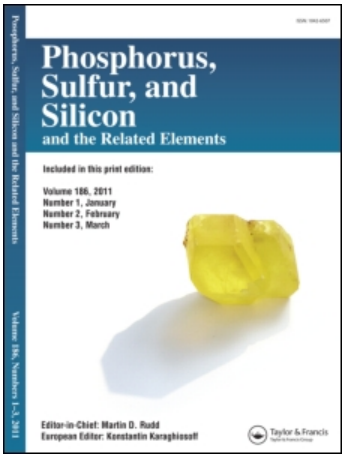


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

AB INITIO MOLECULAR ORBITAL STUDY OF 1,2-DITHIANE AND 1,2,4,5-TETRATHIANE

Issa Yavari[a]; Mina Haghdadi[a]; Rahebeh Amiri[a]
[a] Department of Chemistry, Science & Research Campus, Islamic Azad University, Ponak, Tehran, Iran

Online publication date: 16 August 2010

Phosphorus, Sulfur, and Silicon, 179:2015–2023, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490473537

Taylor & Francis
Taylor & Francis Group

AB INITIO MOLECULAR ORBITAL STUDY OF 1,2-DITHIANE AND 1,2,4,5-TETRATHIANE

Issa Yavari, Mina Haghdadi, and Rahebeh Amiri
Department of Chemistry, Science & Research Campus, Islamic Azad University, Ponak, Tehran, Iran and Department of Chemistry, University of Tarbiat Modarres, Tehran, Iran

(Received December 18, 2003; accepted March 16, 2004)

Ab initio calculations at HF/6-31+G level of theory for geometry optimization, and MP2/6-31+G*//HF/6-31+G* and B3LYP/6-31+G*//HF/6-31+G* levels for a single-point total energy calculation, are reported for the chair and twist conformations of 1,2-dithiane (**1**), 3,3,6,6-tetramethyl-1,2-dithiane (**2**), 1,2,4,5-tetrathiane (**3**), and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane (**4**). The C_2 symmetric chair conformations of **1** and **2** are calculated to be 21.9 and 8.6 kJ mol^{-1} more stable than the corresponding twist forms. The calculated energy barriers for chair-to-twist processes in **1** and **2** are 56.3 and 72.8 kJ mol^{-1}, respectively. The C_{2h} symmetric chair conformation of **3** is 10.7 kJ mol^{-1} more stable than the twist form. Interconversion of these forms takes place via a C_2 symmetric transition state, which is 67.5 kJ mol^{-1} less stable than **3-Chair**. The D_2 symmetric twist-boat conformation of **4** is calculated to be 4.0 kJ mol^{-1} more stable than the C_{2h} symmetric chair form. The calculated strain energy for twist to chair process is 61.1 kJ mol^{-1}.*

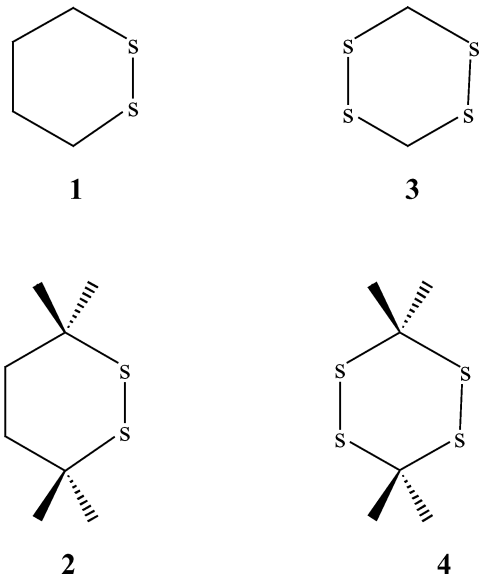
Keywords: Ab initio calculations; conformational analysis; cyclic disulfide; stereochmistry

INTRODUCTION

There has been considerable interest in the synthesis and chemistry of cyclic disulfides due to the importance of compounds such as lipoic acid. The disulfide moiety occurs in proteins and is also found in a variety of natural products[1] and pharmacologically active compounds.[2] In addition, cyclic and acyclic disulfides are useful intermediates in

