**Supporting Information for:**

# The Contributions of Through-Bond Interactions to the Singlet-Triplet Energy Difference in 1,3-Dehydrobenzene

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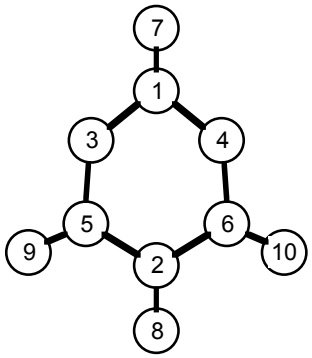
TCSCF, ROHF, and CCSD(T) optimized geometries, absolute VB, GVB(= TCSCF), ROHF, CASPT2, and CCSD(T) energies computed at them, the derivation of eqn. 11 from eqn. 10, a Figure that shows the relationship between the adiabatic and vertical energy differences, and the complete list of authors for ref. 15 (8 pages).

## 1,3-Dehydrobenzene $^1A_1$ TCSCF/6-31G(d) $C_{2v}$ Geometry

| | |
|---|---|
| Nuclear Repulsion Energy | 187.144733 Hartrees |
| Zero-Point Correction | 0.080096 Hartrees |
| Thermal Correction to Energy | 0.084179 Hartrees |
| Thermal Correction to Enthalpy | 0.085123 Hartrees |
| Thermal Correction to Gibbs Free Energy | 0.053585 Hartrees |
| $^1A_1$ VB/6-31G(d) Energy | -229.403721 Hartrees |
| $^3B_2$ VB/6-31G(d) Energy | -229.378444 Hartrees |
| $^1A_1$ TCSCF/6-31G(d) Energy | -229.416006 Hartrees |
| $^3B_2$ ROHF/6-31G(d) Energy | -229.388106 Hartrees |
| $^1A_1$ (2/2)CASPT2/6-31G(d) Energy | -230.138363 Hartrees |
| $^3B_2$ (2/2)CASPT2/6-31G(d) Energy | -230.098800 Hartrees |




| | X | Y | Z |
|---|---|---|---|
| C1 | 0.000000 | 0.000000 | 1.547095 |
| C2 | 0.000000 | 0.000000 | -1.367773 |
| C3 | 0.000000 | 1.099010 | 0.726978 |
| C4 | 0.000000 | -1.099010 | 0.726978 |
| C5 | 0.000000 | 1.185754 | -0.643203 |
| C6 | 0.000000 | -1.185754 | -0.643203 |
| H7 | 0.000000 | 0.000000 | 2.616944 |
| H8 | 0.000000 | 0.000000 | -2.444536 |
| H9 | 0.000000 | 2.144988 | -1.126819 |
| H10 | 0.000000 | -2.144988 | -1.126819 |

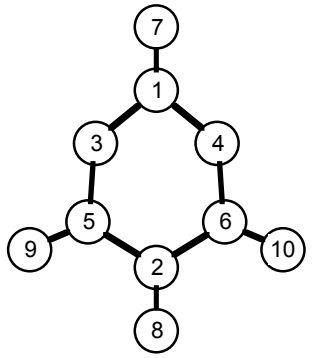
(1-3) 1.371 (1-7) 1.070 (2-5) 1.390 (2-8) 1.077 (3-5) 1.373
(5-9) 1.074 (3,4) 2.198

(3-1-4) 106.5 (3-1-7) 126.7 (5-2-6) 117.1 (5-2-8) 121.4
(1-3-5) 130.4 (2-5-3) 117.8 (2-5-9) 121.8 (3-5-9) 120.4
(4-1-3-5) 0.0 (7-1-3-5) 180.0 (6-2-5-3) 0.0
(6-2-5-9) 180.0 (8-2-5-3) 180.0 (8-2-5-9) 0.0
(1-3-5-2) 0.0 (1-3-5-9) 180.0

Frequencies(cm-1): 447.2 531.6 532.2 655.0 684.9 858.1 952.9 967.0
977.5 1070.8 1103.4 1109.5 1187.3 1206.0 1315.4 1390.2 1548.9 1557.3
1687.5 1792.8 3358.3 3387.9 3394.3 3442.1

