^{bi}$ | $53.50^{ai}$ | $56.66^{bi}$ | 10 | $52.10^{bi}$ | $53.91^{bi}$ | $55.85^{bi}$ |
| 11 | $51.46^{bi}$ | $55.93^{bi}$ | $59.21^{bi}$ | 11 | $51.71^{bi}$ | $56.38^{bi}$ | $59.01^{bi}$ |

**Table 5: The $NH_2$ dicyano structures with energy storage capacities in units of kJ/mol. The storage capacities of the parent dicyano system in vacuum[12]; CAM-B3LYP: 15.87kJ/mol, M06-2X: 27.67kJ/mol, PBE0: 17.12kJ/mol.**

**Vacuum**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 53.80$^k$ | 58.53$^k$ | 53.14$^i$ |
| 4 | 3.80$^i$ | 11.56$^i$ | 0.90$^i$ |
| 5 | 8.72$^i$ | 20.14$^i$ | 8.81$^i$ |
| 6 | 7.64$^i$ | 20.81$^i$ | 7.42$^i$ |
| 7 | -0.29$^i$ | 11.96$^i$ | -4.27$^i$ |
| 8 | -0.84$^i$ | 16.66$^i$ | 5.19$^i$ |
| 9 | 5.41$^i$ | 14.41$^i$ | 4.37$^i$ |
| 10 | 14.11$^i$ | 24.10$^i$ | 15.29$^i$ |
| 11 | 14.98$^i$ | 25.52$^i$ | 17.66$^i$ |

**Dichloromethane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 50.72$^k$ | 55.16$^k$ | 43.83$^i$ |
| 4 | -8.06$^i$ | 4.25$^i$ | -14.46$^i$ |
| 5 | -16.82$^i$ | -3.02$^i$ | -17.47$^i$ |
| 6 | -15.44$^i$ | -0.09$^i$ | -17.21$^i$ |
| 7 | -24.43$^i$ | -10.45$^i$ | -30.04$^i$ |
| 8 | -30.03$^i$ | -6.86$^i$ | -23.96$^i$ |
| 9 | -6.06$^i$ | 7.76$^i$ | -9.00$^i$ |
| 10 | 1.38$^i$ | 14.26$^i$ | 1.13$^i$ |
| 11 | 1.43$^i$ | 14.86$^i$ | 2.81$^i$ |

**Cyclohexane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 53.63$^i$ | 57.00$^k$ | 49.55$^i$ |
| 4 | -0.33$^i$ | 9.48$^i$ | -4.86$^i$ |
| 5 | -2.83$^i$ | 11.92$^i$ | -3.29$^i$ |
| 6 | -3.09$^i$ | 12.74$^i$ | -4.01$^i$ |
| 7 | -13.59$^i$ | 3.09$^i$ | -16.77$^i$ |
| 8 | -13.62$^i$ | 4.55$^i$ | -7.15$^i$ |
| 9 | -0.04$^i$ | 12.74$^i$ | -0.88$^i$ |
| 10 | 8.23$^i$ | 20.14$^i$ | 9.18$^i$ |
| 11 | 8.92$^i$ | 20.72$^i$ | 10.94$^i$ |

**Ethanol**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 49.07$^k$ | 54.33$^k$ | 42.35$^i$ |
| 4 | -12.91$^i$ | 2.80$^i$ | -18.89$^i$ |
| 5 | -19.95$^i$ | -5.24$^i$ | -20.80$^i$ |
| 6 | -18.90$^i$ | -3.00$^i$ | -21.04$^i$ |
| 7 | -29.03$^i$ | -14.31$^i$ | -34.27$^i$ |
| 8 | -35.26$^i$ | -11.41$^i$ | -28.68$^i$ |
| 9 | -7.22$^i$ | 6.89$^i$ | -11.20$^i$ |
| 10 | -0.64$^i$ | 11.89$^i$ | -0.81$^i$ |
| 11 | -0.15$^i$ | 13.46$^i$ | 0.69$^i$ |

**Toluene**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 53.61$^i$ | 56.78$^k$ | 48.79$^i$ |
| 4 | -1.32$^i$ | 8.81$^i$ | -6.01$^i$ |
| 5 | -5.32$^i$ | 9.24$^i$ | -6.04$^i$ |
| 6 | -5.42$^i$ | 9.85$^i$ | -5.95$^i$ |
| 7 | -13.81$^i$ | 0.79$^i$ | -18.54$^i$ |
| 8 | -17.50$^i$ | 3.79$^i$ | -10.10$^i$ |
| 9 | -0.87$^i$ | 11.96$^i$ | -1.70$^i$ |
| 10 | 7.05$^i$ | 19.34$^i$ | 7.94$^i$ |
| 11 | 7.69$^i$ | 19.77$^i$ | 9.50$^i$ |

**Acetonitrile**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 48.77$^k$ | 54.14$^k$ | 42.03$^i$ |
| 4 | -13.74$^i$ | 2.55$^i$ | -19.44$^i$ |
| 5 | -20.54$^i$ | -5.86$^i$ | -21.47$^i$ |
| 6 | -19.60$^i$ | -3.62$^i$ | -21.73$^i$ |
| 7 | -30.00$^i$ | -15.17$^i$ | -35.11$^i$ |
| 8 | -36.17$^i$ | -12.28$^i$ | -29.68$^i$ |
| 9 | -7.33$^i$ | 6.19$^i$ | -11.66$^i$ |
| 10 | -1.05$^i$ | 11.43$^i$ | -1.23$^i$ |
| 11 | -0.43$^i$ | 13.21$^i$ | 0.22$^i$ |

**Table 6: The $NO_2$ monocyano structures with energy storage capacities in units of kJ/mol. The storage capacities of the parent monocyano system in vacuum[12]; CAM-B3LYP: 52.24kJ/mol, M06-2X: 57.70kJ/mol, PBE0: 58.63kJ/mol.**

**Vacuum**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $48.60^{aij}$ | $61.42^{ai}$ | $50.14^{aij}$ |
| 3 | $42.75^{bl}$ | $44.08^{bl}$ | $46.51^{bl}$ |
| 4 | $65.89^{bk}$ | $65.43^{bk}$ | $78.86^{bk}$ |
| 5 | $59.90^{bi}$ | $61.13^{ai}$ | $65.79^{bi}$ |
| 6 | $59.48^{bi}$ | $65.24^{bi}$ | $67.92^{bi}$ |
| 7 | $51.75^{bi}$ | $55.76^{bi}$ | $58.66^{bi}$ |
| 8 | $44.67^{bi}$ | $45.05^{bi}$ | $55.03^{bi}$ |
| 9 | $54.17^{bl}$ | $52.77^{bj}$ | $58.64^{bi}$ |
| 10 | $52.76^{bi}$ | $54.64^{bi}$ | $58.18^{bi}$ |
| 11 | $52.64^{bi}$ | $58.40^{bi}$ | $58.84^{bi}$ |

**Dichloromethane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $25.46^{aij}$ | $43.17^{aj}$ | $25.43^{aj}$ |
| 3 | $32.99^{bl}$ | $38.37^{bl}$ | $36.01^{bl}$ |
| 4 | $68.45^{bl}$ | $69.09^{aj}$ | $79.17^{bi}$ |
| 5 | $64.72^{bi}$ | $65.97^{bi}$ | $69.53^{bi}$ |
| 6 | $64.61^{bi}$ | $70.37^{bi}$ | $71.62^{bi}$ |
| 7 | $53.56^{bi}$ | $62.74^{ai}$ | $61.54^{bi}$ |
| 8 | $45.33^{bi}$ | $51.08^{bk}$ | $55.75^{bi}$ |
| 9 | $49.77^{bi}$ | $49.39^{bj}$ | $52.84^{bi}$ |
| 10 | $50.98^{bi}$ | $55.38^{bi}$ | $57.06^{bi}$ |
| 11 | $52.83^{bi}$ | $58.72^{bi}$ | $59.79^{bi}$ |

**Cyclohexane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $39.81^{ai}$ | $55.05^{aj}$ | $40.53^{aj}$ |
| 3 | $39.02^{bl}$ | $41.55^{bl}$ | $42.62^{bl}$ |
| 4 | $67.49^{bk}$ | $67.04^{ak}$ | $79.83^{bk}$ |
| 5 | $62.01^{bi}$ | $62.97^{ai}$ | $66.48^{bi}$ |
| 6 | $61.51^{bi}$ | $67.01^{bi}$ | $68.44^{bi}$ |
| 7 | $52.49^{bi}$ | $56.35^{bi}$ | $59.57^{bi}$ |
| 8 | $44.65^{bi}$ | $47.78^{bi}$ | $55.48^{bi}$ |
| 9 | $52.23^{bl}$ | $52.62^{bi}$ | $56.45^{bi}$ |
| 10 | $51.24^{bi}$ | $54.95^{bi}$ | $56.98^{bi}$ |
| 11 | $52.42^{bi}$ | $58.28^{bi}$ | $58.10^{bi}$ |

**Ethanol**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $20.57^{aj}$ | $39.15^{aij}$ | $20.87^{ai}$ |
| 3 | $30.94^{bl}$ | $33.93^{bl}$ | $33.97^{bl}$ |
| 4 | $68.38^{bl}$ | $68.89^{bj}$ | $79.76^{bj}$ |
| 5 | $65.28^{bi}$ | $67.45^{bi}$ | $70.73^{bi}$ |
| 6 | $65.38^{bi}$ | $72.36^{bi}$ | $73.45^{bi}$ |
| 7 | $53.41^{bi}$ | $60.31^{bi}$ | $62.47^{bi}$ |
| 8 | $45.79^{bl}$ | $52.50^{bj}$ | $56.19^{bi}$ |
| 9 | $48.74^{bi}$ | $48.46^{bj}$ | $51.76^{bi}$ |
| 10 | $51.91^{bi}$ | $57.26^{bi}$ | $57.23^{bi}$ |
| 11 | $53.37^{bi}$ | $58.75^{bi}$ | $60.35^{bi}$ |

**Toluene**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $37.75^{ai}$ | $53.53^{ai}$ | $38.29^{aj}$ |
| 3 | $37.94^{bl}$ | $40.62^{bl}$ | $41.66^{bl}$ |
| 4 | $67.75^{bk}$ | $67.98^{ak}$ | $80.09^{bi}$ |
| 5 | $62.67^{bi}$ | $63.21^{ai}$ | $66.55^{bi}$ |
| 6 | $61.90^{bi}$ | $67.44^{bi}$ | $68.71^{bi}$ |
| 7 | $52.73^{bi}$ | $56.92^{bi}$ | $59.82^{bi}$ |
| 8 | $44.66^{bi}$ | $48.48^{bi}$ | $55.36^{bi}$ |
| 9 | $51.76^{bl}$ | $51.99^{bj}$ | $55.88^{bi}$ |
| 10 | $50.86^{bi}$ | $54.96^{bi}$ | $56.83^{bi}$ |
| 11 | $52.28^{bi}$ | $58.34^{bi}$ | $58.22^{bi}$ |

**Acetonitrile**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 1 | $19.54^{aij}$ | $38.43^{ai}$ | $19.98^{ai}$ |
| 3 | $30.48^{bl}$ | $33.74^{bl}$ | $33.62^{bl}$ |
| 4 | $68.41^{bl}$ | $69.08^{bj}$ | $79.79^{bj}$ |
| 5 | $65.45^{bi}$ | $67.72^{bi}$ | $70.93^{bi}$ |
| 6 | $65.54^{bi}$ | $72.71^{bi}$ | $73.83^{bi}$ |
| 7 | $53.49^{bi}$ | $59.99^{bi}$ | $62.96^{bi}$ |
| 8 | $45.92^{bi}$ | $55.68^{bj}$ | $56.27^{bi}$ |
| 9 | $48.55^{bi}$ | $48.18^{bj}$ | $51.53^{bj}$ |
| 10 | $51.66^{bi}$ | $58.04^{bi}$ | $57.02^{bi}$ |
| 11 | $53.47^{bi}$ | $58.90^{bi}$ | $60.45^{bi}$ |

**Table 7: The $NO_2$ dicyano structures with energy storage capacities in units of kJ/mol. The storage capacities of the parent dicyano system in vacuum[12]; CAM-B3LYP: 15.87kJ/mol, M06-2X: 27.67kJ/mol, PBE0: 17.12kJ/mol.**

**Vacuum**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 11.65$^k$ | 16.82$^k$ | 13.15$^k$ |
| 4 | 36.67$^i$ | 44.97$^i$ | 46.38$^i$ |
| 5 | 29.89$^i$ | 41.77$^i$ | 29.94$^i$ |
| 6 | 24.35$^i$ | 34.83$^i$ | 27.73$^i$ |
| 7 | 15.91$^i$ | 27.16$^i$ | 17.99$^i$ |
| 8 | -8.85$^i$ | 6.66$^i$ | -2.64$^i$ |
| 9 | 12.37$^i$ | 24.26$^i$ | 11.33$^i$ |
| 10 | 17.45$^i$ | 26.30$^i$ | 18.47$^i$ |
| 11 | 17.64$^i$ | 27.71$^i$ | 19.12$^i$ |

**Dichloromethane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | -4.04$^k$ | 4.49$^k$ | -4.18$^k$ |
| 4 | 26.30$^i$ | 39.18$^i$ | 36.99$^i$ |
| 5 | 20.67$^i$ | 34.37$^i$ | 22.14$^i$ |
| 6 | 17.56$^i$ | 30.79$^i$ | 21.33$^i$ |
| 7 | 9.20$^i$ | 21.33$^i$ | 12.27$^i$ |
| 8 | -13.17$^i$ | 5.36$^i$ | -7.34$^i$ |
| 9 | -2.51$^i$ | 7.80$^i$ | -6.67$^i$ |
| 10 | 3.66$^i$ | 15.12$^i$ | 3.30$^i$ |
| 11 | 5.11$^i$ | 19.50$^i$ | 4.19$^i$ |

**Cyclohexane**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 6.96$^k$ | 13.80$^k$ | 6.08$^k$ |
| 4 | 31.86$^i$ | 41.15$^i$ | 41.34$^i$ |
| 5 | 24.62$^i$ | 38.27$^i$ | 27.15$^i$ |
| 6 | 21.49$^i$ | 32.80$^i$ | 24.67$^i$ |
| 7 | 13.03$^i$ | 24.00$^i$ | 14.63$^i$ |
| 8 | -11.46$^i$ | 5.76$^i$ | -4.89$^i$ |
| 9 | 6.26$^i$ | 16.84$^i$ | 3.91$^i$ |
| 10 | 11.94$^i$ | 20.51$^i$ | 12.49$^i$ |
| 11 | 12.11$^i$ | 24.45$^i$ | 12.66$^i$ |

**Ethanol**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | -6.47$^k$ | 1.91$^k$ | -6.55$^k$ |
| 4 | 26.93$^i$ | 37.98$^i$ | 34.21$^i$ |
| 5 | 20.38$^i$ | 33.44$^i$ | 20.95$^i$ |
| 6 | 16.89$^i$ | 29.92$^i$ | 20.23$^i$ |
| 7 | 8.79$^i$ | 20.76$^i$ | 11.59$^i$ |
| 8 | -13.35$^i$ | 5.01$^i$ | -8.03$^i$ |
| 9 | -5.37$^i$ | 5.02$^i$ | -9.79$^i$ |
| 10 | 1.86$^i$ | 13.56$^i$ | 0.44$^i$ |
| 11 | 2.67$^i$ | 17.41$^i$ | 1.97$^i$ |

**Toluene**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | 5.85$^k$ | 12.54$^k$ | 4.51$^k$ |
| 4 | 31.38$^i$ | 40.62$^i$ | 41.47$^i$ |
| 5 | 24.11$^i$ | 37.35$^i$ | 26.46$^i$ |
| 6 | 20.79$^i$ | 32.51$^i$ | 24.15$^i$ |
| 7 | 11.84$^i$ | 23.51$^i$ | 14.09$^i$ |
| 8 | -11.97$^i$ | 6.13$^i$ | -5.29$^i$ |
| 9 | 4.94$^i$ | 15.66$^i$ | 2.12$^i$ |
| 10 | 10.92$^i$ | 20.01$^i$ | 11.36$^i$ |
| 11 | 11.25$^i$ | 23.92$^i$ | 11.37$^i$ |

**Acetonitrile**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| 3 | -6.68$^k$ | 1.49$^k$ | -7.18$^k$ |
| 4 | 26.59$^i$ | 37.79$^i$ | 33.66$^i$ |
| 5 | 20.32$^i$ | 33.29$^i$ | 20.73$^i$ |
| 6 | 16.82$^i$ | 29.75$^i$ | 19.99$^i$ |
| 7 | 8.77$^i$ | 20.64$^i$ | 11.70$^i$ |
| 8 | -13.42$^i$ | 4.87$^i$ | -8.16$^i$ |
| 9 | -5.92$^i$ | 4.66$^i$ | -10.31$^i$ |
| 10 | 1.42$^i$ | 13.35$^i$ | -0.08$^i$ |
| 11 | 2.22$^i$ | 16.83$^i$ | 1.57$^i$ |

## 4.2 Thermal Back Reaction

**Table 8: The $NH_2$ substituted monocyano structures with TBR barriers in units of kJ/mol. The TBR barriers of the parent monocyano system in vacuum[12]; CAM-B3LYP: 136.13kJ/mol, M06-2X: 133.02kJ/mol, PBE0: 112.10kJ/mol.**

| **Vacuum** | | | | **Dichloromethane** | | | |
|---|---|---|---|---|---|---|---|
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 154.93 | 150.71 | 130.24 | 1 | 148.79 | 146.97 | 125.29 |
| 3 | 126.33 | 120.55 | 97.40 | 3 | 128.59 | 127.00 | 99.10 |
| 4 | 130.23 | 124.37 | 108.37 | 4 | 118.58 | 120.37 | 100.40 |
| 5 | 119.07 | 113.62 | 98.04 | 5 | 107.49 | 105.04 | 87.41 |
| 6 | 132.30 | 132.81 | 111.00 | 6 | 118.12 | 122.46 | 99.76 |
| 7 | 122.68 | 119.60 | 105.19 | 7 | 110.69 | 106.52 | 93.52 |
| 8 | 112.91 | 110.02 | 91.12 | 8 | 111.92 | 107.29 | 92.12 |
| 9 | 134.18 | 131.39 | 111.16 | 9 | 130.35 | 125.44 | 104.57 |
| 10 | 133.61 | 134.85 | 108.98 | 10 | 132.32 | 130.30 | 102.88 |
| 11 | 129.49 | 131.36 | 109.97 | 11 | 124.96 | 129.87 | 108.39 |
| **Cyclohexane** | | | | **Ethanol** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 152.40 | 149.45 | 128.81 | 1 | 147.81 | 146.28 | 124.63 |
| 3 | 124.18 | 119.38 | 95.33 | 3 | 129.27 | 118.59 | 99.14 |
| 4 | 123.17 | 122.24 | 106.20 | 4 | 116.81 | 120.34 | 99.47 |
| 5 | 112.00 | 110.11 | 93.63 | 5 | 106.65 | 104.16 | 87.86 |
| 6 | 124.09 | 128.83 | 108.90 | 6 | 118.15 | 121.09 | 102.92 |
| 7 | 116.88 | 113.63 | 100.96 | 7 | 108.63 | 103.80 | 94.52 |
| 8 | 111.78 | 109.24 | 90.90 | 8 | 108.05 | 107.09 | 87.54 |
| 9 | 133.30 | 129.66 | 111.56 | 9 | 128.48 | 124.24 | 103.80 |
| 10 | 130.97 | 132.72 | 107.96 | 10 | 131.92 | 130.29 | 109.31 |
| 11 | 127.61 | 130.70 | 109.05 | 11 | 131.82 | 129.98 | 108.83 |
| **Toluene** | | | | **Acetonitrile** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 151.74 | 148.99 | 128.37 | 1 | 147.59 | 146.14 | 124.68 |
| 3 | 123.50 | 119.15 | 94.68 | 3 | 129.09 | 118.87 | 98.79 |
| 4 | 122.68 | 121.93 | 101.81 | 4 | 116.39 | 119.83 | 99.35 |
| 5 | 111.20 | 109.29 | 88.14 | 5 | 106.52 | 104.04 | 87.96 |
| 6 | 123.55 | 127.27 | 108.33 | 6 | 118.01 | 120.87 | 103.17 |
| 7 | 115.76 | 112.88 | 100.18 | 7 | 108.18 | 103.55 | 94.74 |
| 8 | 112.01 | 108.96 | 90.89 | 8 | 108.18 | 107.14 | 88.08 |
| 9 | 133.17 | 131.59 | 111.61 | 9 | 128.16 | 124.09 | 103.71 |
| 10 | 130.09 | 126.18 | 107.36 | 10 | 131.78 | 130.32 | 109.26 |
| 11 | 127.24 | 130.56 | 108.81 | 11 | 131.84 | 130.08 | 108.93 |

**Table 9: The $NH_2$ substituted dicyano structures with TBR barriers in units of kJ/mol. The TBR barriers of the parent dicyano system in vacuum[12]; CAM-B3LYP: 107.86kJ/mol, M06-2X: 106.13kJ/mol, PBE0: 91.82kJ/mol.**

| **Vacuum** | | | | **Dichloromethane** | | | |
|---|---|---|---|---|---|---|---|
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 89.54 | 91.71 | 72.85 | 3 | 64.40 | 70.38 | 58.90 |
| 4 | 101.22 | 97.09 | 95.41 | 4 | 94.33 | 90.31 | 90.65 |
| 5 | 88.39 | 83.52 | 74.79 | 5 | 87.25 | 80.13 | 76.87 |
| 6 | 106.61 | 107.59 | 93.42 | 6 | 97.62 | 92.58 | 88.64 |
| 7 | 85.93 | 80.59 | 76.89 | 7 | 82.53 | 75.20 | 78.24 |
| 8 | 89.28 | 87.18 | 73.67 | 8 | 94.89 | 84.22 | 80.52 |
| 9 | 110.90 | 110.71 | 94.00 | 9 | 95.86 | 94.29 | 84.49 |
| 10 | 112.07 | 109.66 | 95.89 | 10 | 95.46 | 93.60 | 84.68 |
| 11 | 108.77 | 109.39 | 95.04 | 11 | 95.70 | 94.16 | 82.53 |
| **Cyclohexane** | | | | **Ethanol** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 75.59 | 82.45 | 66.27 | 3 | 62.16 | 67.41 | 56.67 |
| 4 | 95.47 | 91.86 | 92.13 | 4 | 94.76 | 90.36 | 91.40 |
| 5 | 85.16 | 79.64 | 73.56 | 5 | 88.47 | 80.37 | 77.91 |
| 6 | 101.41 | 100.22 | 91.22 | 6 | 99.11 | 93.41 | 91.80 |
| 7 | 82.67 | 75.33 | 76.81 | 7 | 84.26 | 76.03 | 79.87 |
| 8 | 89.23 | 83.51 | 72.92 | 8 | 96.60 | 85.54 | 81.76 |
| 9 | 103.56 | 103.22 | 88.51 | 9 | 94.36 | 92.06 | 83.87 |
| 10 | 103.63 | 102.29 | 90.72 | 10 | 92.40 | 90.71 | 82.14 |
| 11 | 102.00 | 101.68 | 86.67 | 11 | 94.65 | 92.79 | 81.74 |
| **Toluene** | | | | **Acetonitrile** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 73.52 | 80.71 | 65.20 | 3 | 61.75 | 66.90 | 56.27 |
| 4 | 95.07 | 90.65 | 91.94 | 4 | 94.77 | 89.91 | 91.60 |
| 5 | 85.52 | 79.37 | 74.27 | 5 | 88.71 | 80.46 | 78.15 |
| 6 | 100.96 | 100.67 | 90.49 | 6 | 99.42 | 93.60 | 92.13 |
| 7 | 82.42 | 74.89 | 76.60 | 7 | 84.66 | 76.25 | 80.23 |
| 8 | 89.62 | 82.70 | 75.01 | 8 | 95.77 | 86.13 | 82.14 |
| 9 | 102.00 | 101.78 | 87.54 | 9 | 94.13 | 91.70 | 83.73 |
| 10 | 102.27 | 100.63 | 89.79 | 10 | 92.16 | 90.13 | 82.02 |
| 11 | 100.80 | 100.32 | 86.05 | 11 | 94.44 | 92.55 | 81.62 |

**Table 10: The $NO_2$ substituted monocyano structures with TBR barriers in units of kJ/mol. The TBR barriers of the parent monocyano system in vacuum[12]; CAM-B3LYP: 136.13kJ/mol, M06-2X: 133.02kJ/mol, PBE0: 112.10kJ/mol.**

| **Vacuum** | | | | **Dichloromethane** | | | |
|---|---|---|---|---|---|---|---|
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 69.77 | 68.18 | 58.72 | 1 | 64.32 | 55.95 | 54.58 |
| 3 | 147.30 | 144.13 | 127.31 | 3 | 143.32 | 137.96 | 126.90 |
| 4 | 140.82 | 140.77 | 110.60 | 4 | 123.39 | 135.40 | 95.45 |
| 5 | 136.61 | 133.02 | 110.54 | 5 | 133.71 | 133.54 | 108.63 |
| 6 | 138.77 | 134.63 | 112.36 | 6 | 131.48 | 129.56 | 103.24 |
| 7 | 133.74 | 133.99 | 112.05 | 7 | 138.55 | 133.80 | 112.89 |
| 8 | 134.61 | 134.20 | 107.83 | 8 | 125.87 | 126.78 | 99.04 |
| 9 | 135.48 | 127.32 | 112.89 | 9 | 128.68 | 135.15 | 109.17 |
| 10 | 128.37 | 133.75 | 104.78 | 10 | 123.31 | 128.54 | 101.55 |
| 11 | 128.34 | 131.30 | 111.16 | 11 | 122.68 | 128.90 | 101.24 |
| **Cyclohexane** | | | | **Ethanol** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 63.16 | 60.35 | 54.08 | 1 | 66.14 | 56.64 | 55.70 |
| 3 | 145.20 | 140.56 | 126.63 | 3 | 143.15 | 140.76 | 126.95 |
| 4 | 138.66 | 137.87 | 108.53 | 4 | 123.98 | 134.90 | 95.52 |
| 5 | 135.40 | 132.48 | 109.44 | 5 | 133.74 | 133.82 | 108.30 |
| 6 | 137.94 | 135.24 | 109.68 | 6 | 128.50 | 127.08 | 100.86 |
| 7 | 138.44 | 132.57 | 112.02 | 7 | 138.34 | 134.76 | 112.91 |
| 8 | 131.00 | 131.79 | 104.12 | 8 | 123.87 | 124.97 | 97.62 |
| 9 | 133.04 | 125.87 | 111.81 | 9 | 125.60 | 135.57 | 107.99 |
| 10 | 126.30 | 131.21 | 103.64 | 10 | 122.12 | 127.59 | 100.85 |
| 11 | 125.57 | 129.92 | 103.32 | 11 | 121.79 | 128.82 | 100.74 |
| **Toluene** | | | | **Acetonitrile** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 1 | 62.89 | 59.03 | 53.99 | 1 | 66.57 | 56.86 | 56.01 |
| 3 | 144.88 | 140.08 | 126.42 | 3 | 143.18 | 140.71 | 126.98 |
| 4 | 138.32 | 137.36 | 108.08 | 4 | 124.13 | 134.90 | 95.57 |
| 5 | 135.01 | 132.62 | 109.32 | 5 | 133.78 | 133.84 | 108.30 |
| 6 | 137.31 | 134.97 | 108.83 | 6 | 128.01 | 126.69 | 100.38 |
| 7 | 138.72 | 124.57 | 112.16 | 7 | 138.55 | 134.98 | 113.12 |
| 8 | 130.37 | 131.04 | 103.34 | 8 | 123.86 | 123.98 | 97.37 |
| 9 | 132.58 | 125.86 | 111.60 | 9 | 126.09 | 135.39 | 107.68 |
| 10 | 125.96 | 130.82 | 103.31 | 10 | 121.70 | 127.43 | 100.71 |
| 11 | 124.97 | 129.92 | 102.95 | 11 | 121.43 | 128.81 | 100.64 |