Address correspondence to Issa Yavari, Department of Chemistry, University of Tarbiat Modarres, P.O. Box 14115-175, Tehran, Iran. E-mail: isayavar@yahoo.com

organic synthesis[3–6] and in the preparation of adsorbed monolayers.[7] Cyclic disulfides are typically prepared by the oxidative dimerization of α,ω-dithiols[8–11] and may be prepared by α,ω-dihalogenated compounds with Na_2S/S_8.[12] Thiocyanates have also been used in the preparation of disulfides.[13] This study was undertaken to investigate the structural optimization of chair, twist, and twist-boat geometries of 1,2-dithiane (**1**), 1,2,4,5-tetrathiane (**3**), and their tetramethyl derivatives **2** and **4** (Scheme 1) by comparing their geometries (HF/6-31+G*) and conformational energies (MP2/6-31+G*//HF/6-31+G*) and B3LYP/6-31+G*//HF/6-31+G*. The results from MP2/6-31+G*//HF/6-31+G* calculations are used in the discussions below.



1 **3**

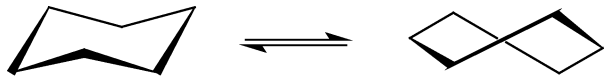
2 **4**

SCHEME 1

RESULTS AND DISCUSSION

1,2-Dithiane (1) and 3,3,6,6-Tetramethyl-1,2-dithiane (2)

The energy-minimum conformations of 1,2-dithiane (**1**) and 3,3,6,6-tetramethyl-1,2-dithiane **2** are the same as those of cyclohexane, a chair and a twist form, but the energy relations between these conformers are quite different in the two systems (Scheme 2). While the



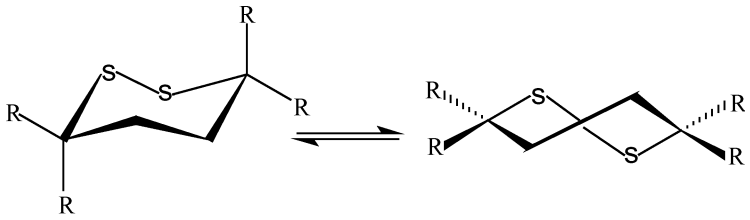
Chair Twist

SCHEME 2

cyclohexane twist is at least 20 kJ mol^{-1} higher in energy than the chair,[14] the twist form is 10–15 kJ mol^{-1} less stable than the chair in **1** and **2**.[15]

The results of ab initio calculations for the chair, twist, and the trasition state for the chair-to-twist process in **1** and **2** are shown in Tables I and II. According to these calculations, the chair conformation is the most stable geometry for **1** and **2**. The twist conformation is 21.9 and 8.6 kJ mol^{-1} higher than the corresponding chair form in **1** and **2**, respectively. The calculated energy barriers for the chair-to-twist processes in **1** and **2** are 56.3 and 61.1 kJ mol^{-1}, respectively, while the dynamic ^{1}H NMR values[15] are 48.50 and 57.0 kJ mol^{-1}, respectively. The energy values calculated with B3LYP/6-31+G* method are in better agreement with the experimental results (see Tables I, II, and III).

The energy difference between the chair and twist conformations of **2** is significantly lower relative to that calculated for the parent ring system **1**. The lower energy difference in **2** can be attributed to an unfavorable repulsion between the axial methyl groups and the gauche sulfur atoms. This repulsion decreases the stability of the chair form of **2** relative to that of **1**, but it has little effect on the twist form (Scheme 3).



