Supporting Information

Methyliminopropadienone CH_3-N=C=C=C=O: Photoelectron Spectrum and Electronic Structure

Anna Chrostowska,*† Alain Dargelos†, Saîd Khayar† and Curt Wentrup*‡

†Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR CNRS 5254, Université de Pau et des Pays de l'Adour, 64 000 Pau, France and

‡School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland 4072, Australia.

E-mail: anna.chrostowska@univ-pau.fr, wentrup@uq.edu.au

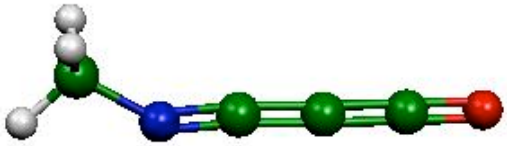
Contents:

1) *N*-Methyliminopropadienone **1a**
[CAM-B3LYP/6-311G(d,p)] Atomic Coordinates of Optimized Geometry.[1]
2) Energies: total, 1st cation, HOMO, LUMO, ΔSCF and ΔE(HOMO-LUMO);
3) Dipole Moment
4) **Table SI-1.** CAM-B3LYP/6-311G(d,p) Total Energy (a.u.), HOMO, LUMO energies and HOMO-LUMO gap (eV), Ground State Dipole Moments (Debye), 1st Radical Cation Energy (a.u.), ΔSCF Ionization Energy (IE, eV), CAM-B3LYP/6-311G++(d,p) Total Energy (a.u.), Radical Anion Energy (a.u.), Electron Affinity (EA, eV), Δ(EA-IE) (eV) for $CH_3N=CH_2$, CH_3-N=C=CH_2, CH_2=C=O, CH_3-N=C=C=C=O **1a**, and CH_2=O.
5) Atomic coordinates for optimized geometry of **2a** [CAM-B3LYP/6-311G(d,p)].
Energies: total, 1st cation, HOMO, LUMO, ΔSCF and ΔE(HOMO-LUMO);
Dipole Moment
Table SI-2. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO visualization of **2a** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.
6) Atomic coordinates for optimized geometry of **2b** [CAM-B3LYP/6-311G(d,p)].
Energies: total, 1st cation, HOMO, LUMO, ΔSCF and ΔE(HOMO-LUMO);
Dipole Moment
Table SI-3. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO visualization of **2b** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.
7) Atomic coordinates for optimized geometry of **2c** [CAM-B3LYP/6-311G(d,p)].
Energies: total, 1st cation, HOMO, LUMO, ΔSCF and ΔE(HOMO-LUMO);
Dipole Moment
Table SI-4. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO

visualization of **2c** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.

Me-N=C=C=C=O 1a

1) Atomic coordinates for optimized geometry of **1a** [CAM-B3LYP/6-311G(d,p)].



6	0.515238	2.924691	0.000294
1	1.130086	3.054506	0.893481
1	1.146389	3.032185	-0.884471
1	-0.245799	3.703818	-0.015921
7	-0.107942	1.643659	0.011585
6	-0.057890	0.462652	0.005806
6	-0.091003	-0.823416	0.001976
6	-0.108353	-2.085097	-0.003794
8	-0.123599	-3.248718	-0.008956

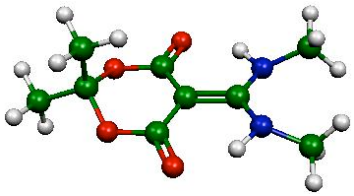
2) E_{tot} (neutral) = -284.068221 A.U.
Zero-point correction= 0.061122 (Hartree/Particle)
Sum of electronic and zero-point Energies= -284.007099
Sum of electronic and thermal Energies= -284.000070
Sum of electronic and thermal Enthalpies= -283.999126
Sum of electronic and thermal Free Energies= -284.040225
E_{tot} (1st cation) = -283.738175 au
$\Delta SCF = E_{tot}$ (1st cation) - E_{tot} (neutral) ΔSCF = 8.98 eV
E(HOMO) = -8.02 eV
E(LUMO) = 0.08 eV
Δ E(HOMO-LUMO) = 7.94 eV

3) Dipole moment (Debye): 4.8755

4) **Table SI-1.** CAM-B3LYP/6-311G(d,p) Total Energy (a.u.), HOMO, LUMO energies and HOMO-LUMO gap (eV), Ground State Dipole Moments (Debye), 1st Radical Cation Energy (a.u.), ΔSCF Ionization Energy (IE, eV), CAM-B3LYP/6-311G++(d,p) Total Energy (a.u.), Radical Anion Energy (a.u.), Electron Affinity (EA, eV), and Δ(EA-IE) (eV) for $CH_3N{=}CH_2$, CH_3-N=C=CH_2, CH_2=C=O, CH_3-N=C=C=C=O **1a**, and CH_2=O.