## 1,3-Dehydrobenzene $^1A_1$ CCSD(T)/6-31G(d,p) $C_{2v}$ Geometry

| | |
|---|---|
| Nuclear Repulsion Energy | 186.035385 Hartrees |
| $^1A_1$ CCSD(T)/6-31G(d,p) Energy | -230.238609 Hartrees |
| $^1A_1$ VB/6-31G(d) Energy | -229.398125 Hartrees |
| $^3B_2$ VB/6-31G(d) Energy | -229.359882 Hartrees |
| $^1A_1$ TCSCF/6-31G(d) Energy | -229.412334 Hartrees |
| $^3B_2$ ROHF/6-31G(d) Energy | -229.370400 Hartrees |
| $^1A_1$ (2/2)CASPT2/6-31G(d) Energy | -230.141013 Hartrees |
| $^3B_2$ (2/2)CASPT2/6-31G(d) Energy | -230.084990 Hartrees |

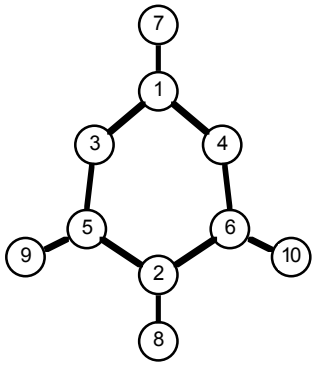



| | X | Y | Z |
|---|---|---|---|
| C1 | 0.000000 | 0.000000 | 1.611341 |
| C2 | 0.000000 | 0.000000 | -1.411517 |
| C3 | 0.000000 | 1.053297 | 0.724382 |
| C4 | 0.000000 | -1.053297 | 0.724382 |
| C5 | 0.000000 | 1.182323 | -0.652480 |
| C6 | 0.000000 | -1.182323 | -0.652480 |
| H7 | 0.000000 | 0.000000 | 2.689341 |
| H8 | 0.000000 | 0.000000 | -2.497517 |
| H9 | 0.000000 | 2.154818 | -1.126797 |
| H10 | 0.000000 | -2.154818 | -1.126797 |

(1-3) 1.377 (1-7) 1.078 (2-5) 1.405 (2-8) 1.086 (3-5) 1.383

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (5-9) | 1.082 | (3,4) | 2.107 | | | | |
| (3-1-4) | 99.8 | (3-1-7) | 130.1 | (5-2-6) | 114.6 | (5-2-8) | 122.7 |
| (1-3-5) | 135.5 | (2-5-3) | 117.3 | (2-5-9) | 121.3 | (3-5-9) | 121.4 |
| (4-1-3-5) | 0.0 | (7-1-3-5) | 180.0 | (6-2-5-3) | 0.0 | | |
| (6-2-5-9) | 180.0 | (8-2-5-3) | 180.0 | (8-2-5-9) | 0.0 | | |
| (1-3-5-2) | 0.0 | (1-3-5-9) | 180.0 | | | | |

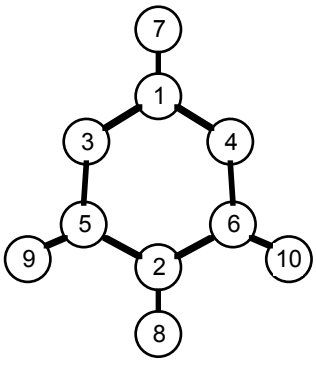
| 1,3-Dehydrobenzene $^1A_1$ CCSD(T)/cc-pVTZ $C_{2v}$ Geometry | |
|---|---|
| Nuclear Repulsion Energy | 187.647946 Hartrees |
| $^1A_1$ VB/6-31G(d) Energy | -229.393750 Hartrees |
| $^3B_2$ VB/6-31G(d) Energy | -229.343613 Hartrees |
| $^1A_1$ TCSCF/6-31G(d) Energy | -229.410339 Hartrees |
| $^3B_2$ ROHF/6-31G(d) Energy | -229.355405 Hartrees |
| $^1A_1$ TCSCF/cc-pVTZ Energy | -229.484757 Hartrees |
| $^3B_2$ ROHF/cc-pVTZ Energy | -229.429858 Hartrees |
| $^1A_1$ (2/2)CASPT2/6-31G(d) Energy | -230.140405 Hartrees |
| $^3B_2$ (2/2)CASPT2/6-31G(d) Energy | -230.070279 Hartrees |