**Table 11: The $NO_2$ substituted dicyano structures with TBR barriers in units of kJ/mol. The TBR barriers of the parent dicyano system in vacuum[12]; CAM-B3LYP: 107.86kJ/mol, M06-2X: 106.13kJ/mol, PBE0: 91.82kJ/mol.**

| **Vacuum** | | | | **Dichloromethane** | | | |
|---|---|---|---|---|---|---|---|
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 115.13 | 113.86 | 100.07 | 3 | 108.50 | 104.05 | 97.87 |
| 4 | 121.61 | 120.03 | 94.33 | 4 | 96.36 | 105.23 | 78.58 |
| 5 | 118.58 | 116.63 | 97.38 | 5 | 104.81 | 105.26 | 89.61 |
| 6 | 111.19 | 110.02 | 89.42 | 6 | 98.89 | 99.65 | 81.61 |
| 7 | 123.61 | 120.54 | 102.31 | 7 | 113.43 | 113.55 | 95.11 |
| 8 | 117.12 | 113.35 | 96.20 | 8 | 99.95 | 101.11 | 83.95 |
| 9 | 104.68 | 104.19 | 91.98 | 9 | 95.79 | 91.93 | 85.65 |
| 10 | 104.96 | 104.10 | 91.23 | 10 | 91.31 | 90.72 | 81.99 |
| 11 | 104.67 | 103.03 | 90.68 | 11 | 89.72 | 88.18 | 80.59 |
| **Cyclohexane** | | | | **Ethanol** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 110.25 | 104.84 | 98.10 | 3 | 108.46 | 104.21 | 97.93 |
| 4 | 113.53 | 111.09 | 78.75 | 4 | 94.99 | 104.75 | 76.64 |
| 5 | 113.79 | 113.58 | 93.73 | 5 | 102.81 | 102.71 | 88.24 |
| 6 | 106.01 | 105.91 | 85.34 | 6 | 98.39 | 96.64 | 80.31 |
| 7 | 118.89 | 119.29 | 100.01 | 7 | 111.34 | 110.84 | 95.76 |
| 8 | 110.90 | 107.92 | 91.59 | 8 | 97.98 | 98.57 | 82.01 |
| 9 | 99.32 | 97.80 | 88.43 | 9 | 95.14 | 92.72 | 85.77 |
| 10 | 96.94 | 95.85 | 85.64 | 10 | 90.72 | 90.02 | 81.73 |
| 11 | 96.96 | 95.09 | 85.45 | 11 | 88.59 | 86.70 | 79.98 |
| **Toluene** | | | | **Acetonitrile** | | | |
| Position | CAM-B3LYP | M06-2X | PBE0 | Position | CAM-B3LYP | M06-2X | PBE0 |
| 3 | 109.49 | 104.01 | 98.02 | 3 | 108.34 | 104.19 | 98.23 |
| 4 | 112.77 | 110.23 | 78.37 | 4 | 94.75 | 104.24 | 76.28 |
| 5 | 112.43 | 112.50 | 93.45 | 5 | 102.42 | 102.22 | 88.02 |
| 6 | 104.99 | 104.94 | 84.75 | 6 | 98.53 | 95.52 | 80.10 |
| 7 | 117.89 | 118.44 | 99.56 | 7 | 111.04 | 110.38 | 95.87 |
| 8 | 109.71 | 106.74 | 90.46 | 8 | 97.12 | 98.10 | 81.33 |
| 9 | 98.07 | 96.47 | 87.73 | 9 | 95.03 | 92.42 | 86.47 |
| 10 | 95.64 | 95.30 | 84.82 | 10 | 90.15 | 89.46 | 81.48 |
| 11 | 95.56 | 93.77 | 84.47 | 11 | 88.58 | 86.46 | 79.86 |

# 5 Optical Properties

## 5.1 Monocyano $NH_2$

Figure 1: **The UV-Vis spectra for the monocyano structure with $NH_2$ substituted on position number 3, using CAM-B3LYP/6-311+G(d) level of theory.**

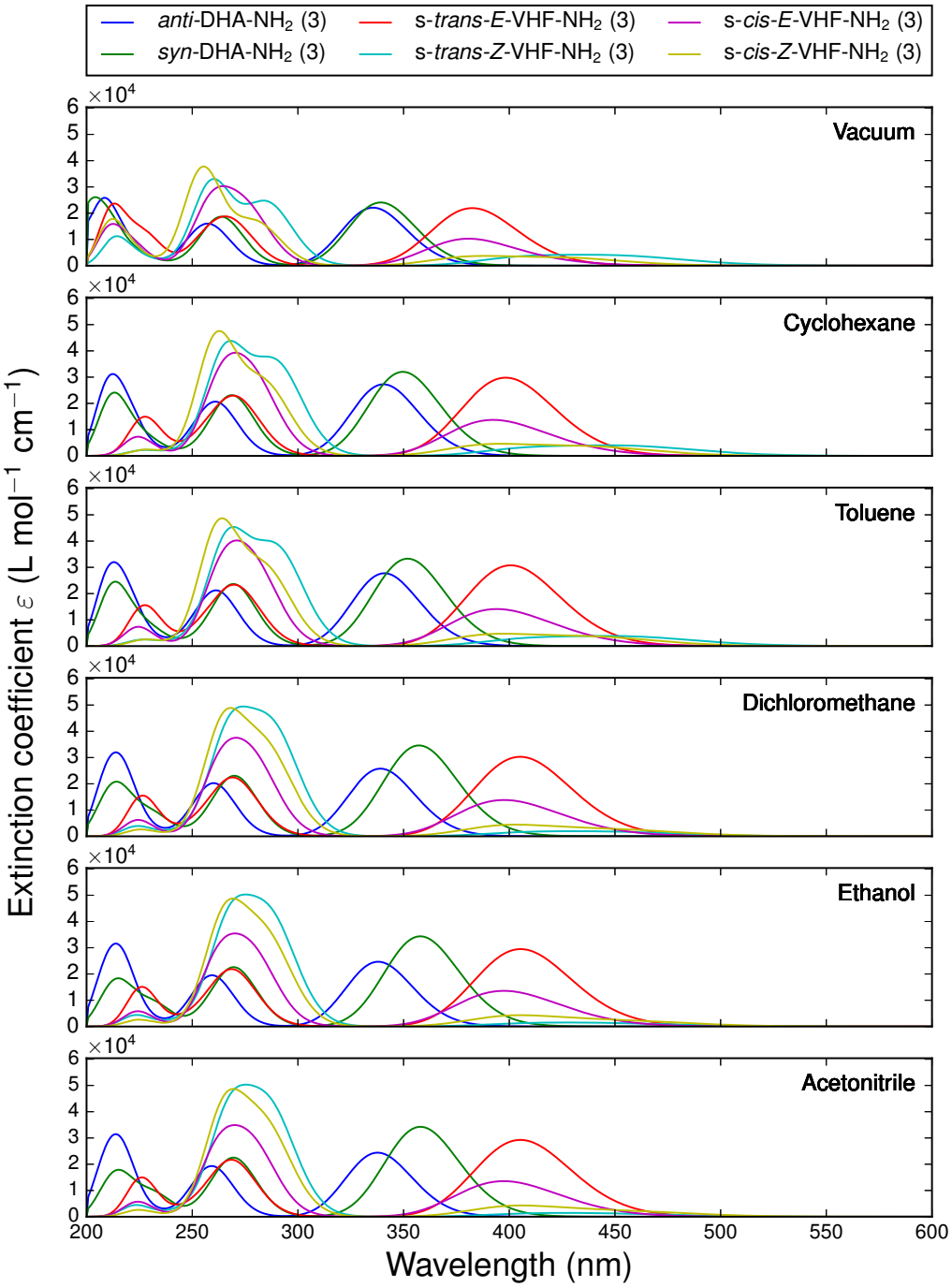


Figure 2: **The UV-Vis spectra for the monocyano structure with $NH_2$ substituted on position number 3, using M06-2X/6-311+G(d) level of theory.**

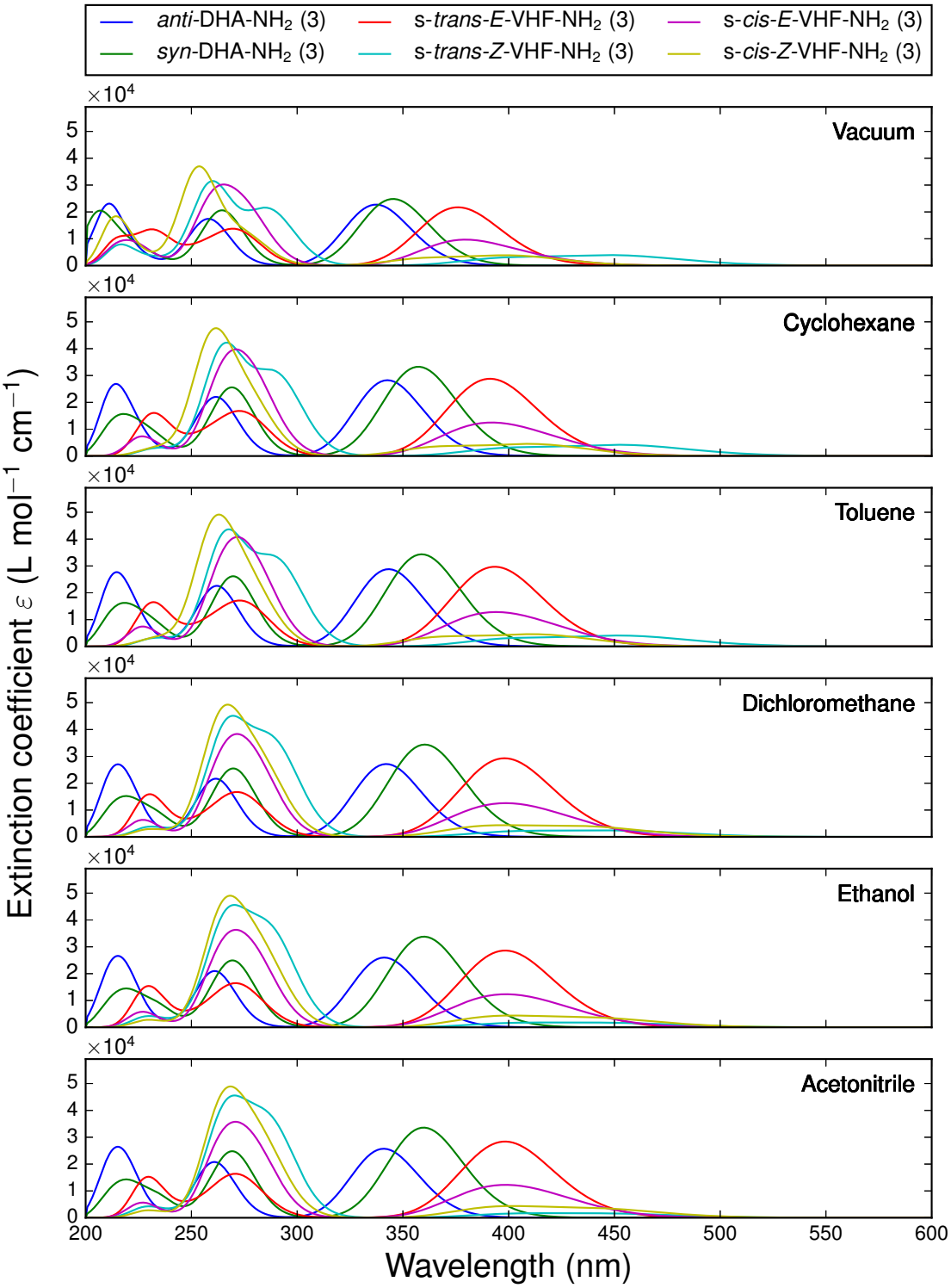
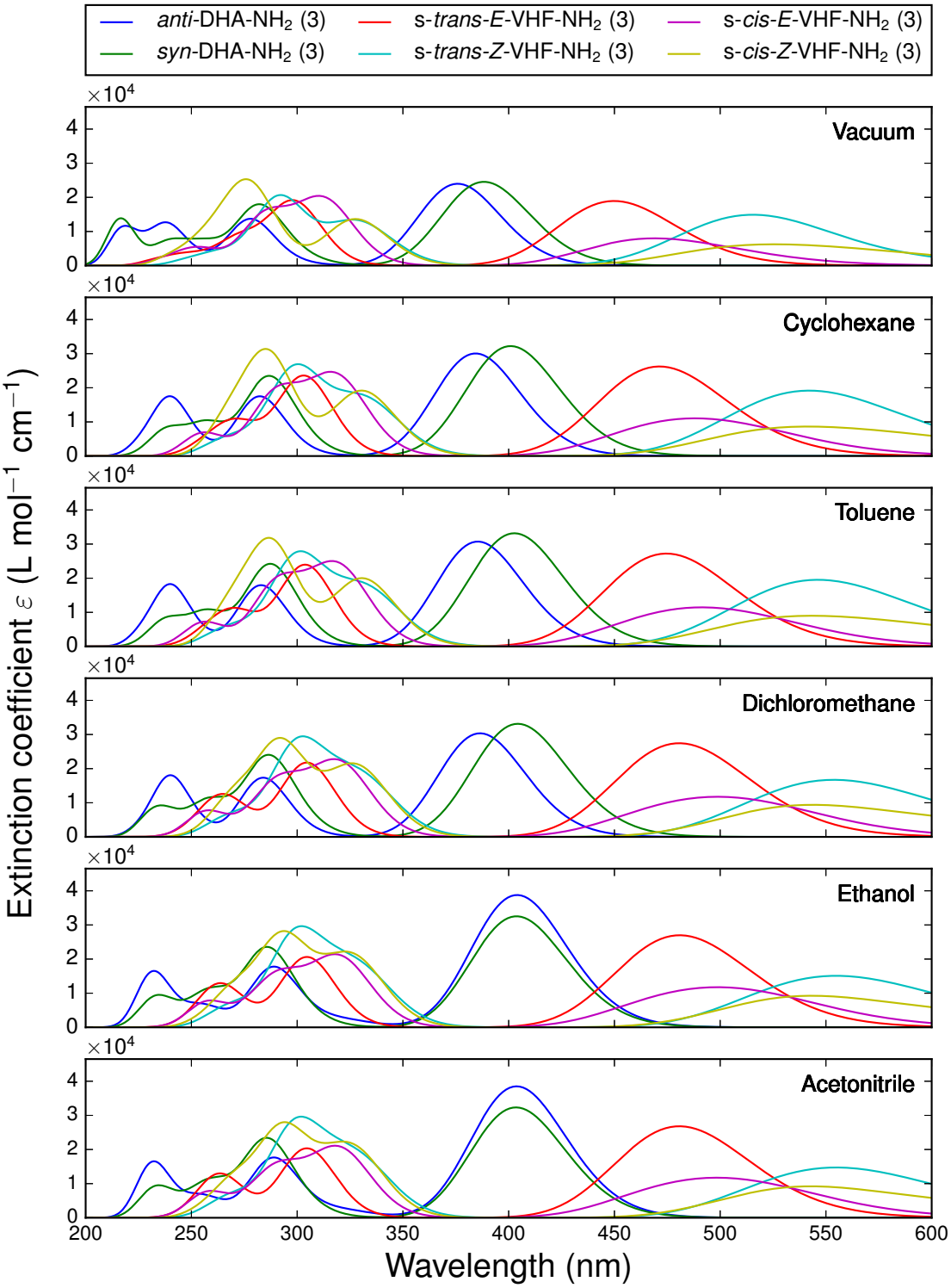


Figure 3: **The UV-Vis spectra for the monocyano structure with $NH_2$ substituted on position number 3, using PBE0/6-311+G(d) level of theory.**



## 5.2 Dicyano $NH_2$

Figure 4: **The UV-Vis spectra for the dicyano structure with $NH_2$ substituted on position number 3, using CAM-B3LYP/6-311+G(d) level of theory.**

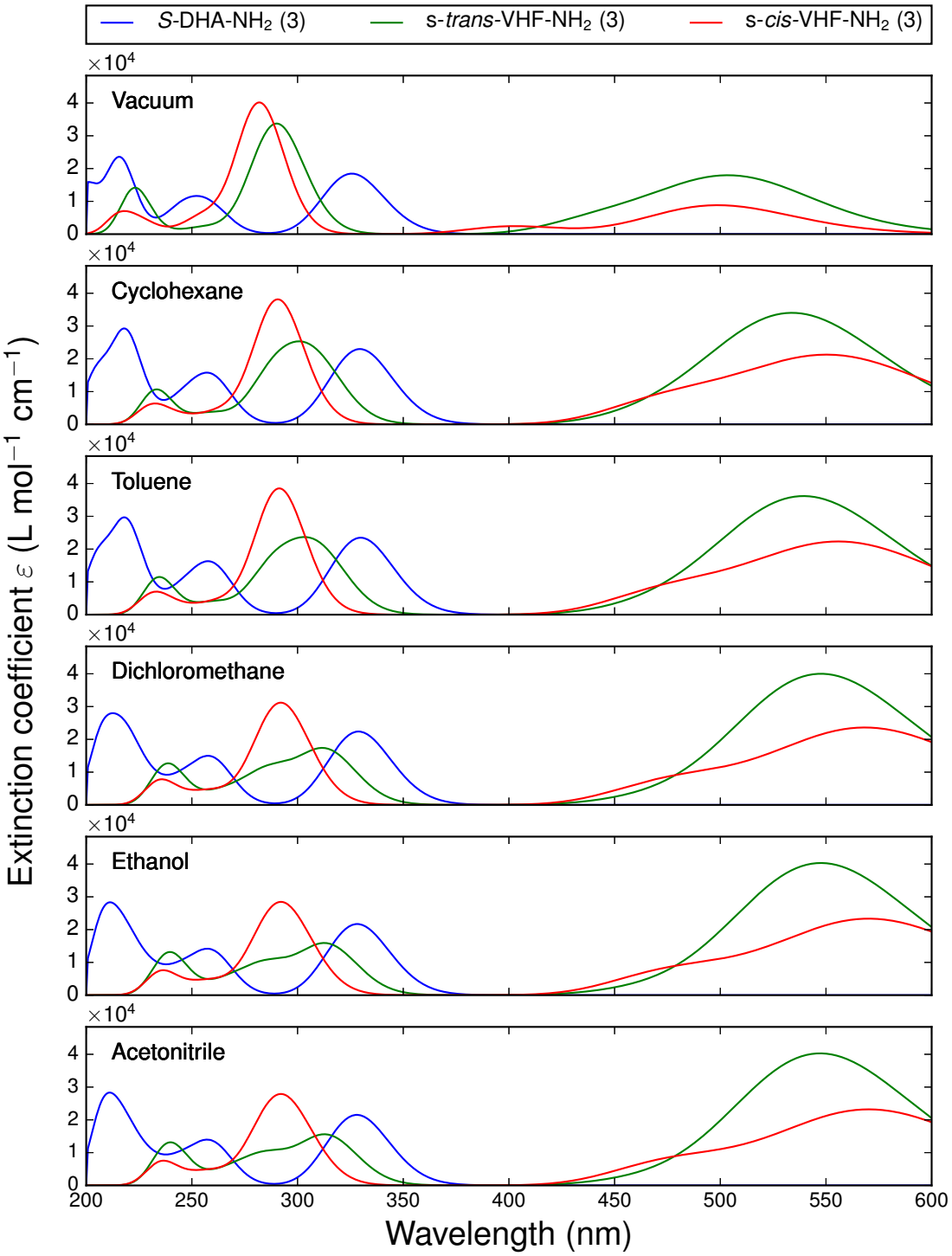


Figure 5: **The UV-Vis spectra for the dicyano structure with $NH_2$ substituted on position number 3, using M06-2X/6-311+G(d) level of theory.**

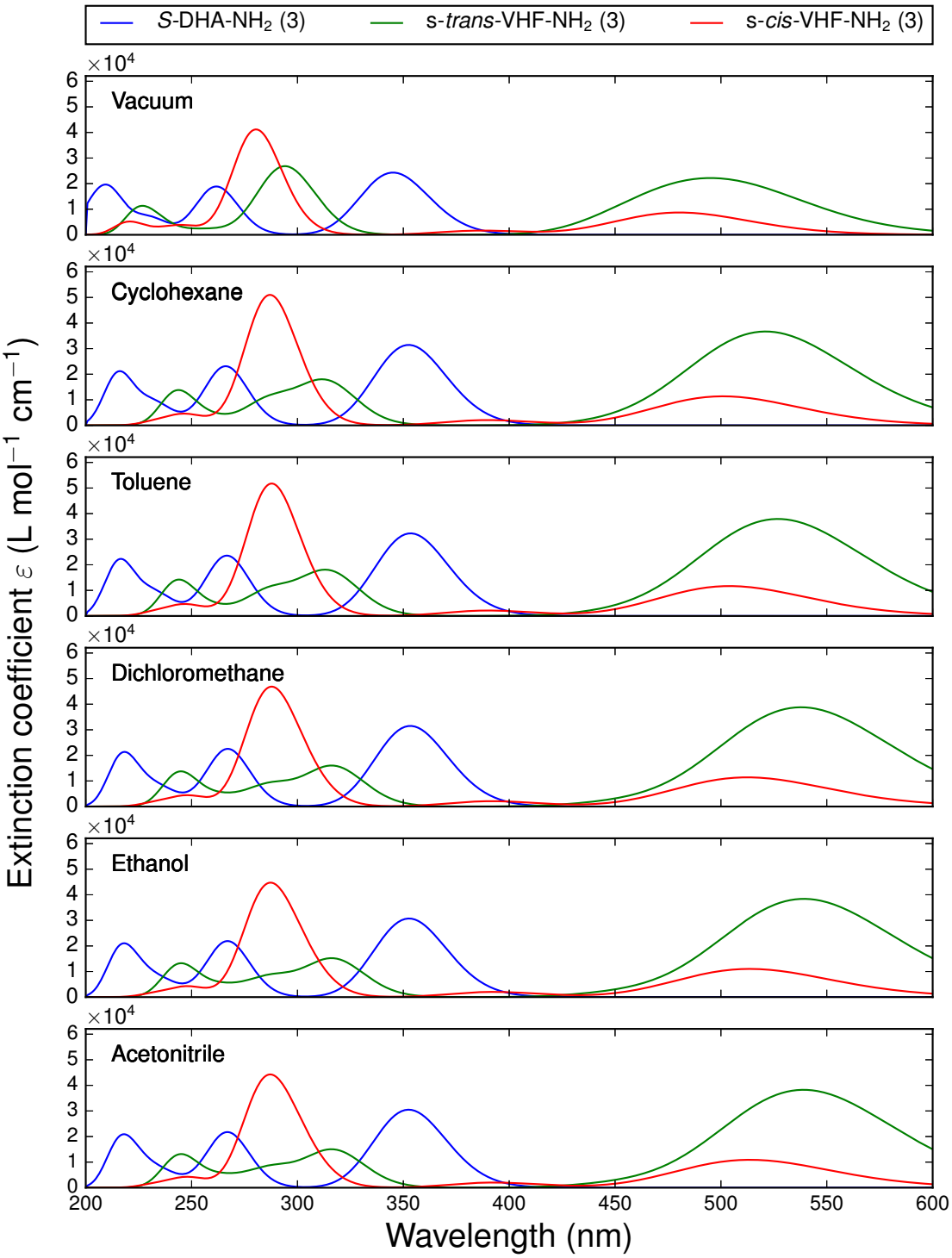
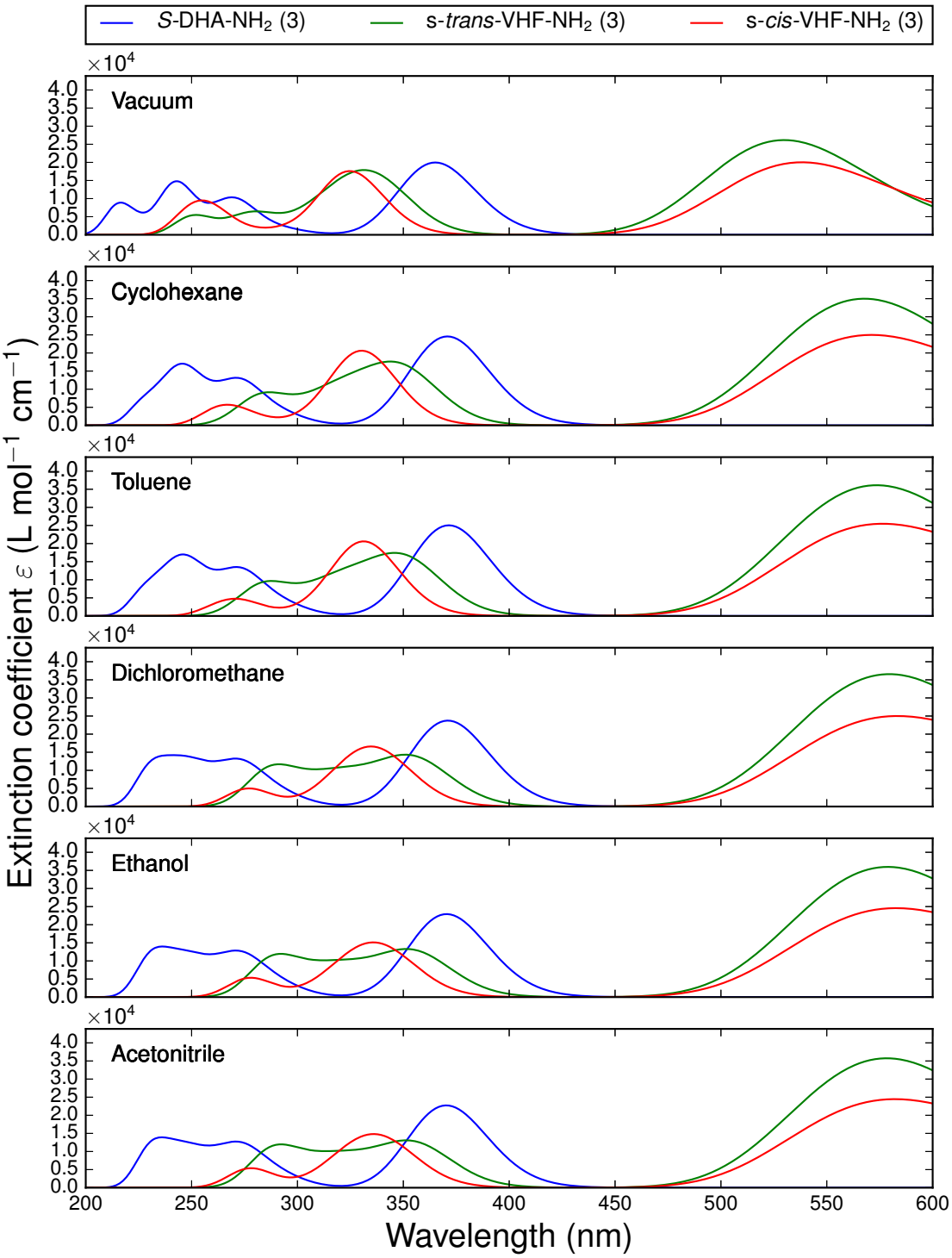