R = H, CH_3

SCHEME 3

TABLE I Calculated Total and Zero-Point Vibrational Energies (Hartree) and Relative Energy (Including Zero-Point Energy, kJ mol^{-1}) for Various Conformations of 1,2 Dithiane (**1**)

Structure	**1-Chair,** C_1	**1-Twist,** C_2	**1-TB,** C_2
HF/6-31+G*//HF/6-31+G*	−951.1591	−951.1503	−951.1381
MP2/6-31+G*//HF/6-31+G*	−951.9318	−951.9234	−951.9102
B3LYP/6-31+G*//HF/6-31+G*	−953.6346	−953.6267	−953.6148
ZPE	0.1249	0.1248	0.1247
E^a_{rel}/ kJ mol^{-1}	0.0	22.9	54.9
E^b_{rel}/ kJ mol^{-1}	0.0 (0.0)[d]	21.9 (16.3)[d]	56.3 (48.5)[d]
E^c_{rel}/ kJ mol^{-1}	0.0	20.5	51.5
r_{12}/Å	2.061	2.056	2.050
r_{23}/Å	1.821	1.831	1.815
r_{34}/Å	1.530	1.540	1.552
r_{45}/Å	1.535	1.533	1.562
r_{56}/Å	1.530	1.540	1.552
r_{61}/Å	1.821	1.831	1.815
θ_{123}/°	99.1	99.9	96.6
θ_{234}/°	112.9	113.9	116.6
θ_{345}/°	114.7	113.9	122.3
θ_{456}/°	114.7	113.9	122.3
θ_{561}/°	112.9	113.9	116.6
θ_{612}/°	99.1	99.9	96.6
ϕ_{1234}/°	62.2	−33.8	55.8
ϕ_{2345}/°	−63.5	−32.2	−13.5
ϕ_{3456}/°	60.4	76.6	14.9
ϕ_{4561}/°	−63.5	−32.2	13.5
ϕ_{5612}/°	62.2	−33.8	55.8
ϕ_{6123}/°	−56.7	63.3	71.0

Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations.

Experimental values are given in parentheses.

[a]Relative energy with respect to the most stable conformation from HF/6-31+G*//HF/6-31+G* calculations.

[b]Relative energy with respect to the most stable conformation from MP2/6-31+G*//HF/6-31+G* calculations.

[c]Relative energy with respect to the most stable conformation from B3LYP/6-31+G*//HF/ 6-31+G* calculations.

[d]^{1}H NMR data, see Claeson et al.[15]

1,2,4,5-Tetrathiane (3) and 3,3,6,6-Tetramethyl-1,2,4,5-tetrathiane (4)

The relation between the conformational features of cyclohexane and tetrathianes **3** and **4** are rather remote. While these appear to be no conformational data on the parent tetrathiane **3**, derivatives of this ring system have been studied by dynamic NMR spectroscopy. The molecular

TABLE II Calculated Total and Zero-Point Vibrational Energies (Hartree) and Relative Energy (Including Zero-Point Energy, kJ mol^{-1}) for Various Conformations of 3,3,6,6-Tetramethyl-1,2-Dithiane (**2**)

Structure	**2-Chair,** C_2	**2-Twist,** C_2	**2-TB,** C_2
HF/6-31+G*//HF/6-31+G*	−1107.2966	−1107.2924	−1107.2736
MP2/6-31+G*//HF/6-31+G*	−1108.6232	−1108.6198	−1108.5999
B3LYP/6-31+G*//HF/6-31+G*	−1110.8947	−1110.8909	−1110.8737
ZPE	0.2442	0.2441	0.2442
E^a_{rel}/kJ · mol^{-1}	0.0	10.51	60.35
E^b_{rel}/kJ · mol^{-1}	0.0 (0.0)[d]	8.63 (10.0)[d]	61.13 (57.0)[d]
E^c_{rel}/kJ · mol^{-1}	0.0	9.70	55.10
r_{12}/Å	2.057	2.051	2.044
r_{23}/Å	1.845	1.854	1.836
r_{34}/Å	1.541	1.549	1.561
r_{45}/Å	1.536	1.534	1.567
r_{56}/Å	1.541	1.549	1.561
r_{61}/Å	1.845	1.854	1.836
θ_{123}/°	101.8	100.6	99.7
θ_{234}/°	109.3	110.5	112.8
θ_{345}/°	117.6	115.4	125.3
θ_{456}/°	117.6	100.6	125.3
θ_{561}/°	109.3	110.5	112.8
θ_{612}/°	101.8	115.4	99.7
ϕ_{1234}/°	−58.3	34.3	−53.2
ϕ_{2345}/°	61.3	32.4	14.2
ϕ_{3456}/°	−63.3	−79.1	0.0
ϕ_{4561}/°	61.3	32.4	14.2
ϕ_{5612}/°	−58.3	34.3	−53.2
ϕ_{6123}/°	56.3	−65.7	70.1