| | X | Y | Z |
|---|---|---|---|
| C1 | 0.000000 | 0.000000 | 1.625918 |
| C2 | 0.000000 | 0.000000 | -1.418345 |
| C3 | 0.000000 | -1.012853 | 0.712340 |
| C4 | 0.000000 | 1.012853 | 0.712340 |
| C5 | 0.000000 | -1.168459 | -0.650811 |
| C6 | 0.000000 | 1.168459 | -0.650811 |
| H7 | 0.000000 | 0.000000 | 2.697918 |
| H8 | 0.000000 | -0.000001 | -2.498345 |
| H9 | 0.000000 | -2.149994 | -1.091679 |
| H10 | 0.000000 | 2.149994 | -1.091679 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (1-3) | 1.364 | (1-7) | 1.072 | (2-5) | 1.398 | (2-8) | 1.080 | (3-5) | 1.372 |
| (5-9) | 1.076 | (3,4) | 2.026 | | | | | | |
| (3-1-4) | 95.9 | (3-1-7) | 132.0 | (5-2-6) | 113.4 | (5-2-8) | 123.3 | | |
| (1-3-5) | 138.6 | (2-5-3) | 116.8 | (2-5-9) | 122.5 | (3-5-9) | 120.7 | | |
| (4-1-3-5) | 0.0 | (7-1-3-5) | 180.0 | (6-2-5-3) | 0.0 | | | | |
| (6-2-5-9) | 180.0 | (8-2-5-3) | 180.0 | (8-2-5-9) | 0.0 | | | | |
| (1-3-5-2) | 0.0 | (1-3-5-9) | 180.0 | | | | | | |

| 1,3-Dehydrobenzene $^3B_2$ ROHF/6-31G(d) $C_{2v}$ Geometry | |
|---|---|
| Nuclear Repulsion Energy | 186.676227 Hartrees |
| Zero-Point Correction | 0.080531 Hartrees |
| Thermal Correction to Energy | 0.084551 Hartrees |
| Thermal Correction to Enthalpy | 0.085496 Hartrees |
| Thermal Correction to Gibbs Free Energy | 0.052997 Hartrees |
| ROHF/6-31G(d) Energy | -229.395708 Hartrees |
| $^3B_2$ VB/6-31G(d) Energy | -229.387126 Hartrees |
| $^3B_2$ (2/2)CASPT2/6-31G(d) Energy | -230.106118 Hartrees |



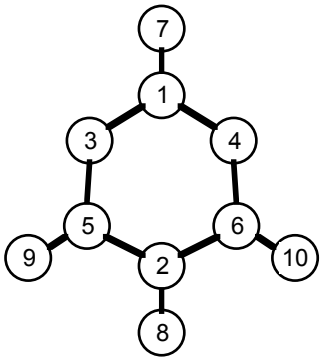

| | X | Y | Z |
|---|---|---|---|
| C1 | 0.000000 | 0.000000 | 1.476228 |
| C2 | 0.000000 | 0.000000 | -1.320042 |
| C3 | 0.000000 | 1.161729 | 0.738240 |
| C4 | 0.000000 | -1.161729 | 0.738240 |
| C5 | 0.000000 | 1.211818 | -0.635096 |
| C6 | 0.000000 | -1.211818 | -0.635096 |
| H7 | 0.000000 | 0.000000 | 2.550732 |
| H8 | 0.000000 | 0.000000 | -2.395804 |
| H9 | 0.000000 | 2.146215 | -1.164883 |
| H10 | 0.000000 | -2.146215 | -1.164883 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1-3) | 1.376 | (1-7) | 1.075 | (2-5) | 1.392 | (2-8) | 1.076 | (3-5) | 1.374 |
| (5-9) | 1.074 | (3,4) | 2.323 | | | | | | |
| (3-1-4) | 115.1 | (3-1-7) | 122.4 | (5-2-6) | 121.0 | (5-2-8) | 119.5 | | |
| (1-3-5) | 124.5 | (2-5-3) | 117.4 | (2-5-9) | 121.0 | (3-5-9) | 121.6 | | |
| (4-1-3-5) | 0.0 | (7-1-3-5) | 180.0 | (6-2-5-3) | 0.0 | | | | |
| (6-2-5-9) | 180.0 | (8-2-5-3) | 180.0 | (8-2-5-9) | 0.0 | | | | |
| (1-3-5-2) | 0.0 | (1-3-5-9) | 180.0 | | | | | | |