Figure 6: **The UV-Vis spectra for the dicyano structure with $NH_2$ substituted on position number 3, using PBE0/6-311+G(d) level of theory.**



## 5.3 Monocyano $NO_2$

Figure 7: **The UV-Vis spectra for the monocyano structure with $NO_2$ substituted on position number 4, using CAM-B3LYP/6-311+G(d) level of theory.**

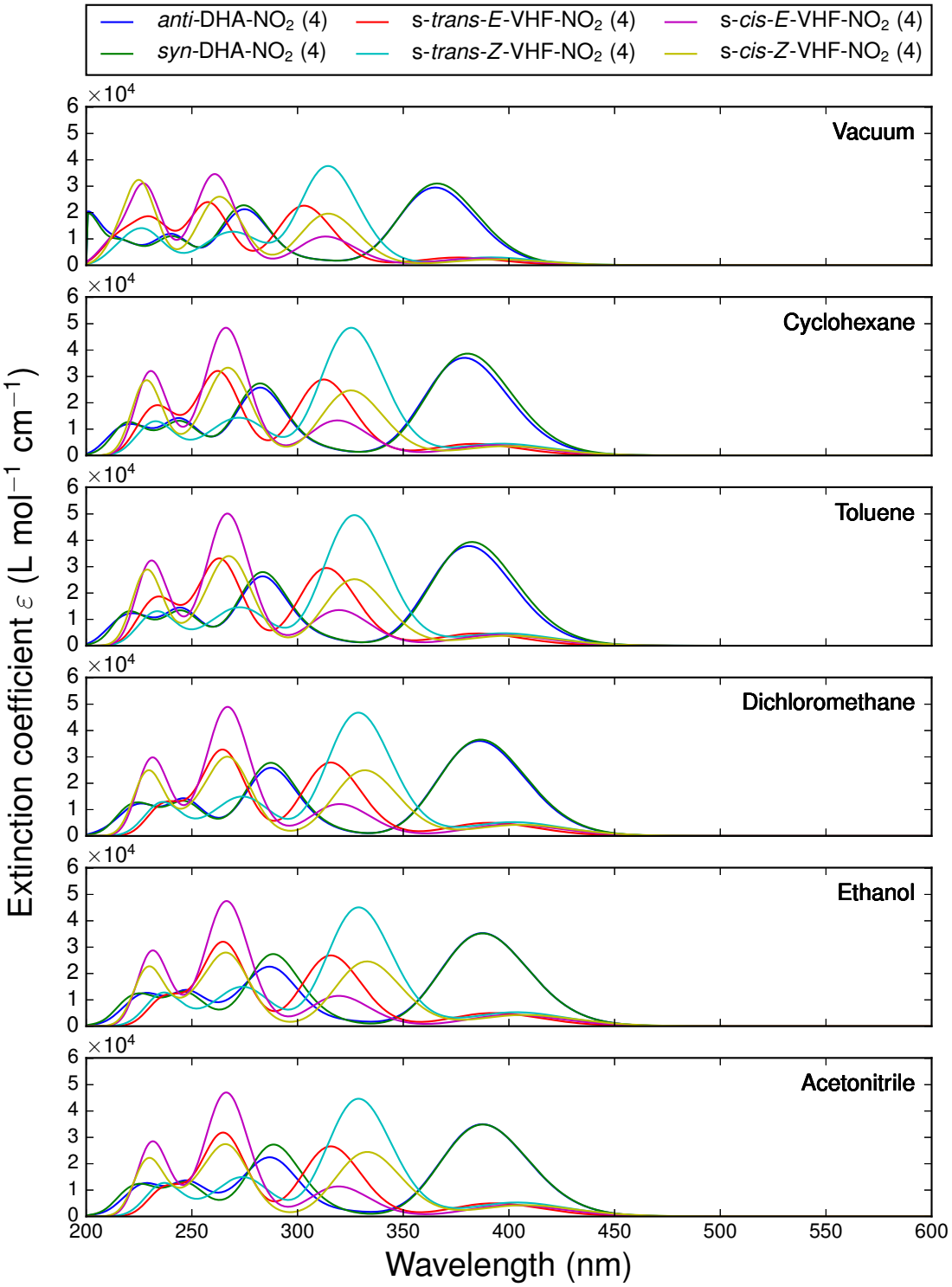


Figure 8: **The UV-Vis spectra for the monocyano structure with $NO_2$ substituted on position number 4, using M06-2X/6-311+G(d) level of theory.**

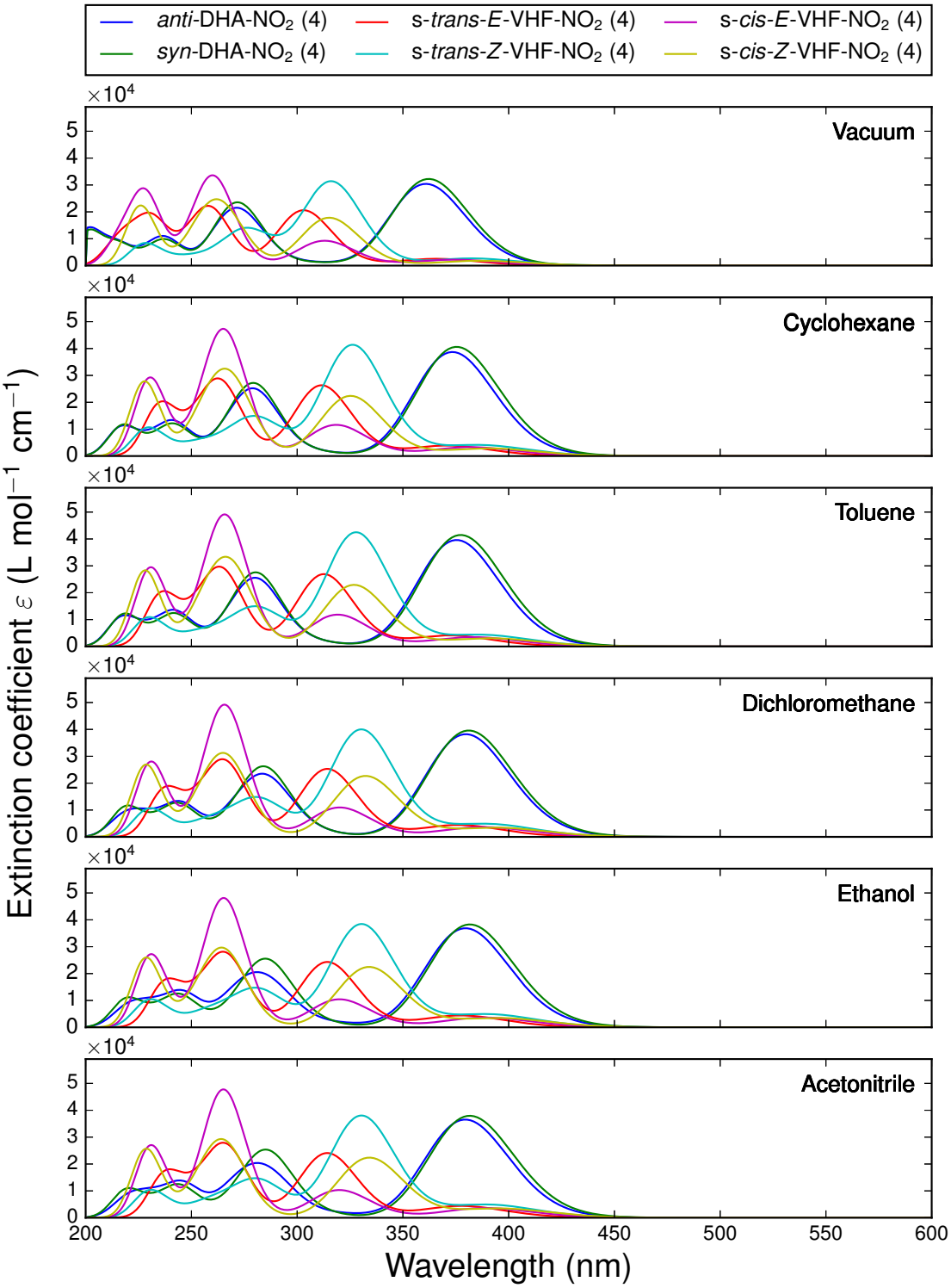
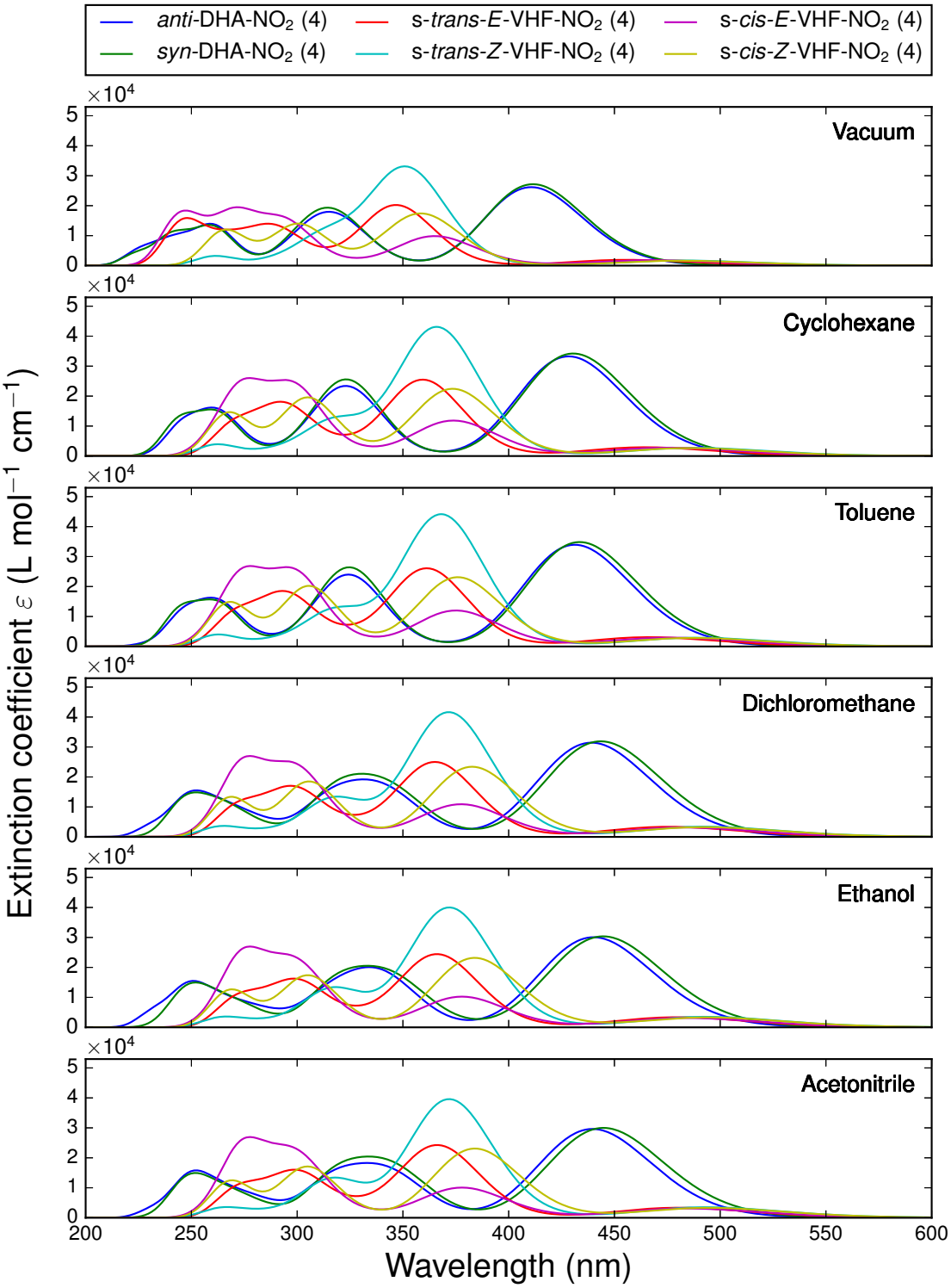


Figure 9: **The UV-Vis spectra for the monocyano structure with $NO_2$ substituted on position number 4, using PBE0/6-311+G(d) level of theory.**



## 5.4 Dicyano $NO_2$

Figure 10: **The UV-Vis spectra for the dicyano structure with $NO_2$ substituted on position number 4, using CAM-B3LYP/6-311+G(d) level of theory.**

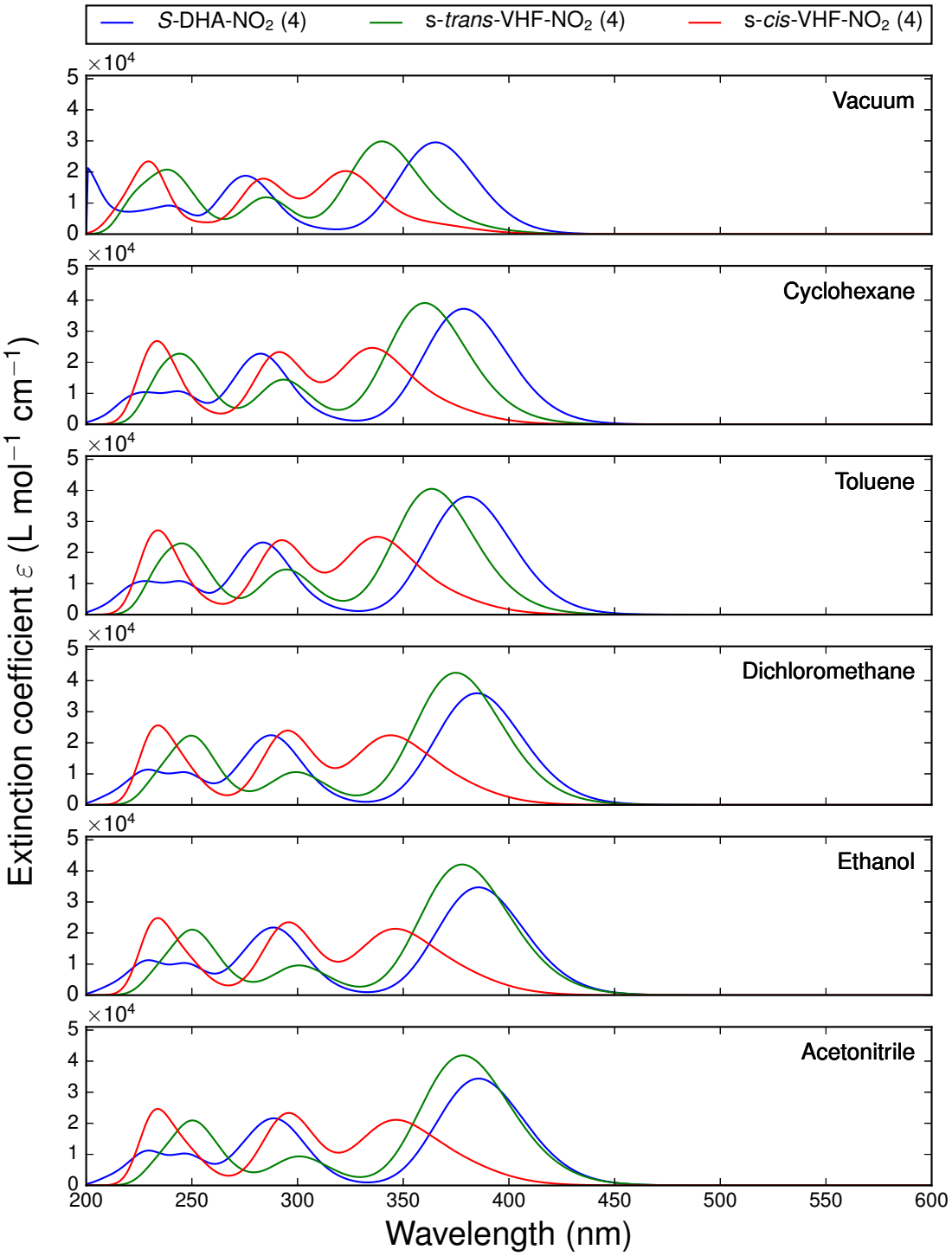


Figure 11: **The UV-Vis spectra for the dicyano structure with $NO_2$ substituted on position number 4, using M06-2X/6-311+G(d) level of theory.**

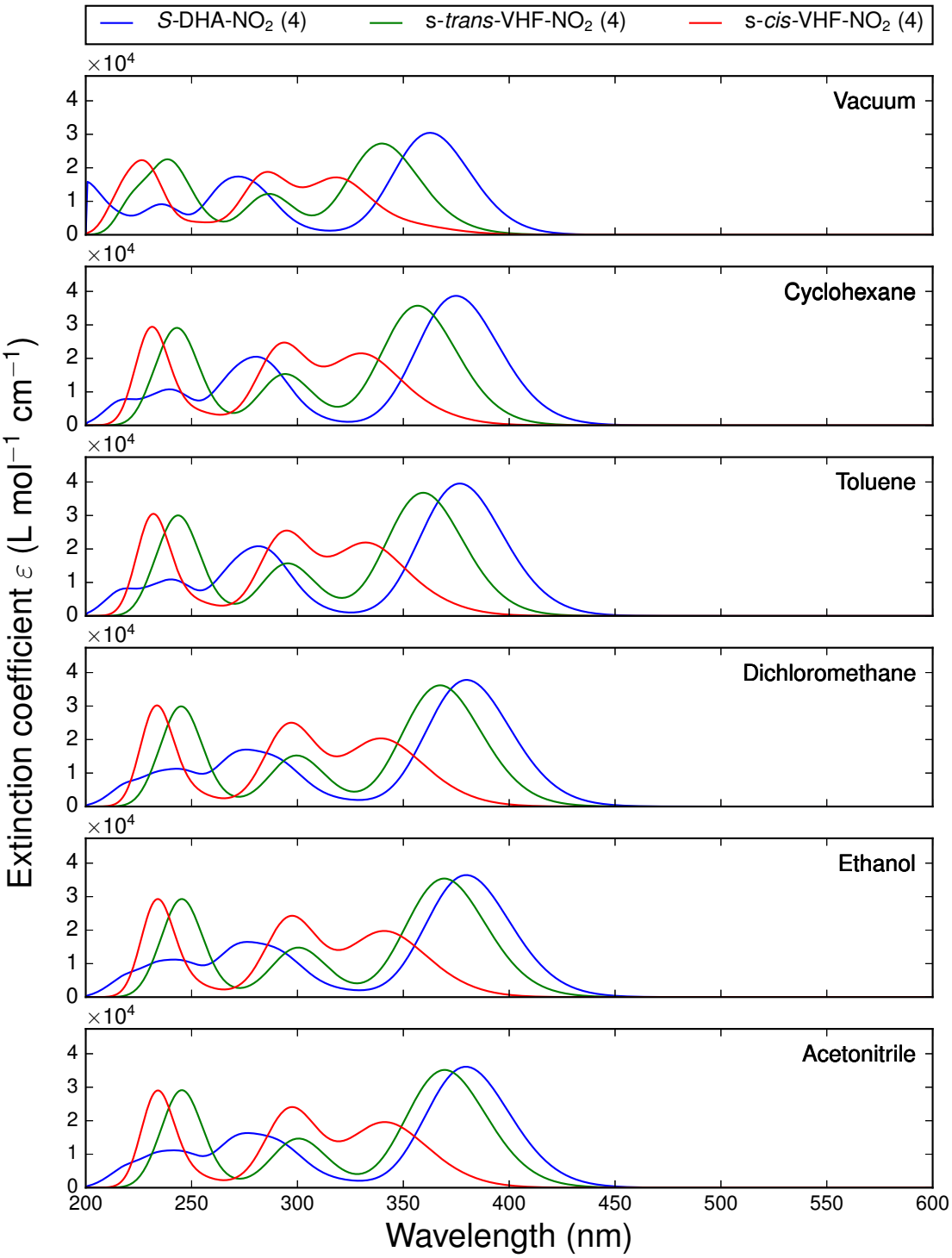
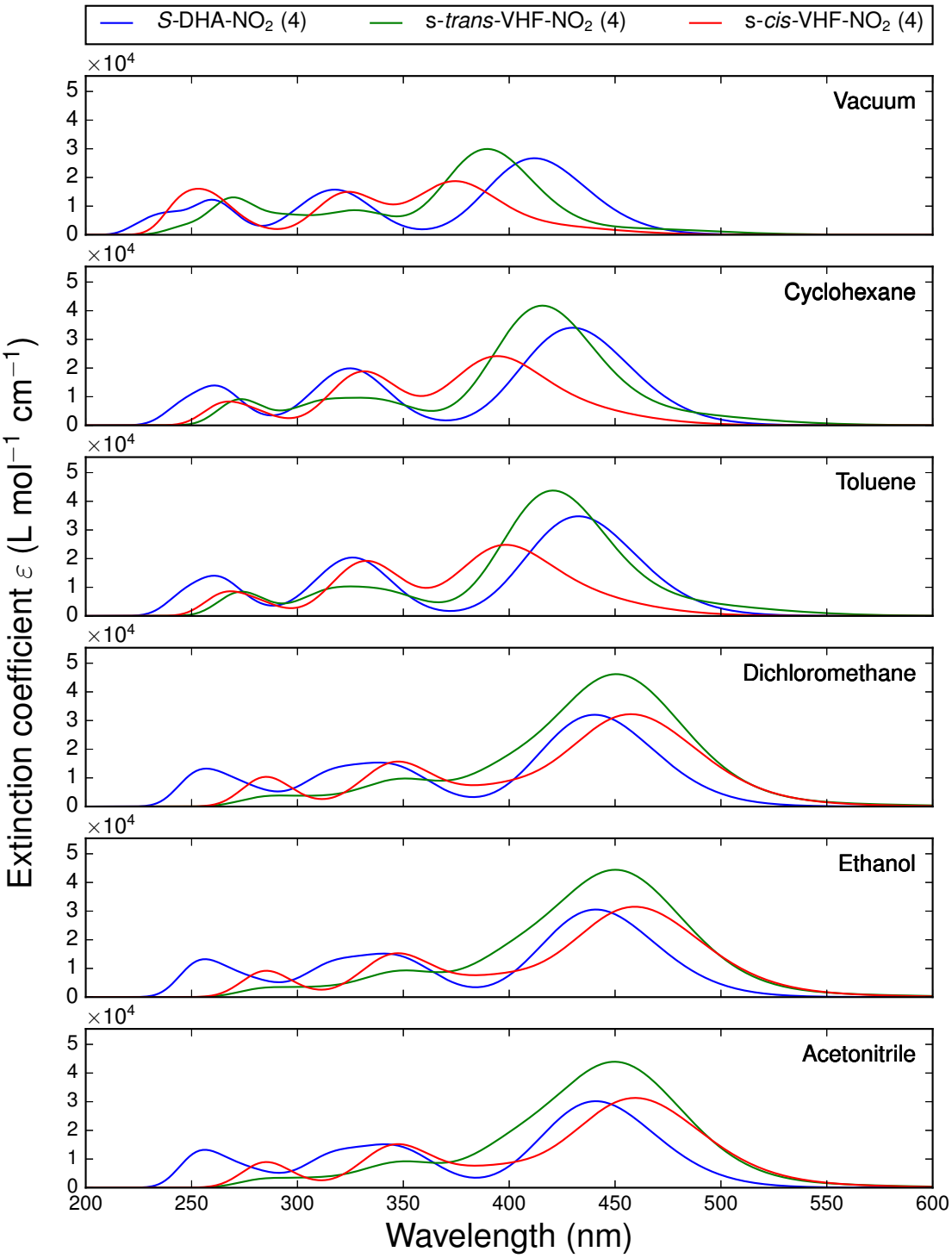


Figure 12: **The UV-Vis spectra for the dicyano structure with $NO_2$ substituted on position number 4, using PBE0/6-311+G(d) level of theory.**