	$CH_3N{=}CH_2$	CH_3-N=C=CH_2	CH_2=C=O	CH_3-N=C=C=C=O	CH_2=O
E_{tot} neutral (6-311G(d,p)) au	-133.901331	-171.971304	-152.574947	-284.068221	-114.485589
HOMO (eV)	-8.672	-7.827	-8.370	-8.025	-9.121
LUMO (eV)	1.227	1.538	0.452	0.083	0.295
HOMO-LUMO gap (eV)	7.445	6.289	7.918	7.942	8.826
ground state dipole moment	1.5010	1.4909	1.415	4.8755	2.304
E_{tot} 1st cation (6-311G(d,p)) au	-133.540844	-171.644995	-152.215779	-283.738175	-114.088769
ΔSCF (ionization energy IE) (eV)	9.809	8.879	9.773	8.979	10.797
E_{tot} neutral (6-311G++(d,p)) au	-133.904892	-171.974715	-152.578845	-284.073837	-114.491280
E_{tot} anion (6-311G++(d,p)) au	-133.873949	-171.947938	-152.572196	-284.090800	-114.467399
electron affinity (EA) (eV)	-0.854	-0.729	-0.181	+0.462	-0.650
Δ(IE+EA) (eV)	8.955	8.150	9.592	9.441	10.147

5) Atomic coordinates for optimized geometry of **2a** [CAM-B3LYP/6-311G(d,p)].