Frequencies(cm-1): 455.4 474.9 653.8 662.1 719.6 832.5 945.9 992.2
1062.2 1096.8 1102.3 1126.7 1167.4 1210.9 1312.5 1383.8 1522.6 1596.1
1738.3 1759.0 3363.5 3387.2 3388.3 3394.8

1,3-Dehydrobenzene $^3B_2$ CCSD(T)/6-31G(d,p) $C_{2v}$ Geometry

| | |
|---|---|
| Nuclear Repulsion Energy | 185.091234 Hartrees |
| Zero-Point Correction | 0.074977 Hartrees |
| Thermal Correction to Energy | 0.079401 Hartrees |
| Thermal Correction to Enthalpy | 0.080345 Hartrees |
| Thermal Correction to Gibbs Free Energy | 0.047230 Hartrees |
| CCSD(T)/6-31G(d,p) Energy | -230.206660 Hartrees |
| ROHF/6-31G(d) Energy | -229.394563 Hartrees |
| $^3B_2$ VB/6-31G(d) Energy | -229.386294 Hartrees |
| $^3B_2$ (2/2)CASPT2/6-31G(d) Energy | -230.107097 Hartrees |




| | X | Y | Z |
|---|---|---|---|
| C1 | 0.000000 | 0.000000 | 1.486164 |
| C2 | 0.000000 | 0.000000 | -1.327141 |
| C3 | 0.000000 | 1.172960 | 0.744168 |
| C4 | 0.000000 | -1.172960 | 0.744168 |
| C5 | 0.000000 | 1.225557 | -0.639974 |
| C6 | 0.000000 | -1.225557 | -0.639974 |
| H7 | 0.000000 | 0.000000 | 2.570226 |
| H8 | 0.000000 | 0.000000 | -2.412063 |
| H9 | 0.000000 | 2.163528 | -1.181314 |
| H10 | 0.000000 | -2.163528 | -1.181314 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1-3) | 1.388 | (1-7) | 1.084 | (2-5) | 1.405 | (2-8) | 1.085 | (3-5) | 1.385 |
| (5-9) | 1.083 | (3,4) | 2.346 | | | | | | |
| (3-1-4) | 115.4 | (3-1-7) | 122.3 | (5-2-6) | 121.4 | (5-2-8) | 119.3 | | |
| (1-3-5) | 124.5 | (2-5-3) | 117.1 | (2-5-9) | 120.7 | (3-5-9) | 122.2 | | |
| (4-1-3-5) | 0.0 | (7-1-3-5) | 180.0 | (6-2-5-3) | 0.0 | | | | |
| (6-2-5-9) | 180.0 | (8-2-5-3) | 180.0 | (8-2-5-9) | 0.0 | | | | |
| (1-3-5-2) | 0.0 | (1-3-5-9) | 180.0 | | | | | | |

Frequencies(cm-1): 385.3 409.7 569.4 604.1 611.6 728.3 791.5 876.4
925.1 970.0 1041.8 1068.7 1096.6 1176.5 1268.6 1280.4 1427.0 1473.3
1610.6 1637.7 3221.8 3237.7 3243.9 3255.5