# 6 Gibbs Free Energies

## 6.1 DHA Structures

### 6.1.1 The $NH_2$ substituted monocyano structures - Vacuum

**Table 12: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2008985.919 | -2009309.023 | -2007715.058 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009024.595 | -2009344.276 | -2007755.775 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009013.074 | -2009331.093 | -2007744.582 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009023.668 | -2009338.988 | -2007754.155 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009024.674 | -2009340.036 | -2007756.720 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009018.514 | -2009335.504 | -2007749.053 |
| *anti*-DHA $NH_2$ (8) conf2 | -2009008.346 | -2009326.089 | -2007742.697 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009017.519 | -2009336.814 | -2007749.455 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009022.770 | -2009339.883 | -2007754.491 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009025.522 | -2009339.931 | -2007757.715 |
| *syn*-DHA $NH_2$ (1) conf3 | -2008983.206 | -2009302.268 | -2007711.456 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009029.061 | -2009344.544 | -2007758.287 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009017.398 | -2009330.844 | -2007749.119 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009026.842 | -2009338.318 | -2007756.591 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009027.002 | -2009340.479 | -2007758.839 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009020.418 | -2009333.656 | -2007749.665 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009028.147 | -2009346.830 | -2007760.831 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009022.003 | -2009337.084 | -2007753.603 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009027.538 | -2009339.424 | -2007758.573 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009030.413 | -2009343.995 | -2007762.564 |

### 6.1.2 The $NH_2$ substituted monocyano structures - Cyclohexane

**Table 13: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2008999.135 | -2009322.445 | -2007728.057 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009037.982 | -2009357.474 | -2007768.713 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009028.163 | -2009346.765 | -2007759.747 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009039.387 | -2009355.130 | -2007769.958 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009040.088 | -2009355.912 | -2007772.218 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009033.503 | -2009350.322 | -2007764.145 |
| *anti*-DHA $NH_2$ (8) conf2 | -2009022.662 | -2009340.702 | -2007757.623 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009032.088 | -2009351.606 | -2007764.237 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009038.415 | -2009355.875 | -2007769.997 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009041.508 | -2009356.027 | -2007773.943 |
| *syn*-DHA $NH_2$ (1) conf3 | -2008995.743 | -2009316.529 | -2007724.242 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009042.603 | -2009358.742 | -2007772.384 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009033.010 | -2009347.324 | -2007764.925 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009043.275 | -2009354.851 | -2007773.765 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009043.317 | -2009357.049 | -2007775.335 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009035.995 | -2009349.805 | -2007765.308 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009041.390 | -2009361.869 | -2007776.230 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009037.021 | -2009352.696 | -2007769.018 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009043.294 | -2009355.802 | -2007775.280 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009046.723 | -2009360.950 | -2007779.698 |

### 6.1.3 The $NH_2$ substituted monocyano structures - Toluene

**Table 14: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2009001.748 | -2009325.136 | -2007730.709 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009040.726 | -2009359.903 | -2007771.273 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009031.159 | -2009349.813 | -2007762.743 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009042.511 | -2009358.388 | -2007773.108 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009043.152 | -2009358.994 | -2007775.322 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009036.467 | -2009353.258 | -2007767.261 |

| | | | |
|---|---|---|---|
| *anti*-DHA $NH_2$ (8) conf2 | -2009025.881 | -2009343.887 | -2007761.078 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009034.892 | -2009354.518 | -2007767.156 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009041.642 | -2009359.070 | -2007773.090 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009044.667 | -2009359.238 | -2007777.157 |
| *syn*-DHA $NH_2$ (1) conf3 | -2008998.539 | -2009319.339 | -2007727.010 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009045.447 | -2009361.273 | -2007775.353 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009036.244 | -2009350.075 | -2007767.960 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009046.549 | -2009358.062 | -2007777.094 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009046.597 | -2009360.357 | -2007778.624 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009039.098 | -2009353.024 | -2007768.485 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009046.014 | -2009364.006 | -2007779.333 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009039.915 | -2009355.760 | -2007772.095 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009046.405 | -2009359.055 | -2007778.609 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009049.873 | -2009364.348 | -2007783.096 |

### 6.1.4 The $NH_2$ substituted monocyano structures - Dichloromethane

**Table 15: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2009015.736 | -2009339.400 | -2007745.194 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009054.575 | -2009374.251 | -2007785.960 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009047.505 | -2009366.188 | -2007779.304 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009059.506 | -2009376.244 | -2007790.200 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009059.582 | -2009375.527 | -2007792.403 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009052.504 | -2009369.305 | -2007783.366 |
| *anti*-DHA $NH_2$ (8) conf2 | -2009043.102 | -2009360.816 | -2007779.129 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009050.104 | -2009369.927 | -2007782.668 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009057.681 | -2009376.113 | -2007790.122 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009061.822 | -2009376.656 | -2007794.874 |
| *syn*-DHA $NH_2$ (1) conf3 | -2009012.342 | -2009334.569 | -2007744.343 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009057.763 | -2009374.267 | -2007790.213 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009053.263 | -2009366.758 | -2007784.876 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009063.752 | -2009375.146 | -2007794.338 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009064.274 | -2009378.520 | -2007796.706 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009055.841 | -2009370.641 | -2007785.887 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009062.174 | -2009379.589 | -2007797.260 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009055.339 | -2009371.725 | -2007788.360 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009063.696 | -2009376.034 | -2007795.026 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009066.598 | -2009381.920 | -2007800.952 |

### 6.1.5 The $NH_2$ substituted monocyano structures - Ethanol

**Table 16: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2009020.113 | -2009343.853 | -2007749.757 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009058.566 | -2009378.255 | -2007788.244 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009052.559 | -2009371.368 | -2007784.592 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009064.736 | -2009381.715 | -2007795.504 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009064.615 | -2009380.870 | -2007797.809 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009057.474 | -2009374.409 | -2007788.244 |
| *anti*-DHA $NH_2$ (8) conf2 | -2009049.080 | -2009367.141 | -2007785.251 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009054.869 | -2009374.598 | -2007787.365 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009062.680 | -2009380.883 | -2007795.451 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009067.215 | -2009382.243 | -2007800.385 |
| *syn*-DHA $NH_2$ (1) conf3 | -2009017.175 | -2009339.350 | -2007747.675 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009062.749 | -2009378.819 | -2007794.506 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009058.230 | -2009372.723 | -2007790.844 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009068.929 | -2009380.610 | -2007799.634 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009069.554 | -2009384.254 | -2007802.485 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009061.142 | -2009376.134 | -2007791.306 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009067.362 | -2009385.793 | -2007803.588 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009060.170 | -2009376.317 | -2007792.939 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009069.047 | -2009381.125 | -2007800.093 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009071.891 | -2009387.103 | -2007806.470 |

### 6.1.6 The $NH_2$ substituted monocyano structures - Acetonitrile

**Table 17: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NH_2$ (1) conf7 | -2009020.930 | -2009344.672 | -2007750.613 |
| *anti*-DHA $NH_2$ (3) conf6 | -2009059.296 | -2009378.935 | -2007789.035 |
| *anti*-DHA $NH_2$ (4) conf1 | -2009053.465 | -2009372.321 | -2007785.574 |
| *anti*-DHA $NH_2$ (5) conf8 | -2009065.694 | -2009382.705 | -2007796.486 |
| *anti*-DHA $NH_2$ (6) conf8 | -2009065.550 | -2009381.865 | -2007798.815 |
| *anti*-DHA $NH_2$ (7) conf4 | -2009058.401 | -2009375.349 | -2007789.137 |

| | | | |
|---|---|---|---|
| *anti*-DHA $NH_2$ (8) conf2 | -2009050.443 | -2009368.467 | -2007786.362 |
| *anti*-DHA $NH_2$ (9) conf6 | -2009055.749 | -2009375.451 | -2007788.223 |
| *anti*-DHA $NH_2$ (10) conf1 | -2009063.589 | -2009381.784 | -2007796.373 |
| *anti*-DHA $NH_2$ (11) conf1 | -2009068.194 | -2009383.262 | -2007801.398 |
| *syn*-DHA $NH_2$ (1) conf3 | -2009018.110 | -2009340.227 | -2007748.528 |
| *syn*-DHA $NH_2$ (3) conf6 | -2009063.213 | -2009379.628 | -2007795.315 |
| *syn*-DHA $NH_2$ (4) conf1 | -2009059.152 | -2009373.781 | -2007791.967 |
| *syn*-DHA $NH_2$ (5) conf8 | -2009069.879 | -2009381.626 | -2007800.603 |
| *syn*-DHA $NH_2$ (6) conf8 | -2009070.517 | -2009385.312 | -2007803.559 |
| *syn*-DHA $NH_2$ (7) conf4 | -2009062.061 | -2009377.139 | -2007792.295 |
| *syn*-DHA $NH_2$ (8) conf2 | -2009068.323 | -2009387.050 | -2007804.814 |
| *syn*-DHA $NH_2$ (9) conf6 | -2009061.063 | -2009377.142 | -2007793.742 |
| *syn*-DHA $NH_2$ (10) conf1 | -2009070.021 | -2009382.059 | -2007801.057 |
| *syn*-DHA $NH_2$ (11) conf1 | -2009072.888 | -2009388.038 | -2007807.442 |

### 6.1.7 The $NH_2$ substituted dicyano structures - Vacuum

**Table 18: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251136.138 | -2251494.128 | -2249694.061 |
| *S*-DHA $NH_2$ (4) conf45 | -2251120.241 | -2251477.540 | -2249679.760 |
| *S*-DHA $NH_2$ (5) conf15 | -2251127.096 | -2251483.397 | -2249685.615 |
| *S*-DHA $NH_2$ (6) conf5 | -2251129.582 | -2251486.611 | -2249689.937 |
| *S*-DHA $NH_2$ (7) conf30 | -2251120.485 | -2251477.196 | -2249677.943 |
| *S*-DHA $NH_2$ (8) conf21 | -2251121.708 | -2251485.091 | -2249686.765 |
| *S*-DHA $NH_2$ (9) conf12 | -2251118.571 | -2251476.965 | -2249676.515 |
| *S*-DHA $NH_2$ (10) conf3 | -2251127.453 | -2251482.877 | -2249686.828 |
| *S*-DHA $NH_2$ (11) conf13 | -2251131.018 | -2251486.359 | -2249691.851 |

### 6.1.8 The $NH_2$ substituted dicyano structures - Cyclohexane

**Table 19: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251152.414 | -2251510.537 | -2249710.182 |
| *S*-DHA $NH_2$ (4) conf45 | -2251137.579 | -2251495.327 | -2249697.044 |
| *S*-DHA $NH_2$ (5) conf15 | -2251143.946 | -2251500.888 | -2249702.707 |
| *S*-DHA $NH_2$ (6) conf5 | -2251146.396 | -2251504.028 | -2249707.617 |
| *S*-DHA $NH_2$ (7) conf30 | -2251137.112 | -2251494.225 | -2249694.959 |
| *S*-DHA $NH_2$ (8) conf21 | -2251136.406 | -2251499.896 | -2249701.620 |
| *S*-DHA $NH_2$ (9) conf12 | -2251134.484 | -2251494.771 | -2249693.158 |
| *S*-DHA $NH_2$ (10) conf3 | -2251144.177 | -2251500.418 | -2249703.920 |
| *S*-DHA $NH_2$ (11) conf13 | -2251148.418 | -2251503.866 | -2249709.777 |

### 6.1.9 The $NH_2$ substituted dicyano structures - Toluene

**Table 20: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251155.527 | -2251513.638 | -2249713.259 |
| *S*-DHA $NH_2$ (4) conf45 | -2251140.937 | -2251498.649 | -2249700.389 |
| *S*-DHA $NH_2$ (5) conf15 | -2251147.223 | -2251504.294 | -2249706.099 |
| *S*-DHA $NH_2$ (6) conf5 | -2251149.720 | -2251507.363 | -2249711.051 |
| *S*-DHA $NH_2$ (7) conf30 | -2251140.294 | -2251497.399 | -2249698.254 |
| *S*-DHA $NH_2$ (8) conf21 | -2251139.252 | -2251502.792 | -2249704.500 |
| *S*-DHA $NH_2$ (9) conf12 | -2251137.695 | -2251497.950 | -2249696.624 |
| *S*-DHA $NH_2$ (10) conf3 | -2251147.464 | -2251503.834 | -2249707.233 |
| *S*-DHA $NH_2$ (11) conf13 | -2251151.749 | -2251507.263 | -2249713.225 |

### 6.1.10 The $NH_2$ substituted dicyano structures - Dichloromethane

**Table 21: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251171.842 | -2251529.737 | -2249729.343 |
| *S*-DHA $NH_2$ (4) conf45 | -2251158.058 | -2251516.219 | -2249718.166 |
| *S*-DHA $NH_2$ (5) conf15 | -2251164.858 | -2251522.646 | -2249724.094 |
| *S*-DHA $NH_2$ (6) conf5 | -2251167.760 | -2251525.665 | -2249729.106 |
| *S*-DHA $NH_2$ (7) conf30 | -2251157.258 | -2251514.139 | -2249715.698 |
| *S*-DHA $NH_2$ (8) conf21 | -2251154.191 | -2251518.269 | -2249719.712 |
| *S*-DHA $NH_2$ (9) conf12 | -2251154.742 | -2251514.378 | -2249712.511 |
| *S*-DHA $NH_2$ (10) conf3 | -2251164.381 | -2251521.449 | -2249724.480 |
| *S*-DHA $NH_2$ (11) conf13 | -2251169.183 | -2251525.382 | -2249731.480 |

### 6.1.11 The $NH_2$ substituted dicyano structures - Ethanol

**Table 22: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251176.713 | -2251534.655 | -2249734.231 |
| *S*-DHA $NH_2$ (4) conf45 | -2251163.273 | -2251521.845 | -2249723.561 |
| *S*-DHA $NH_2$ (5) conf15 | -2251170.364 | -2251528.288 | -2249729.631 |
| *S*-DHA $NH_2$ (6) conf5 | -2251173.483 | -2251531.278 | -2249734.877 |
| *S*-DHA $NH_2$ (7) conf30 | -2251162.362 | -2251519.327 | -2249721.240 |
| *S*-DHA $NH_2$ (8) conf21 | -2251158.599 | -2251522.908 | -2249724.349 |
| *S*-DHA $NH_2$ (9) conf12 | -2251160.642 | -2251519.873 | -2249717.811 |
| *S*-DHA $NH_2$ (10) conf3 | -2251169.422 | -2251526.427 | -2249729.568 |
| *S*-DHA $NH_2$ (11) conf13 | -2251174.447 | -2251530.908 | -2249736.597 |

### 6.1.12 The $NH_2$ substituted dicyano structures - Acetonitrile

**Table 23: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NH_2$ (3) conf39 | -2251177.592 | -2251535.561 | -2249735.129 |
| *S*-DHA $NH_2$ (4) conf45 | -2251164.249 | -2251522.893 | -2249724.559 |
| *S*-DHA $NH_2$ (5) conf15 | -2251171.378 | -2251529.307 | -2249730.629 |
| *S*-DHA $NH_2$ (6) conf5 | -2251174.531 | -2251532.281 | -2249735.975 |
| *S*-DHA $NH_2$ (7) conf30 | -2251163.278 | -2251520.270 | -2249722.230 |
| *S*-DHA $NH_2$ (8) conf21 | -2251159.384 | -2251523.754 | -2249725.205 |
| *S*-DHA $NH_2$ (9) conf12 | -2251161.815 | -2251520.905 | -2249718.783 |
| *S*-DHA $NH_2$ (10) conf3 | -2251170.340 | -2251527.311 | -2249730.482 |
| *S*-DHA $NH_2$ (11) conf13 | -2251175.405 | -2251531.922 | -2249737.484 |

### 6.1.13 The $NO_2$ substituted monocyano structures - Vacuum

**Table 24: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400627.122 | -2400918.613 | -2399084.189 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400630.086 | -2400912.987 | -2399085.531 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400658.678 | -2400942.786 | -2399116.278 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400667.699 | -2400950.069 | -2399123.963 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400669.679 | -2400951.891 | -2399127.384 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400660.776 | -2400942.755 | -2399116.688 |
| *anti*-DHA $NO_2$ (8) conf41 | -2400644.535 | -2400930.617 | -2399102.368 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400645.645 | -2400929.821 | -2399099.693 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400662.795 | -2400943.676 | -2399119.245 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400663.790 | -2400944.734 | -2399120.534 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400622.619 | -2400913.415 | -2399079.012 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400635.059 | -2400916.400 | -2399089.614 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400662.283 | -2400943.327 | -2399119.006 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400670.845 | -2400949.691 | -2399126.678 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400673.888 | -2400954.898 | -2399131.191 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400667.232 | -2400947.386 | -2399122.874 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400655.979 | -2400939.082 | -2399115.204 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400649.783 | -2400931.055 | -2399102.791 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400668.009 | -2400945.690 | -2399123.651 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400668.319 | -2400948.436 | -2399124.635 |

### 6.1.14 The $NO_2$ substituted monocyano structures - Cyclohexane

**Table 25: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400640.405 | -2400931.475 | -2399097.341 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400645.700 | -2400928.603 | -2399100.940 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400675.250 | -2400960.057 | -2399133.215 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400685.492 | -2400967.839 | -2399141.688 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400688.798 | -2400970.207 | -2399145.713 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400679.756 | -2400962.189 | -2399134.481 |

| | | | |
|---|---|---|---|
| *anti*-DHA $NO_2$ (8) conf41 | -2400662.572 | -2400948.266 | -2399120.518 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400661.141 | -2400944.816 | -2399115.065 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400679.837 | -2400960.755 | -2399136.064 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400682.182 | -2400962.183 | -2399137.555 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400635.427 | -2400927.952 | -2399092.882 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400651.763 | -2400932.373 | -2399105.067 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400679.708 | -2400959.786 | -2399135.757 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400689.982 | -2400967.579 | -2399144.628 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400693.398 | -2400974.064 | -2399149.520 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400685.269 | -2400965.268 | -2399140.748 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400672.559 | -2400956.570 | -2399132.396 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400665.260 | -2400946.667 | -2399118.746 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400684.999 | -2400963.257 | -2399140.856 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400686.653 | -2400966.090 | -2399142.208 |

#### 6.1.15 The $NO_2$ substituted monocyano structures - Toluene

**Table 26: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400642.888 | -2400934.001 | -2399099.698 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400648.533 | -2400932.169 | -2399104.372 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400678.535 | -2400964.055 | -2399137.088 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400688.853 | -2400971.162 | -2399145.030 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400692.308 | -2400973.835 | -2399149.451 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400683.544 | -2400966.781 | -2399138.041 |
| *anti*-DHA $NO_2$ (8) conf41 | -2400666.027 | -2400951.392 | -2399124.086 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400664.186 | -2400947.672 | -2399118.187 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400683.108 | -2400964.042 | -2399139.267 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400685.865 | -2400965.565 | -2399140.898 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400638.950 | -2400930.772 | -2399095.555 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400654.779 | -2400935.419 | -2399108.084 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400683.085 | -2400963.052 | -2399139.154 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400693.889 | -2400971.071 | -2399148.036 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400697.102 | -2400977.789 | -2399153.188 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400688.850 | -2400969.164 | -2399144.253 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400675.741 | -2400959.692 | -2399135.418 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400668.146 | -2400949.618 | -2399121.739 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400688.160 | -2400966.534 | -2399144.177 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400690.058 | -2400969.529 | -2399145.786 |

### 6.1.16 The $NO_2$ substituted monocyano structures - Dichloromethane

**Table 27: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400656.278 | -2400947.677 | -2399112.571 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400665.111 | -2400949.702 | -2399119.862 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400697.383 | -2400981.664 | -2399153.093 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400706.570 | -2400988.402 | -2399162.831 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400710.910 | -2400993.750 | -2399169.229 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400702.416 | -2400991.886 | -2399157.987 |
| *anti*-DHA $NO_2$ (8) conf41 | -2400684.329 | -2400969.900 | -2399142.861 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400679.343 | -2400962.220 | -2399133.291 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400700.964 | -2400981.074 | -2399155.540 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400704.811 | -2400983.229 | -2399158.604 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400652.674 | -2400945.952 | -2399109.166 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400671.593 | -2400953.787 | -2399124.987 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400700.665 | -2400980.830 | -2399156.144 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400712.674 | -2400989.339 | -2399166.672 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400717.056 | -2400997.515 | -2399173.060 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400707.134 | -2400988.512 | -2399163.036 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400692.933 | -2400977.117 | -2399152.006 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400684.072 | -2400964.987 | -2399137.889 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400706.034 | -2400984.159 | -2399161.980 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400708.305 | -2400987.509 | -2399164.910 |

### 6.1.17 The $NO_2$ substituted monocyano structures - Ethanol

**Table 28: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400660.461 | -2400952.046 | -2399116.743 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400670.682 | -2400955.538 | -2399124.866 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400701.634 | -2400985.290 | -2399160.313 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400711.884 | -2400993.498 | -2399168.279 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400716.549 | -2401000.844 | -2399174.971 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400707.486 | -2400991.342 | -2399163.330 |

| | | | |
|---|---|---|---|
| *anti*-DHA $NO_2$ (8) conf41 | -2400690.263 | -2400977.500 | -2399148.556 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400683.922 | -2400966.636 | -2399138.025 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400705.916 | -2400985.978 | -2399160.311 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400709.447 | -2400988.265 | -2399164.062 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400656.940 | -2400949.478 | -2399113.380 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400676.542 | -2400958.928 | -2399129.899 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400705.982 | -2400986.700 | -2399161.917 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400718.196 | -2400995.309 | -2399172.461 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400722.908 | -2401004.365 | -2399179.372 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400712.162 | -2400994.587 | -2399169.156 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400698.271 | -2400984.127 | -2399157.178 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400688.737 | -2400969.831 | -2399142.657 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400712.070 | -2400991.324 | -2399167.210 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400713.958 | -2400992.815 | -2399170.537 |

#### 6.1.18 The $NO_2$ substituted monocyano structures - Acetonitrile

**Table 29: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *anti*-DHA $NO_2$ (1) conf57 | -2400661.238 | -2400952.858 | -2399117.517 |
| *anti*-DHA $NO_2$ (3) conf42 | -2400671.790 | -2400956.405 | -2399125.801 |
| *anti*-DHA $NO_2$ (4) conf39 | -2400702.642 | -2400986.209 | -2399159.961 |
| *anti*-DHA $NO_2$ (5) conf42 | -2400712.882 | -2400994.414 | -2399169.224 |
| *anti*-DHA $NO_2$ (6) conf21 | -2400717.623 | -2401001.382 | -2399175.993 |
| *anti*-DHA $NO_2$ (7) conf20 | -2400708.355 | -2400992.424 | -2399164.246 |
| *anti*-DHA $NO_2$ (8) conf41 | -2400691.384 | -2400978.937 | -2399149.638 |
| *anti*-DHA $NO_2$ (9) conf18 | -2400684.765 | -2400967.450 | -2399138.910 |
| *anti*-DHA $NO_2$ (10) conf15 | -2400706.764 | -2400986.852 | -2399161.206 |
| *anti*-DHA $NO_2$ (11) conf22 | -2400710.316 | -2400989.355 | -2399165.239 |
| *syn*-DHA $NO_2$ (1) conf72 | -2400657.712 | -2400950.137 | -2399114.154 |
| *syn*-DHA $NO_2$ (3) conf42 | -2400677.414 | -2400959.957 | -2399130.858 |
| *syn*-DHA $NO_2$ (4) conf39 | -2400706.990 | -2400987.821 | -2399162.991 |
| *syn*-DHA $NO_2$ (5) conf42 | -2400719.259 | -2400996.433 | -2399173.556 |
| *syn*-DHA $NO_2$ (6) conf21 | -2400723.959 | -2401005.583 | -2399180.527 |
| *syn*-DHA $NO_2$ (7) conf20 | -2400713.141 | -2400995.181 | -2399170.608 |
| *syn*-DHA $NO_2$ (8) conf41 | -2400699.250 | -2400988.475 | -2399158.129 |
| *syn*-DHA $NO_2$ (9) conf18 | -2400689.596 | -2400970.748 | -2399143.534 |
| *syn*-DHA $NO_2$ (10) conf15 | -2400712.748 | -2400993.075 | -2399167.906 |
| *syn*-DHA $NO_2$ (11) conf22 | -2400714.987 | -2400993.923 | -2399171.556 |

### 6.1.19 The $NO_2$ substituted dicyano structures - Vacuum

**Table 30: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642727.292 | -2643050.940 | -2641009.511 |
| *S*-DHA $NO_2$ (4) conf45 | -2642756.157 | -2643081.309 | -2641041.658 |
| *S*-DHA $NO_2$ (5) conf37 | -2642768.583 | -2643091.197 | -2641050.947 |
| *S*-DHA $NO_2$ (6) conf45 | -2642767.276 | -2643089.469 | -2641052.580 |
| *S*-DHA $NO_2$ (7) conf30 | -2642759.937 | -2643083.231 | -2641043.585 |
| *S*-DHA $NO_2$ (8) conf21 | -2642730.752 | -2643062.261 | -2641019.002 |
| *S*-DHA $NO_2$ (9) conf12 | -2642741.588 | -2643069.946 | -2641023.888 |
| *S*-DHA $NO_2$ (10) conf12 | -2642765.514 | -2643086.746 | -2641049.379 |
| *S*-DHA $NO_2$ (11) conf9 | -2642764.934 | -2643086.505 | -2641049.526 |

### 6.1.20 The $NO_2$ substituted dicyano structures - Cyclohexane

**Table 31: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642744.213 | -2643065.144 | -2641024.991 |
| *S*-DHA $NO_2$ (4) conf45 | -2642773.065 | -2643097.989 | -2641058.443 |
| *S*-DHA $NO_2$ (5) conf37 | -2642784.648 | -2643108.827 | -2641069.425 |
| *S*-DHA $NO_2$ (6) conf45 | -2642786.457 | -2643108.281 | -2641071.231 |
| *S*-DHA $NO_2$ (7) conf30 | -2642779.298 | -2643100.669 | -2641061.924 |
| *S*-DHA $NO_2$ (8) conf21 | -2642749.800 | -2643082.076 | -2641037.733 |
| *S*-DHA $NO_2$ (9) conf12 | -2642759.659 | -2643086.368 | -2641041.169 |
| *S*-DHA $NO_2$ (10) conf12 | -2642783.680 | -2643105.025 | -2641067.926 |
| *S*-DHA $NO_2$ (11) conf9 | -2642783.903 | -2643104.791 | -2641067.763 |

### 6.1.21 The $NO_2$ substituted dicyano structures - Toluene

**Table 32: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642747.358 | -2643068.147 | -2641028.003 |
| *S*-DHA $NO_2$ (4) conf45 | -2642776.354 | -2643101.208 | -2641061.646 |
| *S*-DHA $NO_2$ (5) conf37 | -2642788.088 | -2643111.954 | -2641072.820 |
| *S*-DHA $NO_2$ (6) conf45 | -2642790.083 | -2643111.991 | -2641074.873 |
| *S*-DHA $NO_2$ (7) conf30 | -2642782.569 | -2643104.159 | -2641065.563 |
| *S*-DHA $NO_2$ (8) conf21 | -2642753.513 | -2643085.586 | -2641041.414 |
| *S*-DHA $NO_2$ (9) conf12 | -2642763.140 | -2643089.411 | -2641044.296 |
| *S*-DHA $NO_2$ (10) conf12 | -2642787.158 | -2643108.470 | -2641071.344 |
| *S*-DHA $NO_2$ (11) conf9 | -2642787.647 | -2643108.262 | -2641071.255 |