6	-4.920401	1.576144	-0.487502
6	-5.781859	2.677909	-0.107775
6	-7.198780	2.562644	-0.371760
6	-6.866046	0.198256	-0.180429
6	-6.862404	0.015089	1.330092
1	-7.880623	-0.157049	1.679643
1	-6.245292	-0.845282	1.590035
1	-6.465945	0.896927	1.832142
6	-7.435874	-0.993878	-0.912600
1	-6.839579	-1.880003	-0.696188
1	-8.466925	-1.163053	-0.602784
1	-7.410636	-0.799078	-1.983727
8	-7.683042	1.309012	-0.543425
8	-5.548398	0.373989	-0.674211
8	-7.993726	3.479052	-0.485877
8	-3.737877	1.626276	-0.716179
6	-5.237663	3.959756	0.197659
7	-5.954004	5.061820	-0.062782
1	-6.890219	4.855664	-0.416193
6	-5.652112	6.379831	0.447180
1	-4.800796	6.837380	-0.068100
1	-6.516095	7.018864	0.277233
1	-5.444482	6.361608	1.521967
7	-4.041656	4.144429	0.781446
1	-3.681740	5.083377	0.763678
6	-3.236527	3.172026	1.501451
1	-2.528887	2.666646	0.848557
1	-2.717178	3.697492	2.303878
1	-3.886153	2.420237	1.947081

```
E(RCAM-B3LYP) =  -761.692129534     A.U.

Zero-point correction=                           0.238529(Hartree/Particle)
 Thermal correction to Energy=                    0.253657
 Thermal correction to Enthalpy=                  0.254601
 Thermal correction to Gibbs Free Energy=         0.197451
 Sum of electronic and zero-point Energies=           -761.453600
 Sum of electronic and thermal Energies=              -761.438473
 Sum of electronic and thermal Enthalpies=            -761.437529
 Sum of electronic and thermal Free Energies=         -761.494679
 Dipole moment (Debye): 5.4382
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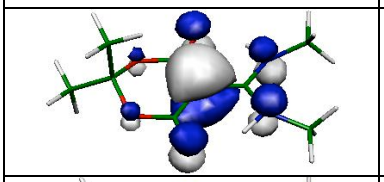
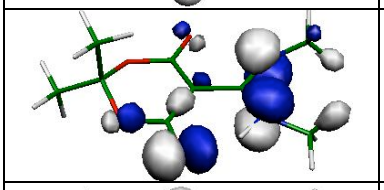
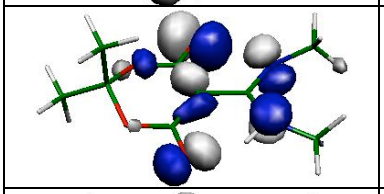
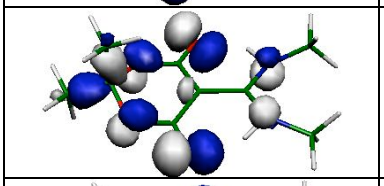
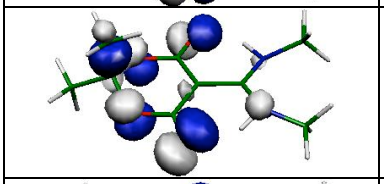
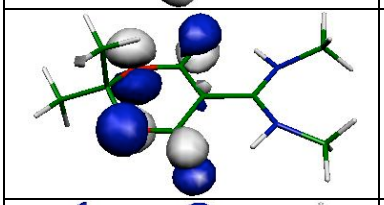
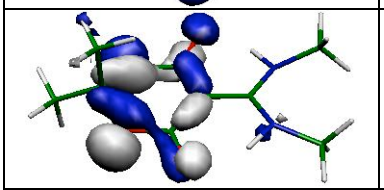
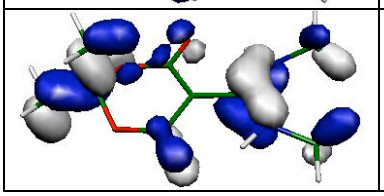
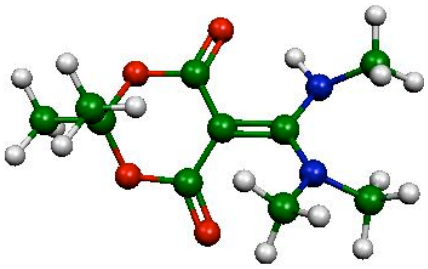
Table SI-2. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO visualization of **2a** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.

O.M.	$-\varepsilon^{KS}$	TD-DFT	OVGF	SAC-CI	P3	IEs exp
	7.71	8.24	7.76	7.59	8.18	8.25
	8.87	9.43	9.37	8.78	9.51	9.4
	9.03	9.74	9.81	8.89	9.63	
	9.57	10.20	10.22	9.39	10.24	10.1
	9.88	10.51	10.61	9.71	10.52	10.6
	10.09	10.72	10.84	10.05	10.80	11.1
	11.24	11.91	12.25	11.11	12.24	12.1
	11.68	12.30	12.25	11.80	12.34	

6) Atomic coordinates for optimized geometry of **2b** [CAM-B3LYP/6-311G(d,p)].



6	-0.437887	1.162734	0.433116
6	0.268689	-0.007258	-0.032417
6	-0.411845	-1.058267	-0.756614
6	-2.460629	-0.083657	0.042477
6	-3.786779	0.242252	-0.603863
1	-4.345899	-0.674958	-0.788124
1	-4.365174	0.898857	0.045728
1	-3.605340	0.746415	-1.552100
6	-2.613741	-0.794385	1.379579
1	-3.186663	-0.168849	2.064257
1	-3.132525	-1.742413	1.235994
1	-1.639401	-0.992148	1.827505
8	-1.766550	-0.917279	-0.876652
8	-1.792376	1.155813	0.226595
8	0.107857	-1.999609	-1.306882
8	0.041844	2.132629	0.969120
6	1.684358	-0.083475	0.103425