# Supporting Information -- Derivation of Eqn. 11 from Eqn. 10

Starting with $\Psi(VB) = |\ldots(c_1\phi_1 + c_3\phi_3)(c_3\phi_1 + c_1\phi_3)(\alpha\beta - \beta\alpha)>/\sqrt{2}$ (10)

symmetry-adapted MOs, $\psi_+$ and $\psi_-$, can be written as the sum and the difference of the VB orbitals in eqn. 10,

$$\psi_+ = (c_1\phi_1 + c_3\phi_3 + c_3\phi_1 + c_1\phi_3)/\sqrt{2} = (c_1 + c_3)(\phi_1 + \phi_3)/\sqrt{2} = (c_1 + c_3)\psi_S \quad (10a)$$

$$\psi_- = (c_1\phi_1 + c_3\phi_3 - c_3\phi_1 - c_1\phi_3)/\sqrt{2} = (c_1 - c_3)(\phi_1 - \phi_3)/\sqrt{2} = (c_1 - c_3)\psi_A \quad (10b)$$

In eqn. 10a and 10b, $\psi_S$ and $\psi_A$ are defined implicitly as,

$$\psi_S = (\phi_1 + \phi_3)/\sqrt{2} \quad (8)$$

and

$$\psi_A = (\phi_1 - \phi_3)/\sqrt{2} \quad (9)$$

The VB orbitals in eqn. 10 can be written in terms of $\psi_S$ and $\psi_A$ as

$$(c_1\phi_1 + c_3\phi_3) = (\psi_+ + \psi_-)/\sqrt{2} = [(c_1 + c_3)\psi_S + (c_1 - c_3)\psi_A]/\sqrt{2} \quad (10c)$$

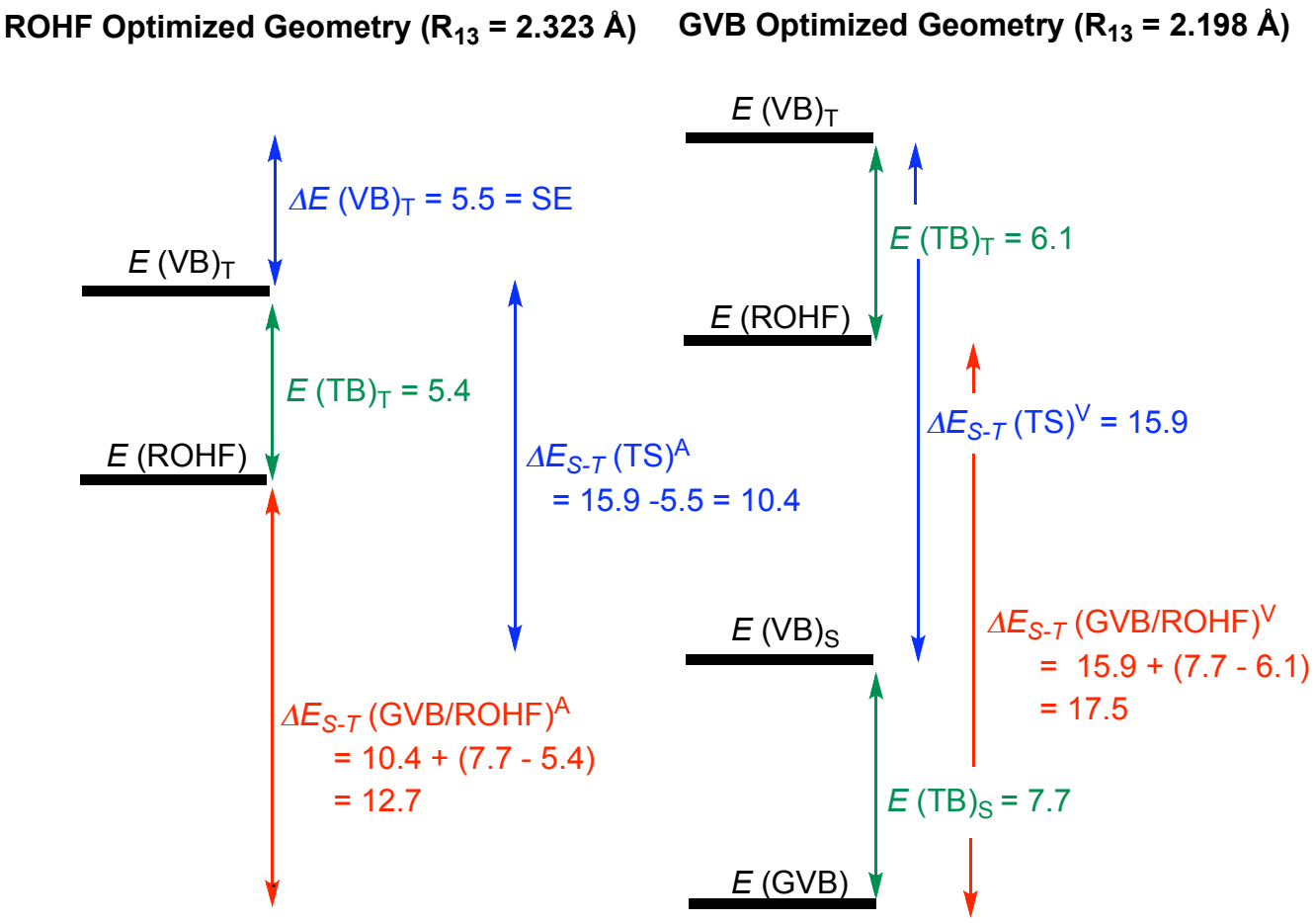
$$(c_3\phi_1 + c_1\phi_3) = (\psi_+ - \psi_-)/\sqrt{2} = [(c_1 + c_3)\psi_S - (c_1 - c_3)\psi_A]/\sqrt{2} \quad (10d)$$