Zero-point vibrational energy is scaled by a factor to 0.9135 to eliminate known systematic errors in calculations.

Experimental values are given in parentheses.

[a]Relative energy with respect to the most stable conformation from HF/6-31+G*//HF/6-31+G* calculations.

[b]Relative energy with respect to the most stable conformation from MP2/6-31+G*//HF/6-31+G*calculations.

[c]Relative energy with respect to the most stable conformation from B3LYP/6-31+G*//HF/6-31+G*calculations.

[d]^{1}HNMR data, see Claeson et al.[15]

structure of 3,3:6,6-bis(pentamethylene)-*s*-tetrathiane has been determined by X-ray crystallography.[16]

These studies revealed that, in contrast to the solution conformational preference, the solid state has the heterocyclic ring in chair conformation. The calculated energy difference between the chair and twist conformations in **3** is 10.7 kJ mol^{-1}, which is much lower than that in

TABLE III Calculated Total and Zero-Point Vibrational Energies (Hartree) and Relative Energy (Including Zero-Point Energy, kJ mol^{-1}) and Structural Parameters for Various Conformations of 3,3,6,6-Tetramethyl-1,2,4,5-Tetrathiane (**4**)

Structure	**3-Chair,** C_2	**3-Twist,** D_2	**3-TB,** C_2
HF/6-31+G*//HF/6-31+G*	−1824.2391	−1824.2386	−1824.2146
MP2/6-31+G*//HF/6-31+G*	−1825.5543	−1825.5556	−1825.5277
B3LYP/6-31+G*//HF/6-31+G*	−1828.6416	−1828.6419	−1828.6189
ZPE	0.1861	0.1859	0.1857
E^a_{rel}/kJ · mol^{-1}	0.0	1.0	63.4
E^b_{rel}/kJ · mol^{-1}	4.0 (1.7)[d]	0.0 (0.0)[d]	72.8 (67.0)[d]
E^c_{rel}/kJ · mol^{-1}	1.3	0.0	59.9
r_{12}/Å	2.055(2.035)[e]	2.042	2.014
r_{23}/Å	1.841(1.841)[e]	1.849	1.855
r_{34}/Å	1.841(1.841)[e]	1.849	1.855
r_{45}/Å	2.055(2.035)[e]	2.042	2.055
r_{56}/Å	1.841(1.841)[e]	1.849	1.855
r_{61}/Å	1.841(1.841)[e]	1.849	1.855
θ_{123}/°	104.8(104.7)[e]	103.6	107.4
θ_{234}/°	110.2(108.0)[e]	112.4	114.7
θ_{345}/°	104.8(104.7)[e]	103.6	117.5
θ_{456}/°	104.8(104.7)[e]	103.6	117.5
θ_{561}/°	110.2(108.0)[e]	112.4	114.7
θ_{612}/°	104.8(104.7)[e]	103.6	107.4
ϕ_{1234}/°	67.7	35.0	53.8
ϕ_{2345}/°	−67.7	35.0	−19.0
ϕ_{3456}/°	63.9	−77.2	0.0
ϕ_{4561}/°	−67.7	35.0	−19.0
ϕ_{5612}/°	67.7	35.0	53.8
ϕ_{6123}/°	−63.9	−77.2	−70.2

Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations.

Experimental values are given in parentheses.

[a]Relative energy with respect to the most stable conformation from HF/6-31+G*//HF/6-31+G* calculations.