7	2.302353	-1.225812	0.457768
6	3.689118	-1.492989	0.113642
1	4.372034	-1.274139	0.942325
1	3.788543	-2.548969	-0.139347
1	3.980428	-0.907865	-0.756992
7	2.485607	0.965759	-0.144558
1	3.395233	0.958990	0.287450
6	2.140424	2.161319	-0.894243
1	1.766596	2.946691	-0.239804
1	3.026342	2.494888	-1.436274
1	1.361919	1.915380	-1.614313
6	1.612875	-2.317857	1.124149
1	0.714273	-1.940892	1.605423
1	1.329334	-3.089387	0.406889
1	2.272919	-2.733152	1.888581

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E(RCAM-B3LYP) =  -800.971306906     A.U.
Zero-point correction=                          0.266509 (Hartree/Particle)
 Thermal correction to Energy=                   0.283148
 Thermal correction to Enthalpy=                 0.284093
 Thermal correction to Gibbs Free Energy=        0.223628
 Sum of electronic and zero-point Energies=          -800.704797
 Sum of electronic and thermal Energies=             -800.688159
 Sum of electronic and thermal Enthalpies=           -800.687214
 Sum of electronic and thermal Free Energies=        -800.747679
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Dipole moment (Debye): 5.0977
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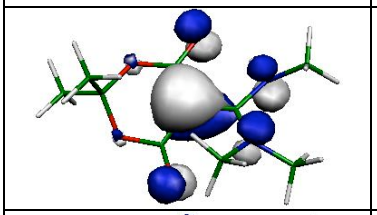
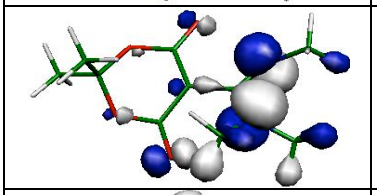
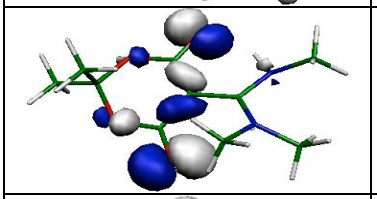
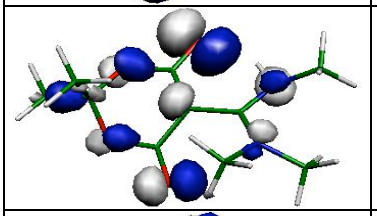
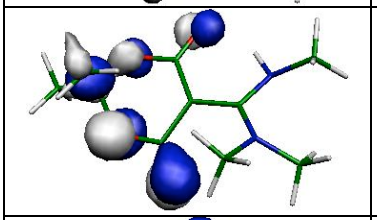
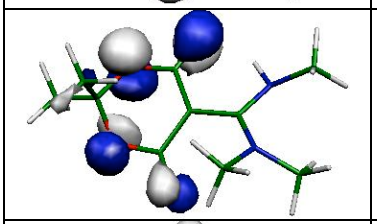
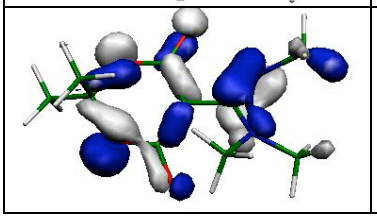
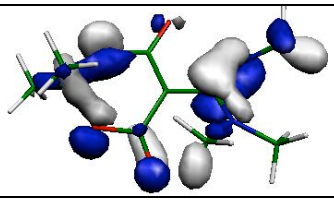
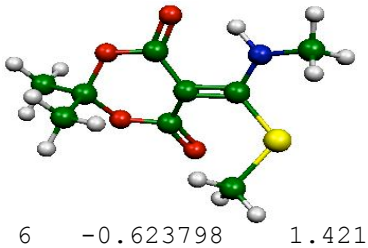
Table SI-3. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO visualization of **2b** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.

O.M.	$-\varepsilon^{KS}$	TD-DFT	OVGF	SAC-CI	P3	IEs exp
	7.68	8.14	7.67	7.23	8.11	8.05
	8.50	8.98	8.90	8.01	9.01	8.9
	8.84	9.51	9.61	8.45	9.41	9.4
	9.50	10.12	10.15	9.05	10.17	10.05
	9.63	10.26	10.37	9.17	10.27	10.5
	9.94	10.56	10.66	9.59	10.60	
	10.76	11.61	11.71	10.61	11.77	11.4

	11.45	12.06	12.21	11.18	12.23	12.1

7) Atomic coordinates for optimized geometry of **2c** [CAM-B3LYP/6-311G(d,p)].



6	-0.623798	1.421860	-0.019730
6	0.118499	0.188073	-0.222520
6	-0.603627	-0.960855	-0.751387
6	-2.558014	0.034967	0.236454
6	-3.998514	0.173982	-0.194428
1	-4.504389	-0.787316	-0.107684
1	-4.504240	0.909968	0.430124
1	-4.030267	0.501761	-1.232417
6	-2.412346	-0.417960	1.680978
1	-2.905775	0.296558	2.339969
1	-2.876582	-1.396693	1.803452
1	-1.363383	-0.488755	1.967720
8	-1.965227	-0.898387	-0.650568
8	-1.968339	1.322340	0.060618
8	-0.132034	-1.911567	-1.316861
8	-0.147858	2.539635	0.058148
6	1.529567	0.229174	-0.170955
6	1.703267	-2.479748	0.732771
1	1.119315	-3.054377	0.022808
1	2.472560	-3.090958	1.202846
1	1.061476	-2.060535	1.505050
7	2.164590	1.395506	-0.146017
1	1.529754	2.199456	-0.185858
6	3.581817	1.617132	0.067669
1	4.177828	1.271849	-0.779762
1	3.735951	2.688286	0.182597
1	3.931083	1.106157	0.966475
16	2.611905	-1.158135	-0.107501