### 6.1.22 The $NO_2$ substituted dicyano structures - Dichloromethane

**Table 33: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642762.119 | -2643085.021 | -2641043.637 |
| *S*-DHA $NO_2$ (4) conf45 | -2642793.783 | -2643117.764 | -2641077.685 |
| *S*-DHA $NO_2$ (5) conf37 | -2642806.939 | -2643129.873 | -2641090.227 |
| *S*-DHA $NO_2$ (6) conf45 | -2642809.410 | -2643131.493 | -2641094.220 |
| *S*-DHA $NO_2$ (7) conf30 | -2642801.830 | -2643123.351 | -2641085.897 |
| *S*-DHA $NO_2$ (8) conf21 | -2642773.354 | -2643104.209 | -2641061.136 |
| *S*-DHA $NO_2$ (9) conf12 | -2642781.448 | -2643106.031 | -2641061.827 |
| *S*-DHA $NO_2$ (10) conf12 | -2642804.970 | -2643125.811 | -2641088.111 |
| *S*-DHA $NO_2$ (11) conf9 | -2642805.936 | -2643126.202 | -2641089.053 |

### 6.1.23 The $NO_2$ substituted dicyano structures - Ethanol

**Table 34: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642767.693 | -2643089.700 | -2641048.200 |
| *S*-DHA $NO_2$ (4) conf45 | -2642799.194 | -2643122.479 | -2641082.463 |
| *S*-DHA $NO_2$ (5) conf37 | -2642813.159 | -2643135.389 | -2641095.832 |
| *S*-DHA $NO_2$ (6) conf45 | -2642815.443 | -2643137.243 | -2641100.138 |
| *S*-DHA $NO_2$ (7) conf30 | -2642807.931 | -2643129.293 | -2641092.238 |
| *S*-DHA $NO_2$ (8) conf21 | -2642779.537 | -2643110.166 | -2641067.230 |
| *S*-DHA $NO_2$ (9) conf12 | -2642786.746 | -2643111.274 | -2641066.928 |
| *S*-DHA $NO_2$ (10) conf12 | -2642810.205 | -2643130.679 | -2641092.892 |
| *S*-DHA $NO_2$ (11) conf9 | -2642811.224 | -2643131.595 | -2641094.520 |

### 6.1.24 The $NO_2$ substituted dicyano structures - Acetonitrile

**Table 35: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *S*-DHA $NO_2$ (3) conf39 | -2642768.806 | -2643090.561 | -2641049.051 |
| *S*-DHA $NO_2$ (4) conf45 | -2642800.212 | -2643123.380 | -2641083.369 |
| *S*-DHA $NO_2$ (5) conf37 | -2642814.306 | -2643136.418 | -2641096.883 |
| *S*-DHA $NO_2$ (6) conf45 | -2642816.554 | -2643138.301 | -2641101.217 |
| *S*-DHA $NO_2$ (7) conf30 | -2642809.066 | -2643130.327 | -2641093.651 |
| *S*-DHA $NO_2$ (8) conf21 | -2642780.681 | -2643111.269 | -2641068.349 |
| *S*-DHA $NO_2$ (9) conf12 | -2642787.702 | -2643112.235 | -2641067.879 |
| *S*-DHA $NO_2$ (10) conf12 | -2642811.155 | -2643131.543 | -2641093.753 |
| *S*-DHA $NO_2$ (11) conf9 | -2642812.211 | -2643132.572 | -2641095.541 |

## 6.2 VHF Structures

### 6.2.1 The $NH_2$ substituted monocyano structures - Vacuum

**Table 36: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008958.466 | -2009271.770 | -2007683.114 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008954.814 | -2009273.739 | -2007676.687 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2008981.479 | -2009295.995 | -2007709.550 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2008976.832 | -2009285.165 | -2007701.860 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2008981.804 | -2009290.576 | -2007708.755 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2008980.597 | -2009289.340 | -2007707.568 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2008980.544 | -2009290.335 | -2007706.092 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2008974.072 | -2009286.953 | -2007700.350 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2008976.078 | -2009285.449 | -2007700.739 |
| *E-trans*-VHF $NH_2$ (11) conf51 | -2008977.504 | -2009286.381 | -2007702.346 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008959.955 | -2009273.419 | -2007685.259 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008958.335 | -2009274.277 | -2007678.527 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2008971.623 | -2009286.016 | -2007699.051 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2008970.502 | -2009280.597 | -2007695.414 |
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2008975.616 | -2009285.740 | -2007702.818 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2008976.160 | -2009286.478 | -2007703.519 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2008975.325 | -2009286.651 | -2007701.385 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2008971.331 | -2009285.262 | -2007697.087 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2008971.295 | -2009281.637 | -2007696.428 |
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2008972.279 | -2009281.605 | -2007697.079 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008959.482 | -2009272.095 | -2007682.439 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008958.600 | -2009273.353 | -2007677.968 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2008974.235 | -2009283.687 | -2007699.770 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2008971.917 | -2009278.657 | -2007695.464 |
| *E-cis*-VHF $NH_2$ (6) conf35 | -2008976.926 | -2009286.930 | -2007702.023 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2008979.153 | -2009288.930 | -2007704.764 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2008977.753 | -2009288.471 | -2007703.186 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2008966.619 | -2009278.840 | -2007690.846 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2008970.998 | -2009280.282 | -2007693.661 |
| *E-cis*-VHF $NH_2$ (11) conf3 | -2008973.786 | -2009280.754 | -2007696.780 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008953.394 | -2009266.191 | -2007675.497 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008957.700 | -2009272.006 | -2007676.319 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2008973.437 | -2009283.188 | -2007698.549 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2008971.828 | -2009279.098 | -2007694.664 |

| | | | |
|---|---|---|---|
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2008976.798 | -2009282.188 | -2007701.432 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2008976.989 | -2009282.516 | -2007701.876 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2008970.289 | -2009274.779 | -2007692.736 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2008967.039 | -2009277.785 | -2007689.596 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2008971.943 | -2009279.245 | -2007693.947 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2008973.910 | -2009280.040 | -2007696.425 |

### 6.2.2 The $NH_2$ substituted monocyano structures - Cyclohexane

**Table 37: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008972.463 | -2009286.449 | -2007697.764 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008969.210 | -2009289.256 | -2007691.794 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2008995.980 | -2009310.816 | -2007724.978 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2008994.304 | -2009302.987 | -2007720.745 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2008999.773 | -2009307.852 | -2007728.254 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2008998.156 | -2009307.264 | -2007726.960 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2008998.004 | -2009307.653 | -2007724.342 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2008989.434 | -2009301.711 | -2007716.061 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2008992.679 | -2009302.289 | -2007718.543 |
| *E-trans*-VHF $NH_2$ (11) conf51 | -2008995.024 | -2009304.870 | -2007720.462 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008973.022 | -2009287.142 | -2007698.749 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008972.261 | -2009288.993 | -2007692.521 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2008988.447 | -2009302.651 | -2007716.980 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2008988.799 | -2009299.099 | -2007715.977 |
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2008994.677 | -2009304.316 | -2007723.725 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2008993.711 | -2009305.090 | -2007722.720 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2008992.979 | -2009307.083 | -2007720.417 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2008987.552 | -2009300.561 | -2007714.119 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2008988.387 | -2009297.991 | -2007714.699 |
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2008989.642 | -2009299.550 | -2007715.350 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008973.030 | -2009286.095 | -2007696.588 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008972.757 | -2009287.722 | -2007692.148 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2008988.864 | -2009299.390 | -2007716.187 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2008988.967 | -2009296.389 | -2007713.717 |
| *E-cis*-VHF $NH_2$ (6) conf35 | -2008994.591 | -2009305.571 | -2007721.459 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2008995.284 | -2009305.660 | -2007722.630 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2008993.168 | -2009304.221 | -2007719.301 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2008981.589 | -2009294.436 | -2007706.804 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2008987.268 | -2009296.494 | -2007711.018 |

| | | | |
|---|---|---|---|
| *E-cis*-VHF $NH_2$ (11) conf3 | -2008991.086 | -2009298.823 | -2007715.061 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008967.251 | -2009280.773 | -2007689.557 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008972.303 | -2009286.704 | -2007691.516 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2008989.907 | -2009298.986 | -2007716.014 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2008989.920 | -2009296.841 | -2007713.691 |
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2008994.942 | -2009299.879 | -2007720.982 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2008994.147 | -2009299.721 | -2007720.737 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2008989.135 | -2009293.887 | -2007713.969 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2008983.535 | -2009294.782 | -2007705.683 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2008988.822 | -2009296.405 | -2007712.089 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2008991.259 | -2009297.114 | -2007714.449 |

### 6.2.3 The $NH_2$ substituted monocyano structures - Toluene

**Table 38: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008975.199 | -2009289.319 | -2007700.679 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008972.001 | -2009292.181 | -2007694.795 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2008998.786 | -2009313.550 | -2007727.950 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2008997.862 | -2009306.440 | -2007724.439 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2009003.276 | -2009311.236 | -2007732.077 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2009001.535 | -2009310.814 | -2007730.748 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2009001.370 | -2009311.313 | -2007727.958 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2008992.288 | -2009304.568 | -2007719.117 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2008995.835 | -2009305.571 | -2007721.950 |
| *E-trans*-VHF $NH_2$ (11) conf51 | -2008998.411 | -2009308.417 | -2007723.885 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008975.501 | -2009289.778 | -2007701.359 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008975.096 | -2009291.844 | -2007695.228 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2008991.718 | -2009306.030 | -2007720.506 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2008992.377 | -2009302.441 | -2007720.168 |
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2008998.574 | -2009307.852 | -2007727.923 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2008997.156 | -2009308.703 | -2007726.710 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2008996.465 | -2009310.898 | -2007724.216 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2008990.757 | -2009303.594 | -2007717.576 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2008991.682 | -2009301.341 | -2007718.259 |
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2008992.992 | -2009303.013 | -2007718.923 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008975.679 | -2009288.794 | -2007699.316 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008975.516 | -2009290.513 | -2007694.926 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2008990.574 | -2009302.575 | -2007719.524 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2008992.414 | -2009299.886 | -2007717.390 |

| | | | |
|---|---|---|---|
| *E-cis*-VHF $NH_2$ (6) conf35 | -2008998.056 | -2009308.671 | -2007725.182 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2008998.471 | -2009308.810 | -2007726.240 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2008996.688 | -2009307.298 | -2007722.557 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2008984.580 | -2009297.487 | -2007709.928 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2008990.524 | -2009299.640 | -2007714.350 |
| *E-cis*-VHF $NH_2$ (11) conf3 | -2008994.362 | -2009302.415 | -2007718.611 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008970.013 | -2009283.637 | -2007692.340 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008975.230 | -2009289.684 | -2007694.732 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2008993.173 | -2009302.016 | -2007719.535 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2008993.317 | -2009300.296 | -2007717.406 |
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2008998.773 | -2009303.389 | -2007724.867 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2008997.565 | -2009303.179 | -2007724.537 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2008992.976 | -2009297.673 | -2007718.157 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2008986.848 | -2009297.463 | -2007709.022 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2008991.857 | -2009299.721 | -2007715.389 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2008994.683 | -2009300.469 | -2007718.020 |

### 6.2.4 The $NH_2$ substituted monocyano structures - Dichloromethane

**Table 39: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008990.106 | -2009304.463 | -2007716.405 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008986.927 | -2009307.440 | -2007710.768 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2009013.463 | -2009328.132 | -2007743.855 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2009015.952 | -2009325.913 | -2007744.272 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2009021.673 | -2009329.633 | -2007752.719 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2009020.092 | -2009329.618 | -2007753.540 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2009018.961 | -2009331.030 | -2007747.554 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2009007.311 | -2009319.903 | -2007735.214 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2009012.163 | -2009323.261 | -2007739.310 |
| *E-trans*-VHF $NH_2$ (11) conf51 | -2009015.524 | -2009325.761 | -2007741.923 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008988.576 | -2009303.402 | -2007714.814 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008990.238 | -2009307.017 | -2007709.731 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2009008.732 | -2009322.972 | -2007739.533 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2009011.769 | -2009321.137 | -2007741.983 |
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2009019.299 | -2009327.990 | -2007751.414 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2009016.422 | -2009327.530 | -2007748.741 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2009015.240 | -2009329.155 | -2007744.727 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2009007.091 | -2009319.987 | -2007735.041 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2009008.561 | -2009318.992 | -2007736.251 |

| | | | |
|---|---|---|---|
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2009010.766 | -2009320.872 | -2007738.173 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008989.710 | -2009303.788 | -2007713.877 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008990.398 | -2009306.088 | -2007710.243 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2009007.277 | -2009320.948 | -2007737.304 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2009010.948 | -2009318.861 | -2007737.396 |
| *E-cis*-VHF $NH_2$ (6) conf35 | -2009016.582 | -2009326.275 | -2007745.879 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2009016.931 | -2009325.341 | -2007745.315 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2009014.038 | -2009323.645 | -2007741.592 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2009000.582 | -2009313.865 | -2007726.671 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2009008.267 | -2009316.718 | -2007732.263 |
| *E-cis*-VHF $NH_2$ (11) conf3 | -2009012.111 | -2009322.261 | -2007737.769 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008984.973 | -2009298.524 | -2007707.639 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008991.435 | -2009307.314 | -2007710.868 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2009009.538 | -2009318.336 | -2007738.347 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2009011.819 | -2009319.328 | -2007738.399 |
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2009017.422 | -2009322.285 | -2007747.720 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2009015.876 | -2009322.476 | -2007746.050 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2009013.279 | -2009319.189 | -2007740.542 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2009003.292 | -2009314.363 | -2007727.516 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2009007.865 | -2009316.687 | -2007732.526 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2009012.399 | -2009317.853 | -2007736.947 |

### 6.2.5 The $NH_2$ substituted monocyano structures - Ethanol

**Table 40: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008994.845 | -2009309.375 | -2007721.357 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008991.737 | -2009312.077 | -2007715.660 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2009017.868 | -2009332.642 | -2007748.804 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2009021.386 | -2009332.587 | -2007750.290 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2009027.236 | -2009335.257 | -2007759.849 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2009025.824 | -2009334.995 | -2007758.151 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2009024.471 | -2009336.431 | -2007753.719 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2009011.940 | -2009324.621 | -2007740.108 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2009017.028 | -2009327.402 | -2007744.307 |
| *E-trans*-VHF $NH_2$ (11) conf51 | -2009020.313 | -2009330.736 | -2007747.428 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008992.417 | -2009307.290 | -2007718.760 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008994.984 | -2009311.037 | -2007714.179 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2009013.904 | -2009328.244 | -2007745.640 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2009018.094 | -2009327.323 | -2007748.523 |

| | | | |
|---|---|---|---|
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2009025.810 | -2009334.766 | -2007759.437 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2009022.634 | -2009333.763 | -2007756.035 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2009021.426 | -2009335.417 | -2007751.527 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2009012.006 | -2009325.270 | -2007740.190 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2009013.791 | -2009324.241 | -2007741.726 |
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2009016.164 | -2009326.480 | -2007744.115 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008994.055 | -2009308.535 | -2007718.364 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008994.824 | -2009311.956 | -2007715.187 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2009011.901 | -2009327.570 | -2007743.044 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2009016.689 | -2009324.991 | -2007743.810 |
| *E-cis*-VHF $NH_2$ (6) conf35 | -2009022.463 | -2009331.692 | -2007753.215 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2009022.631 | -2009330.694 | -2007751.729 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2009019.328 | -2009328.945 | -2007747.252 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2009005.591 | -2009319.024 | -2007731.778 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2009013.686 | -2009322.329 | -2007737.732 |
| *E-cis*-VHF $NH_2$ (11) conf3 | -2009017.942 | -2009328.538 | -2007743.973 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008989.594 | -2009303.034 | -2007712.569 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008996.633 | -2009310.255 | -2007716.075 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2009014.421 | -2009323.482 | -2007744.047 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2009017.774 | -2009325.585 | -2007745.567 |
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2009023.626 | -2009328.701 | -2007756.216 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2009021.765 | -2009328.370 | -2007753.559 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2009019.840 | -2009326.987 | -2007747.806 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2009008.036 | -2009320.126 | -2007732.584 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2009012.749 | -2009321.885 | -2007737.522 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2009017.157 | -2009322.833 | -2007742.550 |

### 6.2.6 The $NH_2$ substituted monocyano structures - Acetonitrile

**Table 41: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (1) conf8 | -2008995.696 | -2009310.297 | -2007722.276 |
| *E-trans*-VHF $NH_2$ (3) conf65 | -2008992.645 | -2009312.930 | -2007716.560 |
| *E-trans*-VHF $NH_2$ (4) conf17 | -2009018.669 | -2009333.469 | -2007749.715 |
| *E-trans*-VHF $NH_2$ (5) conf46 | -2009022.382 | -2009333.782 | -2007751.364 |
| *E-trans*-VHF $NH_2$ (6) conf22 | -2009028.263 | -2009336.276 | -2007761.420 |
| *E-trans*-VHF $NH_2$ (7) conf37 | -2009026.890 | -2009335.932 | -2007759.453 |
| *E-trans*-VHF $NH_2$ (8) conf26 | -2009025.490 | -2009337.384 | -2007754.858 |
| *E-trans*-VHF $NH_2$ (9) conf31 | -2009012.780 | -2009325.485 | -2007741.017 |
| *E-trans*-VHF $NH_2$ (10) conf50 | -2009017.918 | -2009328.150 | -2007745.204 |

| | | | |
|---|---|---|---|
| *E-trans*-VHF $NH_2$ (11) conf51 | -2009021.182 | -2009331.655 | -2007748.436 |
| *Z-trans*-VHF $NH_2$ (1) conf38 | -2008993.110 | -2009307.968 | -2007719.480 |
| *Z-trans*-VHF $NH_2$ (3) conf20 | -2008996.019 | -2009311.759 | -2007715.072 |
| *Z-trans*-VHF $NH_2$ (4) conf27 | -2009014.886 | -2009329.242 | -2007746.785 |
| *Z-trans*-VHF $NH_2$ (5) conf71 | -2009019.344 | -2009328.496 | -2007749.810 |
| *Z-trans*-VHF $NH_2$ (6) conf71 | -2009027.092 | -2009336.034 | -2007761.081 |
| *Z-trans*-VHF $NH_2$ (7) conf27 | -2009023.810 | -2009334.924 | -2007757.489 |
| *Z-trans*-VHF $NH_2$ (8) conf65 | -2009022.594 | -2009336.583 | -2007752.821 |
| *Z-trans*-VHF $NH_2$ (9) conf25 | -2009013.001 | -2009326.265 | -2007741.224 |
| *Z-trans*-VHF $NH_2$ (10) conf26 | -2009014.778 | -2009325.230 | -2007742.739 |
| *Z-trans*-VHF $NH_2$ (11) conf25 | -2009017.146 | -2009327.520 | -2007745.199 |
| *E-cis*-VHF $NH_2$ (1) conf50 | -2008994.858 | -2009309.396 | -2007719.188 |
| *E-cis*-VHF $NH_2$ (3) conf19 | -2008995.633 | -2009313.221 | -2007716.098 |
| *E-cis*-VHF $NH_2$ (4) conf55 | -2009012.720 | -2009328.265 | -2007744.120 |
| *E-cis*-VHF $NH_2$ (5) conf53 | -2009017.664 | -2009326.152 | -2007745.013 |
| *E-cis*-VHF $NH_2$ (6) conf35 | -2009023.518 | -2009332.742 | -2007754.738 |
| *E-cis*-VHF $NH_2$ (7) conf29 | -2009023.608 | -2009331.749 | -2007752.968 |
| *E-cis*-VHF $NH_2$ (8) conf30 | -2009020.355 | -2009329.980 | -2007748.310 |
| *E-cis*-VHF $NH_2$ (9) conf47 | -2009006.510 | -2009319.985 | -2007732.718 |
| *E-cis*-VHF $NH_2$ (10) conf65 | -2009014.613 | -2009323.390 | -2007738.725 |
| *E-cis*-VHF $NH_2$ (11) conf3 | -2009019.045 | -2009329.591 | -2007745.144 |
| *Z-cis*-VHF $NH_2$ (1) conf45 | -2008990.442 | -2009303.856 | -2007713.486 |
| *Z-cis*-VHF $NH_2$ (3) conf64 | -2008997.615 | -2009311.087 | -2007717.009 |
| *Z-cis*-VHF $NH_2$ (4) conf32 | -2009015.319 | -2009324.430 | -2007745.086 |
| *Z-cis*-VHF $NH_2$ (5) conf73 | -2009018.892 | -2009326.766 | -2007746.911 |
| *Z-cis*-VHF $NH_2$ (6) conf43 | -2009024.776 | -2009329.880 | -2007757.694 |
| *Z-cis*-VHF $NH_2$ (7) conf51 | -2009022.880 | -2009329.337 | -2007754.984 |
| *Z-cis*-VHF $NH_2$ (8) conf16 | -2009021.087 | -2009328.791 | -2007749.324 |
| *Z-cis*-VHF $NH_2$ (9) conf1 | -2009008.971 | -2009321.166 | -2007733.584 |
| *Z-cis*-VHF $NH_2$ (10) conf53 | -2009013.662 | -2009322.712 | -2007738.457 |
| *Z-cis*-VHF $NH_2$ (11) conf55 | -2009017.994 | -2009323.881 | -2007743.553 |

### 6.2.7 The $NH_2$ substituted dicyano structures - Vacuum

**Table 42: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251082.339 | -2251435.600 | -2249636.132 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251105.945 | -2251454.905 | -2249669.229 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251110.161 | -2251454.262 | -2249667.488 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251113.228 | -2251457.602 | -2249672.716 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251115.570 | -2251461.080 | -2249675.628 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251116.969 | -2251463.968 | -2249675.016 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251099.809 | -2251450.421 | -2249657.320 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251104.790 | -2251449.533 | -2249660.783 |
| *cis*-VHF $NH_2$ (11) conf54 | -2251109.560 | -2251455.677 | -2249666.449 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251082.092 | -2251434.736 | -2249640.924 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251116.436 | -2251465.977 | -2249678.865 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251118.377 | -2251463.257 | -2249676.801 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251121.945 | -2251465.804 | -2249682.514 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251120.779 | -2251465.237 | -2249682.210 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251122.548 | -2251468.432 | -2249681.572 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251113.162 | -2251462.553 | -2249672.141 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251113.338 | -2251458.778 | -2249671.540 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251116.040 | -2251460.842 | -2249674.191 |

### 6.2.8 The $NH_2$ substituted dicyano structures - Cyclohexane

**Table 43: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251096.963 | -2251453.540 | -2249656.585 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251129.551 | -2251476.734 | -2249694.297 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251136.435 | -2251480.008 | -2249695.072 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251139.942 | -2251483.085 | -2249701.439 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251140.783 | -2251484.051 | -2249703.080 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251141.523 | -2251486.642 | -2249700.131 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251120.503 | -2251470.186 | -2249678.497 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251126.392 | -2251470.774 | -2249683.675 |

| | | | |
|---|---|---|---|
| *cis*-VHF $NH_2$ (11) conf54 | -2251132.181 | -2251477.196 | -2249690.722 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251098.788 | -2251450.631 | -2249660.631 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251137.905 | -2251485.844 | -2249701.901 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251146.774 | -2251488.968 | -2249705.997 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251149.489 | -2251491.284 | -2249711.626 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251150.699 | -2251491.135 | -2249711.731 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251150.030 | -2251495.346 | -2249708.774 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251134.523 | -2251482.035 | -2249694.040 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251135.946 | -2251480.281 | -2249694.741 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251139.493 | -2251483.145 | -2249698.842 |

### 6.2.9 The $NH_2$ substituted dicyano structures - Toluene

**Table 44: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251100.733 | -2251456.861 | -2249660.615 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251134.639 | -2251481.234 | -2249699.488 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251142.116 | -2251485.217 | -2249700.985 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251145.579 | -2251488.758 | -2249706.601 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251145.850 | -2251488.785 | -2249708.131 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251146.480 | -2251491.376 | -2249705.498 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251124.434 | -2251473.974 | -2249682.669 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251130.635 | -2251474.956 | -2249688.051 |
| *cis*-VHF $NH_2$ (11) conf54 | -2251136.624 | -2251481.425 | -2249695.618 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251101.915 | -2251454.120 | -2249664.469 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251142.255 | -2251489.838 | -2249706.401 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251152.540 | -2251495.057 | -2249712.138 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251155.141 | -2251497.509 | -2249717.000 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251154.104 | -2251496.611 | -2249716.798 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251156.751 | -2251499.003 | -2249714.595 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251138.569 | -2251485.989 | -2249698.320 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251140.410 | -2251484.495 | -2249699.291 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251144.057 | -2251487.493 | -2249703.728 |

### 6.2.10 The $NH_2$ substituted dicyano structures - Dichloromethane

**Table 45: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251121.125 | -2251474.576 | -2249682.735 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251162.897 | -2251508.907 | -2249727.846 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251170.971 | -2251513.627 | -2249731.089 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251172.814 | -2251515.515 | -2249735.457 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251172.609 | -2251516.016 | -2249735.814 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251175.030 | -2251519.172 | -2249734.289 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251145.797 | -2251493.899 | -2249705.718 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251152.558 | -2251496.462 | -2249711.174 |
| *cis*-VHF $NH_2$ (11) conf54 | -2251159.778 | -2251503.918 | -2249720.258 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251120.871 | -2251472.438 | -2249685.513 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251166.113 | -2251511.971 | -2249732.630 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251181.677 | -2251525.670 | -2249741.567 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251183.198 | -2251525.760 | -2249746.316 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251181.688 | -2251524.591 | -2249745.734 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251184.216 | -2251525.124 | -2249743.673 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251160.805 | -2251506.620 | -2249721.511 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251163.000 | -2251507.189 | -2249723.351 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251167.757 | -2251510.524 | -2249728.668 |