Substituting eqns. 10c and 10d in eqn. 10 gives eqn. 11 of the text

$$\Psi(VB) = (|\ldots\psi_+^2> - |\ldots\psi_-^2>)/2 = [(c_1 + c_3)^2|\ldots\psi_S^2> - (c_1 - c_3)^2|\ldots\psi_A^2>]/\sqrt{2} \quad (11)$$

It is worth noting that, because the VB orbitals in eqn. 10 are not orthogonal, the correct normalization for $\Psi(VB)$ is $1/\sqrt{2}$ only if $c_1 = 1$ and $c_3 = 0$ or *vice versa*. For example, if $c_1 = c_3 = 1/\sqrt{2}$, $\Psi(VB)$ is correctly normalized only if $1/\sqrt{2}$ is replaced by 1/2 in eqn. 10 and 11.

**Figure S1. Tripet VB and ROHF Energies and the Singlet VB Energy (kcal/mol), Relative to the GVB (TCSCF) Energy of the Singlet at the GVB Optimized Geometry. Both Adiabatic and Vertical Singlet-Triplet Energy Differences Are Shown.**




## Key to Abbreviations

VB = valence-bond
T = triplet
S = singlet
SE = strain energy
TS = through-space
TB = through-bond
V = vertical
A = adiabatic

## Adiabatic and Vertical Singlet-Triplet Energy Differences

As shown graphically in Fig. S1, the adiabatic, VB, singlet-triplet energy difference is equal to the vertical TS interaction energy, minus the increase in the VB "strain energy" in the triplet in going from the triplet equilibrium geometry to the geometry of the singlet. One way to think about this "strain energy" is that it represents the cost to the singlet of having a shorter C(1)-C(3) distance than the triplet, which is at least partially compensated for in the singlet by TS bonding at the geometry of the singlet.

It should be noted that, by the manner in which the adiabatic TS interaction energy is defined, all of the "strain energy" at a given geometry of the singlet gets deducted from the vertical TS interaction energy. The TB interaction energy in the singlet, like the vertical TS interaction energy, increases as the C(1)-C(3) bond length decreases, but none of the increase in the "strain energy" with decreasing $R_{13}$ is included in the TB interaction energy.

This happens because the TS interaction energy is the difference between the VB energy of the triplet state minus the VB energy of the singlet state. Therefore, if there is a difference between the geometries of the two states, the energy associated with this difference gets incorporated into the TS interaction energy. In contrast, the TB interaction energy is defined as the difference between two energies -- either triplet VB and triplet ROHF or singlet VB and singlet GVB -- at the same geometry, Therefore, a difference in geometries does not enter into the computation of the TB interaction energy for either the singlet or the triplet.

Complete citation for Reference 15:

(15) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.