```
E(RCAM-B3LYP) =  -1104.54257429     A.U.
Zero-point correction=                          0.221579 (Hartree/Particle)
 Thermal correction to Energy=                   0.237164
 Thermal correction to Enthalpy=                 0.238109
 Thermal correction to Gibbs Free Energy=        0.179302
 Sum of electronic and zero-point Energies=         -1104.320995
 Sum of electronic and thermal Energies=            -1104.305410
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Sum of electronic and thermal Enthalpies=          -1104.304466
Sum of electronic and thermal Free Energies=       -1104.363272
Dipole moment (Debye):  3.9201
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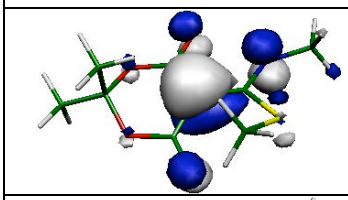
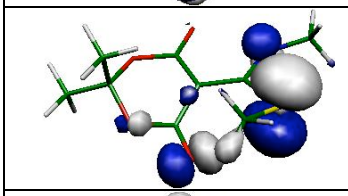
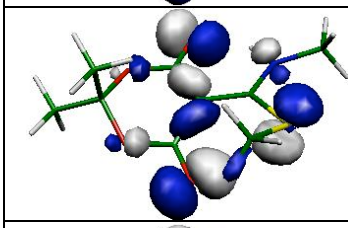
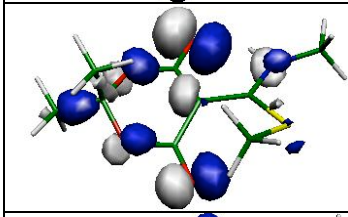
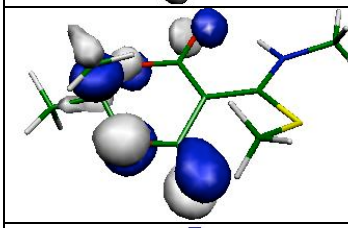
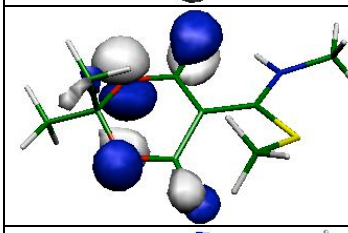
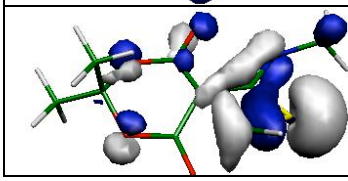
Table SI-4. Calculated CAM-B3LYP Kohn-Sham energies of MO ($-\varepsilon^{K-S}$), ΔSCF/TD-DFT (CAM-B3LYP), OVGF, SAC-CI and P3 ionization energies with the MOLEKEL MO visualization of **2c** compared with experimental values (in eV). The 6-311G(d,p) basis set was applied for all calculations; iso value = ±0.05.

O.M.	$-\varepsilon^{KS}$	TD-DFT	OVGF	SAC-CI	P3	IEs exp
	7.92	8.37	7.87	7.54	8.36	8.4
	8.59	9.30	9.07	8.55	9.08	9.1
	9.16	9.83	9.87	8.91	9.75	9.8
	9.66	10.28	10.32	9.26	10.36	10.1
	9.87	10.52	10.58	9.46	10.66	10.5
	10.20	10.81	10.97	9.86	10.97	
	10.91	11.61	11.37	10.85	11.25	11.35

[1]All calculation were performed using the Gaussian package:
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.;. Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.1.*: Gaussian, Inc., Wallingford CT, 2009.