### 6.2.11 The $NH_2$ substituted dicyano structures - Ethanol

**Table 46: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251127.642 | -2251480.328 | -2249689.338 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251172.068 | -2251517.820 | -2249736.337 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251180.383 | -2251522.677 | -2249740.388 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251182.200 | -2251524.552 | -2249744.943 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251181.688 | -2251524.473 | -2249744.739 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251183.775 | -2251527.600 | -2249743.184 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251152.253 | -2251500.064 | -2249712.852 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251159.232 | -2251502.624 | -2249718.344 |

| | | | |
|---|---|---|---|
| *cis*-VHF $NH_2$ (11) conf54 | -2251166.828 | -2251511.251 | -2249727.557 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251126.936 | -2251478.109 | -2249691.882 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251176.187 | -2251519.046 | -2249742.452 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251190.313 | -2251533.528 | -2249750.436 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251192.384 | -2251534.274 | -2249755.915 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251191.394 | -2251533.634 | -2249755.508 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251193.860 | -2251534.314 | -2249753.025 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251167.859 | -2251512.984 | -2249729.012 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251170.060 | -2251514.541 | -2249730.374 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251174.599 | -2251517.453 | -2249735.909 |

### 6.2.12 The $NH_2$ substituted dicyano structures - Acetonitrile

**Table 47: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NH_2$ (3) conf1 | -2251128.818 | -2251481.420 | -2249690.582 |
| *cis*-VHF $NH_2$ (4) conf30 | -2251173.693 | -2251519.424 | -2249737.891 |
| *cis*-VHF $NH_2$ (5) conf42 | -2251182.137 | -2251524.384 | -2249742.137 |
| *cis*-VHF $NH_2$ (6) conf28 | -2251183.964 | -2251526.261 | -2249746.705 |
| *cis*-VHF $NH_2$ (7) conf42 | -2251183.418 | -2251526.090 | -2249746.416 |
| *cis*-VHF $NH_2$ (8) conf39 | -2251185.411 | -2251529.217 | -2249744.799 |
| *cis*-VHF $NH_2$ (9) conf10 | -2251153.487 | -2251501.232 | -2249714.128 |
| *cis*-VHF $NH_2$ (10) conf68 | -2251160.492 | -2251503.750 | -2249719.673 |
| *cis*-VHF $NH_2$ (11) conf54 | -2251168.130 | -2251512.569 | -2249728.902 |
| *trans*-VHF $NH_2$ (3) conf32 | -2251128.083 | -2251479.210 | -2249693.095 |
| *trans*-VHF $NH_2$ (4) conf11 | -2251177.994 | -2251520.338 | -2249743.998 |
| *trans*-VHF $NH_2$ (5) conf66 | -2251191.922 | -2251535.164 | -2249752.095 |
| *trans*-VHF $NH_2$ (6) conf13 | -2251194.135 | -2251535.899 | -2249757.701 |
| *trans*-VHF $NH_2$ (7) conf76 | -2251193.277 | -2251535.440 | -2249757.336 |
| *trans*-VHF $NH_2$ (8) conf41 | -2251195.558 | -2251536.036 | -2249754.889 |
| *trans*-VHF $NH_2$ (9) conf13 | -2251169.148 | -2251514.719 | -2249730.440 |
| *trans*-VHF $NH_2$ (10) conf40 | -2251171.388 | -2251515.880 | -2249731.716 |
| *trans*-VHF $NH_2$ (11) conf76 | -2251175.838 | -2251518.710 | -2249737.261 |

### 6.2.13 The $NO_2$ substituted monocyano structures - Vacuum

**Table 48: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400578.524 | -2400857.197 | -2399034.048 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400585.190 | -2400863.386 | -2399033.945 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400593.978 | -2400874.187 | -2399038.409 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400610.947 | -2400888.937 | -2399060.891 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400614.404 | -2400889.662 | -2399063.269 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400615.481 | -2400891.626 | -2399064.217 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400611.314 | -2400894.033 | -2399060.177 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400594.637 | -2400876.960 | -2399044.156 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400615.252 | -2400891.045 | -2399065.475 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400615.680 | -2400890.037 | -2399065.793 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400578.524 | -2400857.182 | -2399034.048 |
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400589.816 | -2400871.485 | -2399038.191 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400591.008 | -2400872.541 | -2399036.825 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400606.491 | -2400882.119 | -2399056.527 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400608.560 | -2400886.677 | -2399058.018 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400609.450 | -2400886.997 | -2399058.496 |
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400605.052 | -2400884.384 | -2399054.046 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400591.857 | -2400878.283 | -2399042.342 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400611.506 | -2400888.475 | -2399061.222 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400610.676 | -2400887.286 | -2399060.780 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400570.301 | -2400849.253 | -2399024.596 |
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400589.536 | -2400867.492 | -2399038.002 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400596.391 | -2400877.897 | -2399040.141 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400609.271 | -2400884.109 | -2399056.595 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400611.191 | -2400887.485 | -2399058.354 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400609.744 | -2400884.524 | -2399057.021 |
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400608.360 | -2400887.186 | -2399055.322 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400591.531 | -2400872.688 | -2399039.790 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400611.283 | -2400884.697 | -2399059.862 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400611.185 | -2400884.975 | -2399059.497 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400570.299 | -2400849.253 | -2399024.598 |
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400592.313 | -2400872.315 | -2399043.103 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400594.017 | -2400872.664 | -2399038.437 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400607.392 | -2400880.819 | -2399054.185 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400610.253 | -2400882.893 | -2399056.737 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400609.923 | -2400883.216 | -2399056.073 |

| | | | |
|---|---|---|---|
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400606.087 | -2400881.447 | -2399052.736 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400595.614 | -2400873.969 | -2399042.465 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400612.661 | -2400884.350 | -2399060.240 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400611.230 | -2400882.153 | -2399059.042 |

### 6.2.14 The $NO_2$ substituted monocyano structures - Cyclohexane

**Table 49: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400600.597 | -2400876.411 | -2399056.811 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400604.475 | -2400881.218 | -2399053.159 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400611.556 | -2400891.473 | -2399055.613 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400627.976 | -2400904.871 | -2399078.153 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400631.890 | -2400907.053 | -2399081.078 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400632.775 | -2400908.922 | -2399081.178 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400627.910 | -2400908.791 | -2399076.912 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400612.598 | -2400894.052 | -2399062.298 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400633.759 | -2400908.305 | -2399083.880 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400634.237 | -2400907.809 | -2399084.105 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400600.594 | -2400876.421 | -2399056.813 |
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400609.954 | -2400887.291 | -2399059.948 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400609.353 | -2400890.943 | -2399054.750 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400624.182 | -2400900.253 | -2399074.026 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400626.789 | -2400904.252 | -2399076.329 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400628.466 | -2400904.454 | -2399077.347 |
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400622.683 | -2400902.154 | -2399071.490 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400610.364 | -2400893.600 | -2399061.673 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400629.727 | -2400905.381 | -2399079.815 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400628.579 | -2400905.809 | -2399079.456 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400592.660 | -2400869.653 | -2399048.212 |
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400609.067 | -2400885.716 | -2399058.134 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400612.217 | -2400893.020 | -2399055.931 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400626.093 | -2400901.219 | -2399073.110 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400630.748 | -2400905.751 | -2399076.344 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400628.490 | -2400901.014 | -2399074.906 |
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400626.075 | -2400905.197 | -2399072.640 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400608.720 | -2400889.785 | -2399057.170 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400629.296 | -2400902.319 | -2399077.161 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400629.370 | -2400902.839 | -2399077.171 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400592.660 | -2400869.642 | -2399048.210 |

| | | | |
|---|---|---|---|
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400612.742 | -2400890.822 | -2399062.445 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400611.183 | -2400889.559 | -2399055.613 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400624.623 | -2400898.481 | -2399070.965 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400628.343 | -2400899.998 | -2399074.690 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400627.823 | -2400900.991 | -2399074.199 |
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400625.313 | -2400898.313 | -2399070.277 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400613.026 | -2400891.182 | -2399060.689 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400630.669 | -2400901.852 | -2399078.235 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400629.406 | -2400900.321 | -2399077.245 |

### 6.2.15 The $NO_2$ substituted monocyano structures - Toluene

**Table 50: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400605.139 | -2400880.470 | -2399061.403 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400609.040 | -2400884.910 | -2399056.456 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400614.901 | -2400894.732 | -2399059.069 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400631.223 | -2400907.948 | -2399081.490 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400635.204 | -2400910.345 | -2399084.473 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400636.120 | -2400912.241 | -2399084.431 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400631.081 | -2400911.209 | -2399080.054 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400616.158 | -2400897.370 | -2399065.856 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400637.301 | -2400911.569 | -2399087.343 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400637.782 | -2400911.193 | -2399087.563 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400605.136 | -2400880.467 | -2399061.405 |
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400614.410 | -2400890.153 | -2399064.824 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400612.900 | -2400894.487 | -2399058.228 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400627.569 | -2400903.745 | -2399077.313 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400630.068 | -2400907.599 | -2399079.941 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400632.266 | -2400908.059 | -2399080.902 |
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400626.075 | -2400905.409 | -2399074.940 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400613.892 | -2400897.627 | -2399065.189 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400633.297 | -2400908.838 | -2399083.428 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400632.079 | -2400909.413 | -2399083.063 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400597.507 | -2400873.612 | -2399053.132 |
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400613.404 | -2400888.832 | -2399060.717 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400615.334 | -2400896.071 | -2399058.882 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400629.181 | -2400904.554 | -2399076.368 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400634.358 | -2400909.261 | -2399079.758 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400632.294 | -2400904.378 | -2399078.492 |

| | | | |
|---|---|---|---|
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400629.483 | -2400908.424 | -2399075.953 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400612.015 | -2400893.217 | -2399060.542 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400632.675 | -2400905.803 | -2399080.532 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400632.885 | -2400906.646 | -2399080.621 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400597.514 | -2400873.602 | -2399053.127 |
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400616.836 | -2400894.795 | -2399066.428 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400614.491 | -2400892.891 | -2399058.872 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400627.923 | -2400901.639 | -2399074.170 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400631.882 | -2400903.238 | -2399078.124 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400631.297 | -2400904.666 | -2399077.712 |
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400629.170 | -2400901.579 | -2399073.640 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400616.389 | -2400894.490 | -2399064.304 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400634.114 | -2400905.273 | -2399081.645 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400632.972 | -2400903.813 | -2399080.776 |

### 6.2.16 The $NO_2$ substituted monocyano structures - Dichloromethane

**Table 51: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400630.816 | -2400904.501 | -2399087.133 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400628.222 | -2400905.887 | -2399078.145 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400631.985 | -2400911.915 | -2399076.975 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400647.956 | -2400923.365 | -2399097.146 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400652.443 | -2400927.141 | -2399101.439 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400653.577 | -2400929.147 | -2399101.494 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400647.599 | -2400925.174 | -2399096.256 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400634.303 | -2400915.279 | -2399085.048 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400655.052 | -2400928.779 | -2399104.920 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400655.478 | -2400928.784 | -2399105.117 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400630.816 | -2400904.512 | -2399087.140 |
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400638.446 | -2400911.915 | -2399087.663 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400631.580 | -2400912.574 | -2399076.512 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400644.876 | -2400920.656 | -2399094.957 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400649.707 | -2400925.172 | -2399099.094 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400649.489 | -2400926.503 | -2399099.102 |
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400644.201 | -2400924.783 | -2399093.258 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400632.814 | -2400915.596 | -2399084.599 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400652.109 | -2400927.325 | -2399102.689 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400651.027 | -2400927.815 | -2399102.074 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400625.494 | -2400898.541 | -2399080.122 |

| | | | |
|---|---|---|---|
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400633.164 | -2400909.461 | -2399083.641 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400631.704 | -2400912.383 | -2399075.026 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400646.028 | -2400922.252 | -2399092.953 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400651.634 | -2400926.117 | -2399097.136 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400650.844 | -2400923.549 | -2399097.524 |
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400647.168 | -2400926.041 | -2399093.329 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400629.716 | -2400911.537 | -2399078.361 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400650.445 | -2400923.967 | -2399098.645 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400650.825 | -2400925.119 | -2399098.903 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400625.492 | -2400898.536 | -2399080.120 |
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400638.604 | -2400915.415 | -2399088.981 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400632.218 | -2400911.837 | -2399075.672 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400645.501 | -2400918.322 | -2399091.562 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400650.313 | -2400920.509 | -2399096.393 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400650.061 | -2400921.987 | -2399096.086 |
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400647.129 | -2400918.834 | -2399092.260 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400634.075 | -2400910.860 | -2399082.310 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400651.644 | -2400922.817 | -2399099.402 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400651.676 | -2400922.181 | -2399099.714 |

### 6.2.17 The $NO_2$ substituted monocyano structures - Ethanol

**Table 52: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400639.890 | -2400912.895 | -2399095.873 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400635.246 | -2400915.736 | -2399085.326 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400636.881 | -2400917.264 | -2399082.002 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400652.920 | -2400927.863 | -2399101.730 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400657.528 | -2400932.001 | -2399105.921 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400658.752 | -2400934.277 | -2399106.682 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400652.456 | -2400930.016 | -2399100.985 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400639.995 | -2400920.790 | -2399090.900 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400660.162 | -2400934.059 | -2399109.982 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400660.589 | -2400934.062 | -2399110.187 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400639.893 | -2400912.895 | -2399095.868 |
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400644.177 | -2400920.635 | -2399095.337 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400637.146 | -2400917.807 | -2399082.155 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400650.161 | -2400925.852 | -2399100.273 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400655.055 | -2400930.764 | -2399104.713 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400654.992 | -2400932.631 | -2399104.674 |

| | | | |
|---|---|---|---|
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400649.988 | -2400931.625 | -2399098.834 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400638.955 | -2400921.375 | -2399090.832 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400657.644 | -2400932.184 | -2399108.328 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400656.454 | -2400933.090 | -2399107.759 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400634.825 | -2400907.140 | -2399088.603 |
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400640.504 | -2400915.310 | -2399091.163 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400636.585 | -2400917.369 | -2399080.931 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400651.125 | -2400927.584 | -2399097.645 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400655.937 | -2400930.522 | -2399102.106 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400656.423 | -2400929.677 | -2399102.922 |
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400652.361 | -2400931.205 | -2399098.640 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400635.324 | -2400917.214 | -2399083.838 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400656.042 | -2400929.422 | -2399104.201 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400656.320 | -2400930.795 | -2399104.358 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400634.831 | -2400907.132 | -2399088.600 |
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400645.606 | -2400925.001 | -2399095.925 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400637.601 | -2400916.437 | -2399080.992 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400650.823 | -2400923.413 | -2399097.067 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400655.688 | -2400925.613 | -2399101.951 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400655.593 | -2400927.317 | -2399101.959 |
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400652.477 | -2400924.014 | -2399098.228 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400639.362 | -2400916.200 | -2399087.786 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400656.714 | -2400927.879 | -2399104.597 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400657.360 | -2400927.658 | -2399105.466 |

### 6.2.18 The $NO_2$ substituted monocyano structures - Acetonitrile

**Table 53: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *E-trans*-VHF $NO_2$ (1) conf130 | -2400641.696 | -2400914.428 | -2399097.540 |
| *E-trans*-VHF $NO_2$ (3) conf56 | -2400636.598 | - | -2399086.705 |
| *E-trans*-VHF $NO_2$ (4) conf45 | -2400637.758 | -2400918.274 | -2399083.003 |
| *E-trans*-VHF $NO_2$ (5) conf52 | -2400653.808 | -2400928.716 | -2399102.628 |
| *E-trans*-VHF $NO_2$ (6) conf86 | -2400658.416 | -2400932.870 | -2399106.693 |
| *E-trans*-VHF $NO_2$ (7) conf30 | -2400659.650 | -2400935.191 | -2399107.651 |
| *E-trans*-VHF $NO_2$ (8) conf34 | -2400653.327 | -2400931.005 | -2399101.854 |
| *E-trans*-VHF $NO_2$ (9) conf27 | -2400641.048 | -2400921.761 | -2399091.979 |
| *E-trans*-VHF $NO_2$ (10) conf4 | -2400661.091 | -2400935.030 | -2399110.888 |
| *E-trans*-VHF $NO_2$ (11) conf31 | -2400661.514 | -2400935.025 | -2399111.103 |
| *Z-trans*-VHF $NO_2$ (1) conf88 | -2400641.696 | -2400914.399 | -2399097.532 |

| | | | |
|---|---|---|---|
| *Z-trans*-VHF $NO_2$ (3) conf35 | -2400645.619 | -2400925.030 | -2399096.710 |
| *Z-trans*-VHF $NO_2$ (4) conf47 | -2400638.165 | -2400918.744 | -2399083.197 |
| *Z-trans*-VHF $NO_2$ (5) conf53 | -2400651.119 | -2400926.789 | -2399101.229 |
| *Z-trans*-VHF $NO_2$ (6) conf52 | -2400656.097 | -2400931.769 | -2399105.742 |
| *Z-trans*-VHF $NO_2$ (7) conf60 | -2400655.984 | -2400933.980 | -2399105.679 |
| *Z-trans*-VHF $NO_2$ (8) conf77 | -2400651.041 | -2400932.799 | -2399099.908 |
| *Z-trans*-VHF $NO_2$ (9) conf34 | -2400640.124 | -2400922.567 | -2399092.000 |
| *Z-trans*-VHF $NO_2$ (10) conf61 | -2400658.657 | -2400933.130 | -2399109.386 |
| *Z-trans*-VHF $NO_2$ (11) conf77 | -2400657.481 | -2400934.038 | -2399108.751 |
| *E-cis*-VHF $NO_2$ (1) conf198 | -2400636.624 | -2400908.791 | -2399090.202 |
| *E-cis*-VHF $NO_2$ (3) conf28 | -2400641.731 | -2400916.192 | -2399092.552 |
| *E-cis*-VHF $NO_2$ (4) conf13 | -2400637.514 | -2400918.387 | -2399081.666 |
| *E-cis*-VHF $NO_2$ (5) conf74 | -2400652.080 | -2400928.540 | -2399098.525 |
| *E-cis*-VHF $NO_2$ (6) conf89 | -2400656.804 | -2400931.373 | -2399103.014 |
| *E-cis*-VHF $NO_2$ (7) conf3 | -2400657.696 | -2400930.853 | -2399104.093 |
| *E-cis*-VHF $NO_2$ (8) conf9 | -2400653.275 | -2400931.405 | -2399099.614 |
| *E-cis*-VHF $NO_2$ (9) conf12 | -2400636.372 | -2400918.243 | -2399084.846 |
| *E-cis*-VHF $NO_2$ (10) conf45 | -2400657.079 | -2400930.433 | -2399105.196 |
| *E-cis*-VHF $NO_2$ (11) conf41 | -2400657.360 | -2400931.869 | -2399105.354 |
| *Z-cis*-VHF $NO_2$ (1) conf65 | -2400636.629 | -2400908.778 | -2399090.199 |
| *Z-cis*-VHF $NO_2$ (3) conf94 | -2400646.934 | -2400926.214 | -2399097.238 |
| *Z-cis*-VHF $NO_2$ (4) conf23 | -2400638.577 | -2400917.093 | -2399081.973 |
| *Z-cis*-VHF $NO_2$ (5) conf20 | -2400651.847 | -2400924.358 | -2399098.123 |
| *Z-cis*-VHF $NO_2$ (6) conf45 | -2400656.662 | -2400926.495 | -2399102.964 |
| *Z-cis*-VHF $NO_2$ (7) conf89 | -2400656.593 | -2400928.304 | -2399103.085 |
| *Z-cis*-VHF $NO_2$ (8) conf13 | -2400653.262 | -2400924.956 | -2399099.349 |
| *Z-cis*-VHF $NO_2$ (9) conf24 | -2400640.331 | -2400917.245 | -2399088.792 |
| *Z-cis*-VHF $NO_2$ (10) conf45 | -2400657.473 | -2400928.826 | -2399105.532 |
| *Z-cis*-VHF $NO_2$ (11) conf22 | -2400658.389 | -2400928.658 | -2399106.522 |

### 6.2.19 The $NO_2$ substituted dicyano structures - Vacuum

**Table 54: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642715.642 | -2643034.123 | -2640996.357 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642710.536 | -2643026.168 | -2640984.225 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642733.892 | -2643046.290 | -2641013.859 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642736.762 | -2643049.955 | -2641016.379 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642734.743 | -2643047.842 | -2641014.799 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642731.364 | -2643045.749 | -2641010.842 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642719.746 | -2643034.725 | -2641000.009 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642741.343 | -2643052.993 | -2641023.046 |
| *cis*-VHF $NO_2$ (11) conf77 | -2642739.503 | -2643049.921 | -2641021.350 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642710.420 | -2643025.696 | -2640990.736 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642719.491 | -2643036.337 | -2640995.281 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642738.689 | -2643049.427 | -2641021.006 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642742.921 | -2643054.642 | -2641024.852 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642744.024 | -2643056.067 | -2641025.592 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642739.597 | -2643055.605 | -2641021.638 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642729.222 | -2643045.686 | -2641012.559 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642748.065 | -2643060.444 | -2641030.906 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642747.295 | -2643058.793 | -2641030.405 |

### 6.2.20 The $NO_2$ substituted dicyano structures - Cyclohexane

**Table 55: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642737.256 | -2643051.344 | -2641018.910 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642731.259 | -2643044.922 | -2641004.853 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642754.405 | -2643066.362 | -2641034.157 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642758.315 | -2643070.644 | -2641037.685 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642756.818 | -2643069.132 | -2641037.512 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642752.988 | -2643067.029 | -2641032.027 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642742.675 | -2643056.508 | -2641023.655 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642764.398 | -2643074.680 | -2641046.179 |

| | | | |
|---|---|---|---|
| *cis*-VHF $NO_2$ (11) conf77 | -2642762.765 | -2643072.574 | -2641044.724 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642733.701 | -2643047.529 | -2641016.151 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642741.207 | -2643056.839 | -2641017.099 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642760.029 | -2643070.555 | -2641042.277 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642764.968 | -2643075.478 | -2641046.562 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642766.265 | -2643076.664 | -2641047.292 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642761.260 | -2643076.318 | -2641042.621 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642753.400 | -2643069.531 | -2641037.257 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642771.744 | -2643084.512 | -2641055.439 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642771.794 | -2643080.340 | -2641055.100 |

### 6.2.21 The $NO_2$ substituted dicyano structures - Toluene

**Table 56: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642741.509 | -2643055.605 | -2641023.489 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642735.305 | -2643048.761 | -2641009.157 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642758.372 | -2643070.190 | -2641038.100 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642762.497 | -2643074.533 | -2641041.939 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642761.281 | -2643073.343 | -2641041.870 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642757.165 | -2643071.038 | -2641036.199 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642746.970 | -2643060.830 | -2641028.412 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642768.864 | -2643078.935 | -2641050.692 |
| *cis*-VHF $NO_2$ (11) conf77 | -2642767.325 | -2643077.056 | -2641049.361 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642738.450 | -2643051.785 | -2641019.674 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642744.977 | -2643060.586 | -2641020.179 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642763.978 | -2643074.601 | -2641046.357 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642769.289 | -2643079.476 | -2641050.718 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642770.731 | -2643080.653 | -2641051.469 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642765.485 | -2643079.461 | -2641046.699 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642758.204 | -2643073.753 | -2641042.175 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642776.234 | -2643088.458 | -2641059.986 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642776.402 | -2643084.341 | -2641059.887 |

### 6.2.22 The $NO_2$ substituted dicyano structures - Dichloromethane

**Table 57: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642766.157 | -2643080.527 | -2641047.820 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642756.847 | -2643070.248 | -2641034.519 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642779.269 | -2643089.816 | -2641058.920 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642784.751 | -2643095.337 | -2641064.578 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642784.719 | -2643095.922 | -2641063.607 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642778.935 | -2643091.648 | -2641058.485 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642771.660 | -2643083.958 | -2641053.071 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642792.567 | -2643101.877 | -2641074.566 |
| *cis*-VHF $NO_2$ (11) conf77 | -2642792.063 | -2643100.496 | -2641074.130 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642763.216 | -2643076.113 | -2641042.309 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642767.478 | -2643078.586 | -2641040.699 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642786.271 | -2643095.502 | -2641068.089 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642791.845 | -2643100.706 | -2641072.891 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642792.627 | -2643102.016 | -2641073.623 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642786.523 | -2643098.847 | -2641068.480 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642783.955 | -2643098.230 | -2641068.493 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642801.312 | -2643110.694 | -2641084.808 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642800.824 | -2643106.703 | -2641084.868 |

### 6.2.23 The $NO_2$ substituted dicyano structures - Ethanol

**Table 58: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642774.160 | -2643087.786 | -2641054.751 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642763.679 | -2643076.775 | -2641040.327 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642785.554 | -2643095.794 | -2641065.468 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642792.281 | -2643101.160 | -2641071.216 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642791.357 | -2643101.460 | -2641070.940 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642785.473 | -2643098.453 | -2641065.353 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642778.964 | -2643092.073 | -2641061.128 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642799.939 | -2643109.034 | -2641081.964 |

| | | | |
|---|---|---|---|
| *cis*-VHF $NO_2$ (11) conf77 | -2642799.761 | -2643107.622 | -2641081.634 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642771.907 | -2643084.394 | -2641051.514 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642772.264 | -2643084.496 | -2641048.256 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642792.782 | -2643101.953 | -2641074.886 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642798.550 | -2643107.322 | -2641079.909 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642799.139 | -2643108.535 | -2641080.649 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642792.885 | -2643105.154 | -2641075.262 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642792.113 | -2643106.256 | -2641076.716 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642808.344 | -2643117.123 | -2641092.453 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642808.556 | -2643114.188 | -2641092.550 |