[b]Relative energy with respect to the most stable conformation from MP2/6-31+G*//HF/6-31+G* calculations.

[c]Relative energy with respect to the most stable conformation from B3LYP/6-31+G*//HF/6-31+G* calculations.

[d]1H NMR data, see Bushweller et al.[17]

[e]X-ray crystallographic data for bis(pentamethylene)-*s*-tetrathiane, see Bushweller et al.[16]

cyclohexane (Table IV). This energy difference is somewhat higher than the experimental value of 4.6 kJ mol^{-1}.[15]

The structural parameters for various geometries of **4** by ab initio calculation is given in Table III. The D_2 symmetric twist form of **4**

TABLE IV Calculated Total and Zero-Point Vibrational Energies (Hartree) and Relative Energy (Including Zero-Point Energy, kJ mol^{-1}) for Various Conformations of 1,2,4,5-Tetrathiane (**3**)

Structure	**4-Chair,** C_{2h}	**4-Twist,** D_2	**4-TB,** C_2
HF/6-31+G*//HF/6-31+G*	−1668.0979	−1668.0919	−1668.0736
MP2/6-31+G*//HF/6-31+G*	−1668.8536	−1668.8493	−1668.8275
B3LYP/6-31+G*//HF/6-31+G*	−1671.3759	−1671.3713	−1671.3529
ZPE	0.0668	0.0666	0.0664
E^a_{rel}/kJ · mol^{-1}	0.0	15.4	62.7
E^b_{rel}/kJ · mol^{-1}	0.0	10.7	67.5
E^c_{rel}/kJ · mol^{-1}	0.0	11.6	59.4
r_{12}/Å	2.060	2.049	2.115
r_{23}/Å	1.816	1.826	1.833
r_{34}/Å	1.816	1.826	1.803
r_{45}/Å	2.060	2.049	2.049
r_{56}/Å	1.816	1.826	1.803
r_{61}/Å	1.816	1.826	1.833
θ_{123}/°	101.5	102.3	98.9
θ_{234}/°	114.4	116.1	119.0
θ_{345}/°	101.5	102.3	112.3
θ_{456}/°	101.5	102.3	112.3
θ_{561}/°	114.4	116.1	119.0
θ_{612}/°	101.5	102.3	98.9
ϕ_{1234}/°	−71.4	34.7	−62.8
ϕ_{2345}/°	71.4	34.7	17.4
ϕ_{3456}/°	−61.7	−74.7	10.6
ϕ_{4561}/°	71.4	34.7	17.4
ϕ_{5612}/°	−71.4	34.7	−62.8
ϕ_{6123}/°	61.7	−74.7	83.3

Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations.

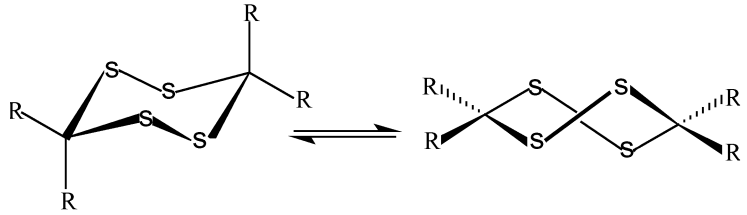
[a]Relative energy with respect to the most stable conformation from HF/6-31+G*//HF/6-31+G* calculations.

[b]Relative energy with respect to the most stable conformation from MP2/6-31+G*//HF/6-31+G* calculations.

[c]Relative energy with respect to the most stable conformation from B3LYP/6-31+G*//HF/6-31+G* calculations.

is 4.0 kJ mol^{-1} more stable than the C_{2h} symmetric chair conformer. According to these calculations, the most probable transition state for chair-twist interconversion in **4** has 72.8 kJ mol^{-1} energy. The twist conformation of **4** is calculated to be the favored form, in agreement with the dynamic NMR measurements.[17]

In conclusion, ab initio calculations at the HF/6-31+G*, MP2/6-31+G*, and B3LYP/6-31+G* levels of theory provide a picture of the conformations of **1–4** from both structural and energetic points of view. The



R = H, CH_3

SCHEME 4

presence of adjacent atoms possessing lone pairs of electrons leads to substantial enhancements in the barriers to ring inversion in these six-membered heterocycles as compared to that for cyclohexane. As shown in Tables I–IV, these calculations predict the chair conformation to be the energy minimum, except for **4**. The agreement between the energy barriers calculated with B3LYP/6-31+G* method and the experimentally determined values is generally better than those calculated with HF/6-31+G* and MP2/6-31+G* methods.