### 6.2.24 The $NO_2$ substituted dicyano structures - Acetonitrile

**Table 59: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| *cis*-VHF $NO_2$ (3) conf98 | -2642775.483 | -2643089.067 | -2641056.227 |
| *cis*-VHF $NO_2$ (4) conf64 | -2642764.947 | -2643078.019 | -2641041.398 |
| *cis*-VHF $NO_2$ (5) conf91 | -2642786.665 | -2643096.912 | -2641066.676 |
| *cis*-VHF $NO_2$ (6) conf78 | -2642793.741 | -2643102.260 | -2641072.410 |
| *cis*-VHF $NO_2$ (7) conf10 | -2642792.501 | -2643102.484 | -2641072.444 |
| *cis*-VHF $NO_2$ (8) conf2 | -2642786.681 | -2643099.740 | -2641066.590 |
| *cis*-VHF $NO_2$ (9) conf52 | -2642780.374 | -2643093.596 | -2641062.638 |
| *cis*-VHF $NO_2$ (10) conf51 | -2642801.281 | -2643110.376 | -2641083.324 |
| *cis*-VHF $NO_2$ (11) conf77 | -2642801.236 | -2643108.937 | -2641082.999 |
| *trans*-VHF $NO_2$ (3) conf5 | -2642772.408 | -2643086.103 | -2641053.373 |
| *trans*-VHF $NO_2$ (4) conf42 | -2642773.627 | -2643085.586 | -2641049.708 |
| *trans*-VHF $NO_2$ (5) conf35 | -2642793.990 | -2643103.129 | -2641076.154 |
| *trans*-VHF $NO_2$ (6) conf62 | -2642799.729 | -2643108.551 | -2641081.224 |
| *trans*-VHF $NO_2$ (7) conf91 | -2642800.296 | -2643109.688 | -2641081.951 |
| *trans*-VHF $NO_2$ (8) conf22 | -2642794.103 | -2643106.398 | -2641076.509 |
| *trans*-VHF $NO_2$ (9) conf23 | -2642793.617 | -2643107.574 | -2641078.192 |
| *trans*-VHF $NO_2$ (10) conf16 | -2642809.735 | -2643118.192 | -2641093.834 |
| *trans*-VHF $NO_2$ (11) conf48 | -2642809.990 | -2643115.740 | -2641093.968 |

## 6.3 Transistion State Structures

### 6.3.1 The $NH_2$ substituted monocyano structures - Vacuum

**Table 60: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008804.552 | -2009121.384 | -2007552.199 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008832.269 | -2009152.803 | -2007580.567 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008826.664 | -2009143.485 | -2007569.488 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008852.843 | -2009164.229 | -2007597.420 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008818.837 | -2009129.247 | -2007563.901 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008856.468 | -2009169.328 | -2007599.571 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008837.234 | -2009151.522 | -2007583.329 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008822.447 | -2009136.460 | -2007569.910 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008824.587 | -2009134.803 | -2007570.047 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008827.803 | -2009136.764 | -2007575.214 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008790.298 | -2009103.741 | -2007538.352 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008823.080 | -2009131.285 | -2007574.258 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008844.008 | -2009159.320 | -2007591.397 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008835.483 | -2009146.846 | -2007581.415 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008844.630 | -2009154.119 | -2007591.022 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008838.628 | -2009149.768 | -2007584.684 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008864.841 | -2009178.454 | -2007612.071 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008831.747 | -2009147.452 | -2007579.685 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008835.218 | -2009145.433 | -2007582.009 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008838.804 | -2009149.395 | -2007586.813 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008805.124 | -2009120.980 | -2007553.960 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008817.157 | -2009131.602 | -2007566.408 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008847.920 | -2009163.754 | -2007595.060 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008839.476 | -2009150.165 | -2007585.540 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008848.518 | -2009159.490 | -2007594.965 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008843.748 | -2009156.080 | -2007590.279 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008863.400 | -2009177.323 | -2007610.227 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008832.860 | -2009149.493 | -2007583.521 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008838.337 | -2009151.280 | -2007584.970 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008844.423 | -2009156.482 | -2007592.540 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008820.693 | -2009137.772 | -2007568.900 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008826.837 | -2009145.271 | -2007576.099 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008822.250 | -2009132.122 | -2007565.941 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008856.797 | -2009165.477 | -2007603.829 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008818.850 | - | -2007567.781 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008860.730 | -2009168.774 | -2007607.321 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008841.787 | -2009151.338 | -2007591.796 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008821.888 | -2009133.235 | -2007573.016 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008826.257 | -2009134.278 | -2007574.854 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008832.154 | -2009140.815 | -2007582.888 |

### 6.3.2 The $NH_2$ substituted monocyano structures - Cyclohexane

**Table 61: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008820.633 | -2009136.649 | -2007567.778 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008848.573 | -2009168.341 | -2007596.822 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008848.172 | -2009163.752 | -2007590.342 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008875.319 | -2009186.985 | -2007620.089 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008845.499 | -2009151.874 | -2007588.221 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008878.402 | -2009192.026 | -2007621.669 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008858.340 | -2009173.256 | -2007604.121 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008840.327 | -2009155.064 | -2007587.905 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008845.536 | -2009154.972 | -2007591.082 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008849.729 | -2009158.188 | -2007597.321 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008807.933 | -2009121.326 | -2007555.491 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008841.314 | -2009149.737 | -2007592.148 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008862.373 | -2009177.150 | -2007609.986 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008855.720 | -2009167.173 | -2007602.246 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008866.170 | -2009176.745 | -2007612.562 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008859.199 | -2009171.177 | -2007605.150 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008881.384 | -2009194.985 | -2007628.399 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008847.339 | -2009162.917 | -2007595.246 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008853.428 | -2009163.775 | -2007600.235 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008857.513 | -2009168.120 | -2007606.014 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008821.872 | -2009137.898 | -2007570.645 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008836.470 | -2009150.409 | -2007585.789 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008866.737 | -2009182.101 | -2007613.908 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008860.131 | -2009170.767 | -2007606.468 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008870.848 | -2009181.266 | -2007617.865 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008863.996 | -2009175.236 | -2007610.275 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008881.022 | -2009194.790 | -2007627.341 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008850.233 | -2009165.127 | -2007601.390 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008857.855 | -2009169.764 | -2007604.126 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008863.652 | -2009176.021 | -2007612.467 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008835.485 | -2009152.774 | -2007583.965 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008842.839 | -2009161.026 | -2007592.314 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008845.124 | -2009154.499 | -2007587.874 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008877.916 | -2009186.730 | -2007625.203 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008842.923 | -2009150.291 | -2007590.631 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008881.862 | -2009190.151 | -2007627.417 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008861.843 | -2009172.025 | -2007610.682 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008841.324 | -2009152.150 | -2007591.639 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008846.969 | -2009154.591 | -2007594.742 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008852.155 | -2009160.352 | -2007603.115 |

### 6.3.3 The $NH_2$ substituted monocyano structures - Toluene

**Table 62: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008823.938 | -2009139.799 | -2007570.947 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008852.015 | -2009171.366 | -2007600.245 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008852.262 | -2009167.259 | -2007594.480 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008879.922 | -2009191.482 | -2007624.684 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008850.372 | -2009156.495 | -2007593.099 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008882.708 | -2009195.935 | -2007626.059 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008862.812 | -2009177.690 | -2007608.466 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008843.874 | -2009158.750 | -2007591.424 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008849.660 | -2009159.089 | -2007595.220 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008854.077 | -2009162.444 | -2007601.674 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008811.444 | -2009124.797 | -2007564.967 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008844.919 | -2009153.284 | -2007595.651 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008865.967 | -2009180.647 | -2007613.530 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008860.362 | -2009171.161 | -2007606.134 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008870.483 | -2009181.403 | -2007616.849 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008863.360 | -2009177.945 | -2007609.041 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008884.682 | -2009198.337 | -2007631.667 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008850.432 | -2009165.897 | -2007598.318 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008856.923 | -2009167.377 | -2007603.790 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008861.123 | -2009171.857 | -2007609.805 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008825.217 | -2009141.356 | -2007573.964 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008840.258 | -2009154.113 | -2007589.620 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008870.489 | -2009185.787 | -2007617.729 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008864.350 | -2009174.771 | -2007610.703 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008875.222 | -2009185.829 | -2007622.557 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008867.792 | -2009179.400 | -2007614.250 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008884.548 | -2009198.214 | -2007632.308 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008853.680 | -2009168.475 | -2007604.759 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008861.772 | -2009173.545 | -2007608.033 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008867.443 | -2009179.938 | -2007616.316 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008838.373 | -2009155.752 | -2007586.887 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008846.189 | -2009164.245 | -2007595.506 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008849.485 | -2009159.026 | -2007592.264 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008882.114 | -2009191.007 | -2007629.270 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008847.689 | -2009154.883 | -2007595.055 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008885.984 | -2009194.378 | -2007631.368 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008865.810 | -2009176.283 | -2007614.399 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008845.176 | -2009155.857 | -2007595.288 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008851.044 | -2009158.608 | -2007598.686 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008856.038 | -2009164.101 | -2007607.098 |

### 6.3.4 The $NH_2$ substituted monocyano structures - Dichloromethane

**Table 63: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008840.923 | -2009156.815 | -2007588.588 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008867.695 | -2009188.326 | -2007617.348 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008875.225 | -2009188.689 | -2007616.902 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008903.901 | -2009215.624 | -2007649.030 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008876.414 | -2009183.585 | -2007620.672 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008906.240 | -2009218.821 | -2007650.043 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008886.835 | -2009200.165 | -2007632.124 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008863.615 | -2009178.806 | -2007610.482 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008871.940 | -2009184.015 | -2007616.676 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008876.984 | -2009185.927 | -2007625.041 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008830.649 | -2009143.606 | -2007576.401 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008864.694 | -2009172.334 | -2007614.588 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008885.785 | -2009200.582 | -2007632.673 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008883.469 | -2009191.745 | -2007628.498 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008893.315 | -2009203.817 | -2007641.405 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008886.349 | -2009195.756 | -2007630.446 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008902.118 | -2009216.353 | -2007649.468 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008866.335 | -2009183.165 | -2007613.861 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008875.944 | -2009186.420 | -2007622.680 |

| | | | |
|---|---|---|---|
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008880.213 | -2009192.391 | -2007629.375 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008843.869 | -2009160.950 | -2007592.492 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008860.698 | -2009174.640 | -2007610.243 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008890.960 | -2009205.957 | -2007637.950 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008887.869 | -2009196.927 | -2007634.314 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008899.301 | -2009208.600 | -2007647.964 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008892.199 | -2009201.049 | -2007636.215 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008904.709 | -2009218.480 | -2007651.842 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008872.941 | -2009188.922 | -2007622.948 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008882.419 | -2009193.966 | -2007629.643 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008887.436 | -2009200.196 | -2007636.601 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008853.811 | -2009171.675 | -2007602.375 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008862.843 | -2009180.313 | -2007611.766 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008873.098 | -2009182.976 | -2007616.195 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008904.334 | -2009214.287 | -2007650.986 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008874.944 | -2009180.116 | -2007620.386 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008907.915 | -2009216.713 | -2007652.532 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008887.239 | -2009198.245 | -2007634.700 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008865.918 | -2009176.118 | -2007614.917 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008872.681 | -2009180.061 | -2007619.771 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008877.207 | -2009184.107 | -2007627.976 |

### 6.3.5 The $NH_2$ substituted monocyano structures - Ethanol

**Table 64: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008846.247 | -2009162.255 | -2007593.737 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008873.694 | -2009193.365 | -2007622.775 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008882.584 | -2009195.623 | -2007624.177 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008911.024 | -2009224.012 | -2007656.187 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008885.577 | -2009192.152 | -2007629.260 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008914.001 | -2009226.892 | -2007657.723 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008894.131 | -2009207.666 | -2007639.843 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008870.260 | -2009185.296 | -2007616.363 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008878.880 | -2009188.970 | -2007623.376 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008883.991 | -2009193.695 | -2007632.421 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008836.769 | -2009149.632 | -2007582.135 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008871.058 | -2009178.699 | -2007620.635 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008891.188 | -2009207.230 | -2007638.803 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008892.170 | -2009200.257 | -2007636.228 |

| | | | |
|---|---|---|---|
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008899.831 | -2009210.606 | -2007647.126 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008895.733 | -2009203.804 | -2007637.761 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008907.314 | -2009221.859 | -2007654.808 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008871.287 | -2009187.355 | -2007618.716 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008881.770 | -2009192.044 | -2007628.422 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008886.126 | -2009198.555 | -2007635.146 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008850.162 | -2009167.096 | -2007598.891 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008867.359 | -2009181.167 | -2007616.938 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008897.607 | -2009212.901 | -2007644.574 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008896.305 | -2009205.064 | -2007641.902 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008905.476 | -2009215.999 | -2007653.296 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008898.513 | -2009208.540 | -2007643.561 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008911.790 | -2009226.286 | -2007660.264 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008879.560 | -2009195.882 | -2007628.785 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008888.835 | -2009200.876 | -2007636.291 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008893.745 | -2009206.395 | -2007642.925 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008858.642 | -2009176.464 | -2007607.164 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008866.931 | -2009185.018 | -2007616.510 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008880.851 | -2009190.204 | -2007623.883 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008911.123 | -2009221.423 | -2007657.710 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008883.624 | -2009188.935 | -2007628.900 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008914.657 | -2009223.545 | -2007659.043 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008894.026 | -2009204.935 | -2007641.279 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008872.324 | -2009182.605 | -2007621.013 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008879.447 | -2009186.625 | -2007626.175 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008883.813 | -2009190.545 | -2007633.881 |

### 6.3.6 The $NH_2$ substituted monocyano structures - Acetonitrile

**Table 65: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NH_2$ (1) | -2008847.266 | -2009163.258 | -2007594.511 |
| TS (E-VHF to anti-DHA WH) $NH_2$ (3) | -2008874.931 | -2009194.352 | -2007623.833 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (4) | -2008883.926 | -2009196.906 | -2007625.471 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (5) | -2008912.302 | -2009225.601 | -2007657.547 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (6) | -2008887.055 | -2009193.793 | -2007630.835 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (7) | -2008915.424 | -2009228.200 | -2007658.954 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (8) | -2008895.586 | -2009208.782 | -2007641.261 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (9) | -2008871.423 | -2009186.478 | -2007617.427 |
| TS (E-VHF to anti-DHA ZI) $NH_2$ (10) | -2008880.156 | -2009190.122 | -2007624.649 |

| | | | |
|---|---|---|---|
| TS (E-VHF to anti-DHA ZI) $NH_2$ (11) | -2008885.294 | -2009195.192 | -2007633.773 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (1) | -2008837.922 | -2009150.755 | -2007583.174 |
| TS (E-VHF to syn-DHA ZI) $NH_2$ (3) | -2008872.248 | -2009179.809 | -2007621.764 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (4) | -2008892.230 | -2009208.435 | -2007639.906 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (5) | -2008894.002 | -2009201.577 | -2007637.522 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (6) | -2008901.044 | -2009211.872 | -2007648.247 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (7) | -2008897.103 | -2009205.529 | -2007639.134 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (8) | -2008908.264 | -2009222.844 | -2007655.801 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (9) | -2008872.261 | -2009188.106 | -2007619.585 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (10) | -2008882.828 | -2009193.068 | -2007629.462 |
| TS (E-VHF to syn-DHA WH) $NH_2$ (11) | -2008887.205 | -2009199.508 | -2007636.212 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (1) | -2008851.391 | -2009168.249 | -2007600.125 |
| TS (Z-VHF to anti-DHA ZI) $NH_2$ (3) | -2008868.527 | -2009182.385 | -2007618.217 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (4) | -2008898.933 | -2009214.124 | -2007645.732 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (5) | -2008898.117 | -2009206.986 | -2007643.367 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (6) | -2008906.762 | -2009217.304 | -2007654.520 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (7) | -2008900.033 | -2009210.307 | -2007645.073 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (8) | -2008912.911 | -2009227.514 | -2007661.241 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (9) | -2008880.815 | -2009197.074 | -2007629.871 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (10) | -2008890.009 | -2009201.459 | -2007637.464 |
| TS (Z-VHF to anti-DHA WH) $NH_2$ (11) | -2008894.948 | -2009207.537 | -2007644.104 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (1) | -2008859.530 | -2009177.323 | -2007608.046 |
| TS (Z-VHF to syn-DHA WH) $NH_2$ (3) | -2008867.776 | -2009185.869 | -2007617.348 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (4) | -2008882.301 | -2009191.577 | -2007625.319 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (5) | -2008912.373 | -2009222.723 | -2007658.952 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (6) | -2008886.709 | -2009190.642 | -2007630.594 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (7) | -2008915.894 | -2009224.810 | -2007660.241 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (8) | -2008895.323 | -2009206.174 | -2007642.487 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (9) | -2008873.497 | -2009183.805 | -2007622.132 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (10) | -2008880.686 | -2009187.833 | -2007627.338 |
| TS (Z-VHF to syn-DHA ZI) $NH_2$ (11) | -2008885.036 | -2009191.742 | -2007634.991 |

### 6.3.7 The $NH_2$ substituted dicyano structures - Vacuum

**Table 66: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2250978.482 | -2251330.601 | -2249553.466 |
| TS WH $NH_2$ (4) | - | -2251347.577 | -2249570.623 |
| TS WH $NH_2$ (5) | -2251021.774 | -2251344.892 | -2249574.181 |
| TS WH $NH_2$ (6) | -2251006.614 | -2251350.014 | -2249579.295 |
| TS WH $NH_2$ (7) | - | -2251354.664 | -2249581.283 |
| TS WH $NH_2$ (8) | -2251027.689 | -2251375.996 | -2249601.344 |
| TS WH $NH_2$ (9) | -2250982.575 | -2251333.733 | -2249556.976 |
| TS WH $NH_2$ (10) | -2250989.619 | -2251335.093 | -2249563.049 |
| TS WH $NH_2$ (11) | -2250995.490 | -2251340.226 | -2249571.414 |
| TS ZI $NH_2$ (3) | -2250992.796 | -2251343.894 | -2249563.285 |
| TS ZI $NH_2$ (4) | -2251004.721 | -2251357.817 | -2249573.819 |
| TS ZI $NH_2$ (5) | -2251021.737 | -2251370.745 | -2249592.698 |
| TS ZI $NH_2$ (6) | -2251003.860 | -2251349.021 | -2249575.131 |
| TS ZI $NH_2$ (7) | -2251029.637 | -2251380.491 | -2249598.735 |
| TS ZI $NH_2$ (8) | -2251027.684 | -2251376.789 | - |
| TS ZI $NH_2$ (9) | -2250988.911 | -2251339.709 | -2249563.317 |
| TS ZI $NH_2$ (10) | -2250992.715 | -2251339.869 | -2249564.889 |
| TS ZI $NH_2$ (11) | -2251000.791 | -2251346.288 | - |

### 6.3.8 The $NH_2$ substituted dicyano structures - Cyclohexane

**Table 67: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2251007.045 | -2251355.226 | -2249579.156 |
| TS WH $NH_2$ (4) | -2251029.976 | -2251376.101 | -2249601.147 |
| TS WH $NH_2$ (5) | -2251051.258 | - | - |
| TS WH $NH_2$ (6) | -2251038.317 | -2251382.869 | -2249610.218 |
| TS WH $NH_2$ (7) | - | - | - |
| TS WH $NH_2$ (8) | -2251052.290 | -2251401.056 | -2249625.887 |
| TS WH $NH_2$ (9) | -2251009.828 | -2251357.342 | -2249581.813 |
| TS WH $NH_2$ (10) | -2251019.282 | -2251360.280 | -2249590.630 |

| | | | |
|---|---|---|---|
| TS WH $NH_2$ (11) | -2251025.418 | -2251367.697 | -2249599.695 |
| TS ZI $NH_2$ (3) | -2251021.370 | -2251371.094 | -2249590.312 |
| TS ZI $NH_2$ (4) | -2251034.085 | -2251384.878 | -2249602.163 |
| TS ZI $NH_2$ (5) | -2251051.277 | -2251400.371 | -2249621.511 |
| TS ZI $NH_2$ (6) | -2251038.532 | -2251381.609 | -2249609.995 |
| TS ZI $NH_2$ (7) | -2251058.108 | -2251408.725 | -2249626.271 |
| TS ZI $NH_2$ (8) | -2251052.282 | -2251403.136 | -2249627.213 |
| TS ZI $NH_2$ (9) | -2251016.943 | -2251366.962 | -2249589.989 |
| TS ZI $NH_2$ (10) | -2251022.758 | -2251368.487 | -2249592.951 |
| TS ZI $NH_2$ (11) | -2251030.181 | -2251375.521 | -2249604.049 |

### 6.3.9 The $NH_2$ substituted dicyano structures - Toluene

**Table 68: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2251013.664 | -2251361.254 | -2249584.622 |
| TS WH $NH_2$ (4) | -2251035.532 | -2251390.588 | -2249604.096 |
| TS WH $NH_2$ (5) | -2251056.601 | -2251405.848 | - |
| TS WH $NH_2$ (6) | -2251044.358 | -2251388.086 | -2249616.016 |
| TS WH $NH_2$ (7) | - | - | - |
| TS WH $NH_2$ (8) | -2251056.864 | -2251405.848 | -2249630.485 |
| TS WH $NH_2$ (9) | -2251015.108 | -2251362.671 | -2249586.744 |
| TS WH $NH_2$ (10) | -2251025.124 | -2251366.069 | -2249596.104 |
| TS WH $NH_2$ (11) | -2251031.165 | -2251373.688 | -2249604.970 |
| TS ZI $NH_2$ (3) | -2251027.214 | -2251376.156 | -2249595.419 |
| TS ZI $NH_2$ (4) | -2251039.567 | -2251390.565 | -2249607.551 |
| TS ZI $NH_2$ (5) | -2251056.601 | -2251405.848 | -2249626.714 |
| TS ZI $NH_2$ (6) | -2251044.624 | -2251387.881 | -2249616.107 |
| TS ZI $NH_2$ (7) | -2251063.430 | -2251413.898 | -2249631.530 |
| TS ZI $NH_2$ (8) | -2251056.864 | -2251408.673 | -2249630.482 |
| TS ZI $NH_2$ (9) | -2251022.433 | -2251372.197 | -2249595.132 |
| TS ZI $NH_2$ (10) | -2251028.364 | -2251374.329 | -2249598.262 |
| TS ZI $NH_2$ (11) | -2251035.826 | -2251381.105 | -2249609.570 |

### 6.3.10 The $NH_2$ substituted dicyano structures - Dichloromethane

**Table 69: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2251052.545 | -2251403.839 | -2249615.028 |
| TS WH $NH_2$ (4) | -2251068.552 | -2251418.581 | -2249634.570 |
| TS WH $NH_2$ (5) | -2251083.717 | -2251433.497 | - |
| TS WH $NH_2$ (6) | -2251073.819 | -2251418.792 | -2249645.382 |
| TS WH $NH_2$ (7) | - | -2251440.814 | - |
| TS WH $NH_2$ (8) | -2251080.144 | -2251431.176 | -2249653.768 |
| TS WH $NH_2$ (9) | -2251044.251 | -2251389.483 | -2249613.857 |
| TS WH $NH_2$ (10) | -2251054.769 | -2251395.874 | -2249624.247 |
| TS WH $NH_2$ (11) | -2251064.058 | -2251403.453 | -2249637.728 |
| TS ZI $NH_2$ (3) | -2251056.725 | -2251404.199 | -2249623.832 |
| TS ZI $NH_2$ (4) | -2251068.566 | -2251418.592 | -2249637.195 |
| TS ZI $NH_2$ (5) | -2251083.717 | -2251433.481 | -2249654.222 |
| TS ZI $NH_2$ (6) | -2251075.198 | -2251422.935 | -2249646.813 |
| TS ZI $NH_2$ (7) | -2251090.082 | -2251440.817 | -2249657.577 |
| TS ZI $NH_2$ (8) | -2251080.144 | -2251434.949 | - |
| TS ZI $NH_2$ (9) | -2251049.932 | -2251399.607 | -2249621.227 |
| TS ZI $NH_2$ (10) | -2251057.100 | -2251402.857 | -2249626.499 |
| TS ZI $NH_2$ (11) | -2251064.079 | -2251409.755 | -2249637.726 |

### 6.3.11 The $NH_2$ substituted dicyano structures - Ethanol

**Table 70: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2251065.483 | -2251412.908 | -2249629.988 |
| TS WH $NH_2$ (4) | -2251075.699 | -2251427.461 | -2249643.683 |
| TS WH $NH_2$ (5) | -2251091.914 | -2251442.308 | - |
| TS WH $NH_2$ (6) | -2251081.730 | -2251427.834 | -2249653.145 |
| TS WH $NH_2$ (6) | - | -2251448.431 | - |
| TS WH $NH_2$ (8) | -2251087.178 | -2251438.614 | -2249661.426 |
| TS WH $NH_2$ (9) | -2251052.051 | -2251398.617 | -2249621.721 |
| TS WH $NH_2$ (10) | -2251066.830 | -2251404.370 | -2249636.206 |

| | | | |
|---|---|---|---|
| TS WH $NH_2$ (11) | -2251072.162 | -2251415.497 | -2249645.802 |
| TS ZI $NH_2$ (3) | -2251065.486 | -2251412.916 | -2249632.666 |
| TS ZI $NH_2$ (4) | -2251077.311 | -2251427.440 | -2249644.935 |
| TS ZI $NH_2$ (5) | -2251091.914 | -2251442.300 | -2249662.482 |
| TS ZI $NH_2$ (6) | -2251083.087 | -2251431.144 | -2249653.145 |
| TS ZI $NH_2$ (7) | -2251097.428 | -2251448.439 | -2249664.871 |
| TS ZI $NH_2$ (8) | -2251087.178 | -2251442.061 | - |
| TS ZI $NH_2$ (9) | -2251057.898 | -2251408.006 | -2249628.983 |
| TS ZI $NH_2$ (10) | -2251065.785 | -2251411.915 | -2249635.071 |
| TS ZI $NH_2$ (11) | -2251072.181 | -2251418.466 | -2249645.815 |

### 6.3.12 The $NH_2$ substituted dicyano structures - Acetonitrile

**Table 71: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NH_2$ (3) | -2251067.056 | -2251414.522 | -2249631.826 |
| TS WH $NH_2$ (4) | -2251078.923 | -2251429.514 | -2249646.290 |
| TS WH $NH_2$ (5) | -2251093.429 | -2251443.923 | - |
| TS WH $NH_2$ (6) | -2251083.176 | -2251429.506 | -2249654.571 |
| TS WH $NH_2$ (7) | - | -2251449.838 | - |
| TS WH $NH_2$ (8) | -2251089.635 | -2251440.019 | -2249662.652 |
| TS WH $NH_2$ (9) | -2251053.451 | -2251400.405 | -2249623.188 |
| TS WH $NH_2$ (10) | -2251068.337 | -2251406.039 | -2249637.658 |
| TS WH $NH_2$ (11) | -2251073.625 | - | -2249647.280 |
| TS ZI $NH_2$ (3) | -2251067.064 | -2251414.525 | -2249634.307 |
| TS ZI $NH_2$ (4) | -2251078.913 | -2251429.498 | -2249646.264 |
| TS ZI $NH_2$ (5) | -2251093.432 | -2251443.920 | -2249663.983 |
| TS ZI $NH_2$ (6) | -2251084.547 | -2251432.665 | -2249654.574 |
| TS ZI $NH_2$ (7) | -2251098.759 | -2251449.835 | -2249666.184 |
| TS ZI $NH_2$ (8) | -2251089.640 | -2251443.088 | -2249662.660 |
| TS ZI $NH_2$ (9) | -2251059.353 | -2251409.529 | -2249630.395 |
| TS ZI $NH_2$ (10) | -2251067.371 | -2251413.625 | -2249636.615 |
| TS ZI $NH_2$ (11) | -2251073.685 | -2251420.015 | -2249647.277 |

### 6.3.13 The $NO_2$ substituted monocyano structures - Vacuum

**Table 72: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400500.534 | -2400767.334 | -2398956.385 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400453.978 | -2400738.987 | -2398925.465 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400449.623 | -2400729.666 | -2398922.915 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400450.337 | -2400728.543 | -2398923.483 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400471.099 | -2400749.476 | -2398945.342 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400448.662 | -2400726.726 | -2398922.115 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400473.748 | -2400752.986 | -2398947.487 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400434.936 | -2400718.474 | -2398903.752 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400464.575 | -2400741.723 | -2398933.856 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400466.807 | -2400742.046 | -2398936.489 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400500.077 | -2400781.076 | -2398965.112 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400449.872 | -2400730.441 | -2398921.889 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400455.572 | -2400737.128 | -2398929.542 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400472.661 | -2400751.085 | -2398946.054 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400472.423 | -2400752.857 | -2398945.999 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400471.703 | -2400750.534 | -2398944.967 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400466.741 | -2400750.980 | -2398939.918 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400444.576 | -2400726.973 | -2398914.795 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400474.027 | -2400750.946 | -2398945.387 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400476.579 | -2400753.674 | -2398948.338 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400500.539 | -2400778.025 | -2398965.882 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400445.012 | -2400727.177 | -2398914.075 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400467.235 | -2400750.355 | -2398940.743 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400479.874 | -2400759.558 | -2398952.862 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400479.598 | -2400760.881 | -2398952.573 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400476.185 | -2400755.774 | -2398949.136 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400475.190 | -2400759.471 | -2398948.099 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400460.135 | -2400746.645 | -2398929.576 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400484.295 | -2400763.588 | -2398955.459 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400482.890 | -2400761.104 | -2398954.385 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | -2400488.535 | -2400760.765 | -2398952.972 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400444.361 | -2400728.183 | -2398915.790 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400457.904 | -2400733.988 | -2398932.947 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400452.839 | -2400728.556 | -2398928.820 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400477.831 | -2400752.054 | -2398954.219 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400449.964 | -2400724.877 | -2398926.481 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400467.888 | -2400745.259 | -2398943.090 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400449.659 | -2400728.167 | -2398919.597 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400470.876 | -2400744.663 | -2398943.014 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400469.671 | -2400743.400 | -2398942.297 |

### 6.3.14 The $NO_2$ substituted monocyano structures - Cyclohexane

**Table 73: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400529.504 | -2400809.298 | -2398994.129 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400472.748 | -2400758.387 | -2398943.533 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400470.404 | -2400749.402 | -2398943.308 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400470.705 | -2400747.761 | -2398943.079 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400492.807 | -2400770.191 | -2398966.669 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400468.303 | -2400745.724 | -2398941.247 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400495.073 | -2400773.407 | -2398968.518 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400458.195 | -2400741.006 | -2398926.402 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400487.603 | -2400765.489 | -2398956.036 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400489.654 | -2400765.024 | -2398958.197 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400528.062 | -2400809.300 | -2398991.809 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400473.793 | -2400753.574 | -2398943.744 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400473.557 | -2400755.152 | -2398947.401 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400490.696 | -2400768.736 | -2398963.666 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400490.896 | -2400770.514 | -2398963.831 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400490.047 | -2400768.440 | -2398962.883 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400486.170 | -2400769.797 | -2398958.940 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400465.651 | -2400746.772 | -2398935.673 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400495.041 | -2400771.105 | -2398965.761 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400497.373 | -2400772.921 | -2398968.271 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400529.501 | -2400809.104 | -2398994.124 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400467.539 | -2400750.261 | -2398935.817 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400485.873 | -2400768.285 | -2398958.690 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400499.100 | -2400777.818 | -2398971.269 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400498.974 | -2400779.837 | -2398971.290 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400496.341 | -2400775.765 | -2398969.093 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400494.608 | -2400778.952 | -2398966.911 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400479.989 | -2400765.313 | -2398948.882 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400504.370 | -2400782.224 | -2398974.593 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400503.834 | -2400780.782 | -2398973.921 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | -2400528.062 | - | - |

| | | | |
|---|---|---|---|
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400463.168 | -2400745.939 | -2398933.383 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400477.813 | -2400753.535 | -2398951.935 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400472.806 | -2400747.961 | -2398947.298 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400498.580 | -2400772.415 | -2398974.648 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400469.474 | -2400743.973 | -2398944.770 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400491.111 | -2400767.471 | -2398965.280 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400471.010 | -2400748.714 | -2398939.758 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400492.615 | -2400765.791 | -2398963.516 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400492.109 | -2400765.371 | -2398963.130 |

### 6.3.15 The $NO_2$ substituted monocyano structures - Toluene

**Table 74: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400534.626 | -2400814.373 | -2398999.139 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400476.526 | -2400762.228 | -2398947.065 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400474.539 | -2400753.469 | -2398947.314 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400474.770 | -2400751.810 | -2398946.970 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400497.044 | -2400774.289 | -2398970.928 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400472.094 | -2400749.912 | -2398945.146 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400499.108 | -2400777.380 | -2398972.614 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400463.015 | -2400745.608 | -2398930.876 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400492.017 | -2400770.075 | -2398960.366 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400494.086 | -2400769.183 | -2398962.471 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400533.395 | -2400814.583 | -2398996.865 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400478.514 | -2400758.258 | -2398948.023 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400477.015 | -2400758.715 | -2398950.798 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400494.172 | -2400771.929 | -2398967.050 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400494.401 | -2400773.759 | -2398967.205 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400493.574 | -2400771.945 | -2398966.333 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400489.969 | -2400773.491 | -2398962.650 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400469.823 | -2400750.941 | -2398939.404 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400499.045 | -2400774.985 | -2398969.605 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400501.300 | -2400776.723 | -2398972.102 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400534.628 | -2400814.415 | -2398999.134 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400471.953 | -2400754.711 | -2398940.013 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400489.567 | -2400771.737 | -2398962.169 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400502.668 | -2400781.601 | -2398974.667 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400502.771 | -2400783.423 | -2398974.916 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400500.678 | -2400780.092 | -2398973.018 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400498.491 | -2400782.788 | -2398970.681 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400483.809 | -2400768.634 | -2398952.707 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400508.150 | -2400785.936 | -2398978.340 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400508.006 | -2400784.537 | -2398977.825 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | -2400533.397 | - | -2398996.863 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400466.851 | -2400749.389 | -2398936.778 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400481.638 | -2400757.505 | -2398955.624 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400476.749 | -2400751.799 | -2398950.940 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400502.666 | -2400776.398 | -2398978.663 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400473.315 | -2400747.698 | -2398948.359 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400495.703 | -2400772.026 | -2398969.715 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400475.114 | -2400752.697 | -2398943.723 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400496.787 | -2400769.774 | -2398967.407 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400496.422 | -2400769.724 | -2398967.181 |

### 6.3.16 The $NO_2$ substituted monocyano structures - Dichloromethane

**Table 75: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400561.172 | -2400841.731 | -2399025.538 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400496.918 | -2400781.620 | -2398967.116 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400497.979 | -2400774.935 | -2398969.434 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400495.650 | -2400771.283 | -2398966.866 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400520.157 | -2400796.561 | -2398993.893 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400493.109 | -2400769.377 | -2398964.805 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400521.301 | -2400799.258 | -2398994.284 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400491.216 | -2400772.499 | -2398956.532 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400516.258 | -2400794.823 | -2398983.914 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400517.883 | -2400791.150 | -2398985.439 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400560.243 | -2400842.594 | -2399022.488 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400502.238 | -2400781.754 | -2398971.198 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400495.201 | -2400776.986 | -2398968.961 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400512.320 | -2400788.711 | -2398984.326 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400512.774 | -2400790.733 | -2398985.205 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400512.299 | -2400789.754 | -2398984.633 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400510.125 | -2400793.340 | -2398982.354 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400493.650 | -2400776.390 | -2398960.673 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400520.004 | -2400795.422 | -2398989.225 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400521.774 | -2400796.215 | -2398991.205 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400561.175 | -2400841.746 | -2399025.538 |

| | | | |
|---|---|---|---|
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400495.283 | -2400777.450 | -2398962.080 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400508.830 | -2400789.898 | -2398980.222 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400521.664 | -2400800.647 | -2398993.003 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400522.790 | -2400802.183 | -2398994.531 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400520.388 | -2400799.838 | -2398992.777 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400519.787 | -2400803.377 | -2398991.480 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400505.396 | -2400787.335 | -2398973.141 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400528.335 | -2400804.617 | -2398997.855 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400528.992 | -2400804.427 | -2398998.477 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | - | -2400842.576 | -2399022.472 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400485.731 | -2400767.762 | -2398954.742 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400501.770 | -2400777.802 | -2398975.055 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400497.318 | -2400771.982 | -2398970.096 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400524.638 | -2400797.533 | -2399000.024 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400494.096 | -2400767.353 | -2398967.662 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400520.020 | -2400798.160 | -2398993.056 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400497.118 | -2400773.549 | -2398963.907 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400518.807 | -2400789.943 | -2398987.597 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400519.078 | -2400791.169 | -2398988.269 |

### 6.3.17 The $NO_2$ substituted monocyano structures - Ethanol

**Table 76: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400568.736 | -2400849.421 | -2399032.903 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400503.251 | -2400787.740 | -2398973.246 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400504.144 | -2400782.003 | -2398976.132 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400502.091 | -2400777.587 | -2398972.965 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400527.440 | -2400803.440 | -2399001.250 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400499.565 | -2400776.230 | -2398971.143 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400528.141 | -2400806.231 | -2399001.016 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400500.269 | -2400781.334 | -2398965.149 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400524.087 | -2400801.269 | -2398991.499 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400525.263 | -2400798.470 | -2398992.541 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400567.663 | -2400850.502 | -2399030.162 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400509.497 | -2400788.953 | -2398977.972 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400501.035 | -2400782.465 | -2398974.415 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400517.389 | -2400793.760 | -2398989.343 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400518.232 | -2400795.792 | -2398990.546 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400518.080 | -2400794.913 | -2398990.010 |

| | | | |
|---|---|---|---|
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400516.576 | -2400799.226 | -2398988.700 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400500.082 | -2400781.646 | -2398967.242 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400526.361 | -2400801.828 | -2398995.240 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400527.923 | -2400801.978 | -2398996.860 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400568.686 | -2400849.418 | -2399032.892 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400502.456 | -2400784.240 | -2398968.975 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400513.622 | -2400795.322 | -2398985.476 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400527.595 | -2400806.425 | -2398998.732 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400528.713 | -2400807.722 | -2399000.457 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400527.007 | -2400806.775 | -2398999.168 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400526.623 | -2400809.896 | -2398998.154 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400513.766 | -2400794.582 | -2398979.794 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400534.592 | -2400810.700 | -2399003.744 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400535.566 | -2400810.519 | -2399004.731 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | -2400567.663 | -2400850.508 | -2399030.167 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400491.373 | -2400773.489 | -2398960.515 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400507.875 | -2400783.405 | -2398980.921 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400503.524 | -2400777.915 | -2398975.859 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400531.538 | -2400804.010 | -2399006.601 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400500.707 | -2400773.394 | -2398973.714 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400528.608 | -2400807.006 | -2399001.077 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400503.868 | - | -2398970.815 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400525.227 | -2400796.281 | -2398993.394 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400525.993 | -2400797.528 | -2398994.531 |

### 6.3.18 The $NO_2$ substituted monocyano structures - Acetonitrile

**Table 77: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS (E-VHF to anti-DHA WH) $NO_2$ (1) | -2400570.057 | -2400850.791 | -2399034.192 |
| TS (E-VHF to anti-DHA WH) $NO_2$ (3) | -2400504.351 | -2400788.695 | -2398974.317 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (4) | -2400505.380 | -2400783.329 | -2398977.384 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (5) | -2400503.280 | -2400778.771 | -2398974.107 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (6) | -2400528.797 | -2400804.680 | -2399002.636 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (7) | -2400500.781 | -2400777.524 | -2398972.325 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (8) | -2400529.417 | -2400807.428 | -2399002.242 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (9) | -2400501.825 | -2400782.856 | -2398966.756 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (10) | -2400525.555 | -2400802.338 | -2398992.956 |
| TS (E-VHF to anti-DHA ZI) $NO_2$ (11) | -2400526.605 | -2400799.835 | -2398993.851 |
| TS (E-VHF to syn-DHA ZI) $NO_2$ (1) | -2400569.015 | -2400851.931 | -2399031.553 |

| | | | |
|---|---|---|---|
| TS (E-VHF to syn-DHA ZI) $NO_2$ (3) | -2400510.852 | -2400790.250 | -2398979.135 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (4) | -2400502.120 | -2400783.484 | -2398975.407 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (5) | -2400518.295 | -2400794.700 | -2398990.223 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (6) | -2400519.212 | -2400796.706 | -2398991.501 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (7) | -2400519.146 | -2400795.871 | -2398990.968 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (8) | -2400517.778 | -2400800.321 | -2398989.892 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (9) | -2400501.332 | -2400782.804 | -2398968.554 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (10) | -2400527.527 | -2400803.002 | -2398996.330 |
| TS (E-VHF to syn-DHA WH) $NO_2$ (11) | -2400528.994 | -2400803.054 | -2398997.897 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (1) | -2400570.062 | -2400850.791 | -2399034.195 |
| TS (Z-VHF to anti-DHA ZI) $NO_2$ (3) | -2400503.755 | -2400785.503 | -2398970.261 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (4) | -2400514.449 | -2400796.299 | -2398986.408 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (5) | -2400528.692 | -2400807.457 | -2398999.785 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (6) | -2400529.798 | -2400808.767 | -2399001.526 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (7) | -2400528.122 | -2400808.161 | -2399000.383 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (8) | -2400527.899 | -2400811.175 | -2398999.399 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (9) | -2400514.241 | -2400795.934 | -2398981.110 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (10) | -2400535.773 | -2400811.850 | -2399004.826 |
| TS (Z-VHF to anti-DHA WH) $NO_2$ (11) | -2400536.963 | -2400811.571 | -2399005.879 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (1) | -2400569.033 | -2400851.941 | -2399031.553 |
| TS (Z-VHF to syn-DHA WH) $NO_2$ (3) | -2400492.410 | -2400774.557 | -2398961.586 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (4) | -2400508.998 | -2400784.458 | -2398981.984 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (5) | -2400504.637 | -2400778.979 | -2398976.909 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (6) | -2400532.817 | -2400805.207 | -2399007.806 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (7) | -2400501.931 | -2400774.507 | -2398974.835 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (8) | -2400530.212 | -2400808.384 | -2399002.594 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (9) | -2400505.291 | -2400781.187 | -2398972.235 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (10) | -2400526.384 | -2400797.415 | -2398994.452 |
| TS (Z-VHF to syn-DHA ZI) $NO_2$ (11) | -2400527.253 | -2400798.707 | -2398995.668 |

### 6.3.19 The $NO_2$ substituted dicyano structures - Vacuum

**Table 78: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642588.332 | -2642905.280 | -2640886.026 |
| TS WH $NO_2$ (4) | - | - | - |
| TS WH $NO_2$ (5) | -2642615.312 | -2642929.660 | -2640916.479 |
| TS WH $NO_2$ (6) | -2642613.954 | -2642927.683 | -2640915.240 |
| TS WH $NO_2$ (7) | -2642611.134 | -2642927.297 | -2640912.491 |
| TS WH $NO_2$ (8) | -2642600.577 | -2642920.389 | -2640902.120 |
| TS WH $NO_2$ (9) | - | -2642926.943 | - |
| TS WH $NO_2$ (10) | -2642624.574 | -2642936.618 | -2640921.751 |
| TS WH $NO_2$ (11) | -2642628.161 | -2642937.810 | -2640925.626 |
| TS ZI $NO_2$ (3) | -2642600.514 | -2642920.263 | -2640896.289 |
| TS ZI $NO_2$ (4) | -2642588.928 | -2642906.138 | -2640889.896 |
| TS ZI $NO_2$ (5) | -2642613.106 | -2642926.843 | -2640913.342 |
| TS ZI $NO_2$ (6) | -2642625.572 | -2642939.939 | -2640926.963 |
| TS ZI $NO_2$ (7) | -2642609.774 | -2642924.370 | -2640910.286 |
| TS ZI $NO_2$ (8) | -2642614.243 | -2642932.398 | -2640914.644 |
| TS ZI $NO_2$ (9) | -2642615.067 | -2642930.537 | -2640908.033 |
| TS ZI $NO_2$ (10) | -2642636.386 | -2642948.894 | -2640931.817 |
| TS ZI $NO_2$ (11) | -2642634.835 | -2642946.891 | -2640930.667 |

### 6.3.20 The $NO_2$ substituted dicyano structures - Cyclohexane

**Table 79: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642615.834 | -2642930.072 | -2640909.603 |
| TS WH $NO_2$ (4) | -2642617.732 | -2642933.835 | -2640916.949 |
| TS WH $NO_2$ (5) | -2642639.818 | -2642952.276 | -2640940.424 |
| TS WH $NO_2$ (6) | -2642639.277 | -2642951.515 | -2640939.247 |
| TS WH $NO_2$ (7) | -2642637.933 | -2642949.262 | -2640937.502 |
| TS WH $NO_2$ (8) | -2642627.838 | -2642945.594 | -2640928.199 |
| TS WH $NO_2$ (9) | - | -2642950.932 | - |
| TS WH $NO_2$ (10) | -2642656.164 | -2642964.852 | -2640950.269 |

| | | | |
|---|---|---|---|
| TS WH $NO_2$ (11) | -2642659.580 | -2642966.181 | -2640954.221 |
| TS ZI $NO_2$ (3) | -2642627.008 | -2642946.505 | -2640920.809 |
| TS ZI $NO_2$ (4) | -2642615.472 | -2642932.257 | -2640926.099 |
| TS ZI $NO_2$ (5) | -2642640.616 | -2642952.780 | -2640938.546 |
| TS ZI $NO_2$ (6) | -2642652.302 | -2642964.734 | -2640952.346 |
| TS ZI $NO_2$ (7) | -2642637.240 | -2642949.837 | -2640935.603 |
| TS ZI $NO_2$ (8) | -2642642.089 | -2642959.105 | -2640940.437 |
| TS ZI $NO_2$ (9) | -2642643.352 | -2642958.711 | -2640935.228 |
| TS ZI $NO_2$ (10) | -2642667.457 | -2642978.833 | -2640960.535 |
| TS ZI $NO_2$ (11) | -2642665.803 | -2642977.484 | -2640959.270 |

### 6.3.21 The $NO_2$ substituted dicyano structures - Toluene

**Table 80: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642621.416 | -2642935.000 | -2640914.347 |
| TS WH $NO_2$ (4) | -2642622.532 | -2642938.529 | -2640921.770 |
| TS WH $NO_2$ (5) | -2642644.652 | -2642956.611 | -2640944.648 |
| TS WH $NO_2$ (6) | -2642644.526 | -2642956.726 | -2640943.624 |
| TS WH $NO_2$ (7) | -2642643.389 | -2642953.584 | -2640942.311 |
| TS WH $NO_2$ (8) | -2642633.349 | -2642950.528 | -2640933.621 |
| TS WH $NO_2$ (9) | - | -2642956.052 | - |
| TS WH $NO_2$ (10) | -2642662.925 | -2642971.033 | -2640955.888 |
| TS WH $NO_2$ (11) | -2642666.044 | -2642971.920 | -2640959.810 |
| TS ZI $NO_2$ (3) | -2642632.020 | -2642951.596 | -2640925.474 |
| TS ZI $NO_2$ (4) | -2642621.075 | -2642937.413 | -2640930.786 |
| TS ZI $NO_2$ (5) | -2642645.938 | -2642957.687 | -2640943.385 |
| TS ZI $NO_2$ (6) | -2642657.509 | -2642969.591 | -2640957.188 |
| TS ZI $NO_2$ (7) | -2642642.483 | -2642954.902 | -2640940.747 |
| TS ZI $NO_2$ (8) | -2642647.450 | -2642964.298 | -2640945.738 |
| TS ZI $NO_2$ (9) | -2642648.905 | -2642964.359 | -2640940.684 |
| TS ZI $NO_2$ (10) | -2642673.225 | -2642983.638 | -2640965.870 |
| TS ZI $NO_2$ (11) | -2642671.762 | -2642983.283 | -2640964.888 |

### 6.3.22 The $NO_2$ substituted dicyano structures - Dichloromethane

**Table 81: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642651.344 | -2642959.743 | -2640940.130 |
| TS WH $NO_2$ (4) | -2642649.052 | -2642959.977 | -2640944.031 |
| TS WH $NO_2$ (5) | -2642672.852 | -2642980.083 | -2640969.288 |
| TS WH $NO_2$ (6) | -2642673.417 | -2642980.051 | -2640970.031 |
| TS WH $NO_2$ (7) | -2642670.045 | -2642978.242 | -2640968.501 |
| TS WH $NO_2$ (8) | -2642666.582 | -2642979.033 | -2640962.638 |
| TS WH $NO_2$ (9) | - | -2642984.950 | - |
| TS WH $NO_2$ (10) | -2642700.307 | -2643002.583 | -2640991.319 |
| TS WH $NO_2$ (11) | -2642702.339 | -2643002.295 | -2640989.182 |
| TS ZI $NO_2$ (3) | -2642657.658 | -2642976.475 | -2640949.949 |
| TS ZI $NO_2$ (4) | -2642660.489 | -2642965.020 | -2640955.938 |
| TS ZI $NO_2$ (5) | -2642674.461 | -2642984.554 | -2640969.307 |
| TS ZI $NO_2$ (6) | -2642685.861 | -2642995.684 | -2640982.965 |
| TS ZI $NO_2$ (7) | -2642671.292 | -2642982.370 | -2640967.010 |
| TS ZI $NO_2$ (8) | -2642678.985 | -2642990.543 | -2640974.539 |
| TS ZI $NO_2$ (9) | -2642675.871 | -2642992.029 | -2640967.422 |
| TS ZI $NO_2$ (10) | -2642701.255 | -2643011.153 | -2640992.579 |
| TS ZI $NO_2$ (11) | -2642702.268 | -2643012.313 | -2640993.538 |

### 6.3.23 The $NO_2$ substituted dicyano structures - Ethanol

**Table 82: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642665.703 | -2642967.911 | -2640947.825 |
| TS WH $NO_2$ (4) | -2642668.184 | -2642967.898 | -2640952.141 |
| TS WH $NO_2$ (5) | -2642681.718 | -2642987.673 | -2640977.168 |
| TS WH $NO_2$ (6) | -2642681.472 | -2642988.910 | -2640976.695 |
| TS WH $NO_2$ (7) | -2642678.450 | -2642986.329 | -2640975.183 |
| TS WH $NO_2$ (8) | -2642675.751 | -2642987.909 | -2640972.426 |
| TS WH $NO_2$ (9) | - | -2642999.349 | - |
| TS WH $NO_2$ (10) | -2642709.194 | -2643014.390 | -2641000.233 |

| | | | |
|---|---|---|---|
| TS WH $NO_2$ (11) | -2642711.150 | -2643013.272 | -2641001.656 |
| TS ZI $NO_2$ (3) | -2642665.671 | -2642983.572 | -2640956.817 |
| TS ZI $NO_2$ (4) | -2642668.685 | -2642972.022 | -2640963.683 |
| TS ZI $NO_2$ (5) | -2642682.740 | -2642993.079 | -2640977.231 |
| TS ZI $NO_2$ (6) | -2642693.890 | -2643004.524 | -2640990.907 |
| TS ZI $NO_2$ (7) | -2642680.020 | -2642990.616 | -2640974.891 |
| TS ZI $NO_2$ (8) | -2642687.497 | -2642999.882 | -2640983.340 |
| TS ZI $NO_2$ (9) | -2642683.821 | -2642998.259 | -2640975.356 |
| TS ZI $NO_2$ (10) | -2642709.215 | -2643019.016 | -2641000.185 |
| TS ZI $NO_2$ (11) | -2642711.166 | -2643020.920 | -2641001.650 |

### 6.3.24 The $NO_2$ substituted dicyano structures - Acetonitrile

**Table 83: Gibbs free energies in kJ/mol, using the 6-311+G(d) basis set and the functionals CAM-B3LYP, M06-2X and PBE0. The number in the parenthesis is the substitution position. The green cells are the structures with lowest free energies used in the calculations of the thermochemical properties.**

| Position | CAM-B3LYP | M06-2X | PBE0 |
|---|---|---|---|
| TS WH $NO_2$ (3) | -2642667.147 | -2642969.310 | -2640949.161 |
| TS WH $NO_2$ (4) | -2642669.633 | -2642969.150 | -2640954.095 |
| TS WH $NO_2$ (5) | -2642683.299 | -2642989.099 | -2640978.517 |
| TS WH $NO_2$ (6) | -2642683.501 | -2642990.708 | -2640978.155 |
| TS WH $NO_2$ (7) | -2642679.781 | -2642987.694 | -2640976.572 |
| TS WH $NO_2$ (8) | -2642678.177 | -2642989.718 | -2640974.298 |
| TS WH $NO_2$ (9) | - | -2643001.176 | - |
| TS WH $NO_2$ (10) | -2642711.132 | -2643020.915 | -2641001.842 |
| TS WH $NO_2$ (11) | -2642712.652 | -2643015.496 | -2641003.139 |
| TS ZI $NO_2$ (3) | -2642667.142 | -2642984.877 | -2640957.999 |
| TS ZI $NO_2$ (4) | -2642670.195 | -2642973.782 | -2640965.114 |
| TS ZI $NO_2$ (5) | -2642684.249 | -2642994.694 | -2640978.656 |
| TS ZI $NO_2$ (6) | -2642695.208 | -2643006.739 | -2640992.314 |
| TS ZI $NO_2$ (7) | -2642681.458 | -2642992.105 | -2640976.369 |
| TS ZI $NO_2$ (8) | -2642689.563 | -2643001.638 | -2640985.259 |
| TS ZI $NO_2$ (9) | -2642685.344 | -2642999.729 | -2640976.167 |
| TS ZI $NO_2$ (10) | -2642710.633 | -2643020.463 | -2641001.532 |
| TS ZI $NO_2$ (11) | -2642712.649 | -2643022.479 | -2641003.136 |

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