CALCULATIONS

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 program.[18] Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraint.[19] The restricted Hartree-Fock calculations with the split-valence 6-31G* basis set, which include a set of d-type polarization functions on all nonhydrogen atoms, were used in these calculations.[20] Single-point energy calculations at MP2/6-31+G*//HF/6-31+G* and B3LYP/6-31+G*//HF/6-31+G*[21] levels were used to evaluate the electron correlation effect in the energies and order of stability of conformers. Vibrational frequencies were calculated at the 6-31+G* level for all minimum energies and transition states, which were confirmed to have zero imaginary frequency, respectively. The frequencies were scaled by a factor of 0.9135[22] and used to compute the zero-point vibrational energies.

Since the theoretical results are free from intermolecular interferences, they are a valuable tool for a systematic study of conformational effects in simple organic molecules.

REFERENCES

[1] a) K. Morita and S. Kobayashi, *Chem. Pharm. Bull*., **15,** 988 (1967); b) K. Morita and S. Kobayashi, *Tetrahedron Lett*., **7,** 573 (1966); c) R. Gemelin, R. Susilo, and G. R. Fenwick, *Phytochemistry*, **20,** 2521 (1981); d) L. N. Nixon, E. Wong, C. B. Johnson, and E. J. Birch, *J. Agric. Food Chem*., **27,** 355 (1979).

[2] F. Freeman, M. Aregullin, and E. Rodriguez, *Rev. Heteroatom Chem*., **9,** 1 (1993).

[3] M. Tazaki and M. Tagaki, *Chem. Lett*., 767 (1979).

[4] M. C. Caserio, C. L. Fisher, and J. K. Kim, *J. Org. Chem*., **50,** 4390 (1985).

[5] D. Scholz, *Synthesis*, 994 (1983).

[6] T. Billard and B. R. Langlois, *Tetrahedron Lett*., **37,** 6865 (1996).

[7] R. G. Nuzzo, A. F. Florence, and D. L. Allara, *J. Am. Chem. Soc*., **109,** 235 (1987).

[8] W. W. Cleland, *Biochemistry*, **3,** 480 (1964).

[9] L. Field and Y. H. Kim, *J. Org. Chem*., **37,** 2710 (1973).

[10] X. Wu, R. D. Rieke, and L. Zhu, *Synth. Commun*., **26,** 191 (1946).

[11] G. Crank and M. I. H. Makin, *Aust. J. Chem*., **37,** 2331 (1984).

[12] A. S. Gopalan and H. K. Jacobs, *J. Chem. Soc., Perkin Trans 1*, 1897 (1990).

[13] C. J. Burns, L. D. Field, J. Morgan, D. D. Ridley, and V. Vignervich, *Tetrahedron Lett.,* 6489 (1999).

[14] G. M. Kellie and F. G. Riddell, *Top. Stereochem.,* **8,** 225 (1974).

[15] G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc*., **83,** 4357 (1961).

[16] C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunelle, H. S. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc*., **97,** 65 (1975).

[17] C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *J. Am. Chem. Soc*., **92,** 3055 (1970).

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rubuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Oritz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head- Gordon, E. S. Replogle, and J. A. Pople, Gaussian 98, Revision A. 6 (Gaussian. Inc., Pittsburgh, PA, 1998).

[19] F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999).

[20] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*. **28,** 213 (1973).

[21] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2000).

[22] R. S. Grev, C. L. Janssen, and H. F. Schaefer, *Chem. Phys*., **95,** 5128 (1991).