J. Phys. Chem. A **2003,** *107,* 7981−7984

Structures and Stabilities of $B_2H_{2n}^{2+}$ Dications ($n = 1-4$)

Jacques F. Dias,[†,‡] Golam Rasul,[*,†] Peter Rudolf Seidl,[§] G. K. Surya Prakash,[*,†,||] and George A. Olah[†]

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, Departamento de Química - Instituto Militar de Engenharia, Rio de Janeiro - Rio de Janeiro, Brazil 22290-270, Instituto de Química - Universidade Federal Fluminense, Niterói - Rio de Janeiro, Brazil 24020-150

Received: June 11, 2003; In Final Form: July 9, 2003

Structures of $B_2H_{2n}^{2+}$ dications ($n = 1-4$) were investigated at the QCISD(T)/6-311G** level of theory. Thermodynamic and kinetic stabilities of the dications were also estimated. Although deprotonations of the dications are exothermic (except the dication $B_2H_2^{2+}$), they show considerable kinetic barriers. The charge distributions and Wiberg bond indices were calculated by the NBO method. ^{11}B NMR chemical shifts were also calculated by GIAO-MP2 and GIAO-DFT methods.

Introduction

The structures of main group hydriodo dications have been a topic of numerous theoretical and experimental investigations.[1,2] Recently, we reported the study of structures and stabilities of hydriodo-borane dications BH_n^{2+} ($n = 1-8$) using ab initio and density functional theory (DFT) methods at the MP2/aug-cc-pVTZ and B3LYP/ aug-cc-pVTZ levels, respectively.[1] The dications BH^{2+} and BH_2^{2+} were characterized as unstable, both kinetically and thermodynamically. The structures of BH_n^{2+} ($n = 3-8$) dications contain one or more two-electron, three-center (2e−3c) bonds. Calculations indicate that the BH_n^{2+} ($n = 3-8$) dications have considerable kinetic barrier for deprotonation. The structures of the $B_2H_2^{2+}$ dication as well as $B_2H_3^{3+}$ trications were recently investigated at the ab initio QCISD(T)/6-311G** level by DiLabio and Matusek.[3] In a recent study, Jursic reported the study of the $B_2H_8^{2+}$ dication at the MP2/6-31G** level.[4] In continuation of our study of the main group hydrido dications, we have now extended our investigations to the structures and stabilities of $B_2H_{2n}^{2+}$ dications ($n = 1-4$) by ab initio calculations at the QCISD(T)/6-311G** level. The thermodynamic and kinetic barriers for deprotonation processes of dications were also estimated. ^{11}B NMR chemical shifts were calculated using GIAO-MP2 and GIAO-DFT methods

TABLE 1: Nimag[a] Total Energies (in au), ZPE,[b] and Relative Energies (in kcal/mol)[c]

	Nimag	MP2/6-311G**	QCISD(T)/6-311G**	ZPE	rel energy
1	0	−49.65406	−49.68435	12.3	0.0
1tsa	1	−49.46687	−49.50749	6.5	105.2
1tsb	1	−49.52260	−49.60227	8.4	47.7
2s	0	−49.54956	−49.59605	5.5	48.7
2t	0	−49.50860	−49.54203	7.7	84.7
3	0	−24.85229	−24.86646	3.6	−35.5
4	0	−50.87663	−50.91407	23.3	0.0
4tsa	1	−50.76885	−50.80572	18.3	63.0
4tsb	1	−50.82639	−50.86472	19.9	27.6
5	0	−50.85940	−50.89651	22.7	10.4
6	0	−50.79653	−50.83304	22.9	50.4
7	0	−50.87731	−50.91471	18.2	−5.5
8	0	−52.09837	−52.14225	35.3	0.0
8ts	1	−52.09412	−52.13759	35.0	2.6
9	0	−52.09830	−52.14072	35.2	0.8
9ts	1	−52.02107	−52.06205	32.0	47.0
10	0	−52.09066	−52.13489	34.6	3.9
11	0	−52.03415	−52.07641	33.6	39.6
12	0	−52.14821	−52.1889	32.5	−32.1
12ts	1	−52.10212	−52.15796	31.9	−13.3
13	0	−53.31855	−53.36898	47.7	0.0
14	0	−53.31421	−53.36469	47.4	2.4
15	0	−53.29916	−53.34844	43.2	8.5

[a] Number of imaginary frequencies (Nimag); [b] Zero-point vibrational energies (ZPE) at MP2/6-311G**//MP2/6-311G** scaled by a factor of 0.96. [c] At QCISD(T)/6-311G**//QCISD(T)/6-311G** + ZPE level.

Calculations

The geometries were optimized at the ab initio MP2/6-311G** level. Vibrational frequencies at the MP2/6-311G**//MP2/6-311G** level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) or transition-state structures (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.96.[5] Further optimizations were carried out at the QCISD(T)/6-311G** level. Final energies were calculated at the QCISD(T)/6-311G**//QCISD(T)/6-311G** + ZPE level. QCISD(T)/6-311G** structures and final energies are discussed throughout the paper unless otherwise stated. Charge distribution and Wiberg bond indices (bond order)[6] were calculated at the QCISD(T)/6-311G**//QCISD(T)/6-311G** level according to the natural orbital (NBO) method.[7] Calculations were performed with the Gaussian 98 program system.[8] ^{11}B NMR chemical shifts were also computed by the gauge-independent atomic orbitals (GIAO) method.[9] GIAO calculations were performed by two different methods, namely, GIAO-MP2 and GIAO-DFT,[10] using QCISD(T)/6-311G** optimized geometries. GIAO-MP2, using the tzp basis set,[11] has been performed with the ACES II

---

[*] Corresponding authors.

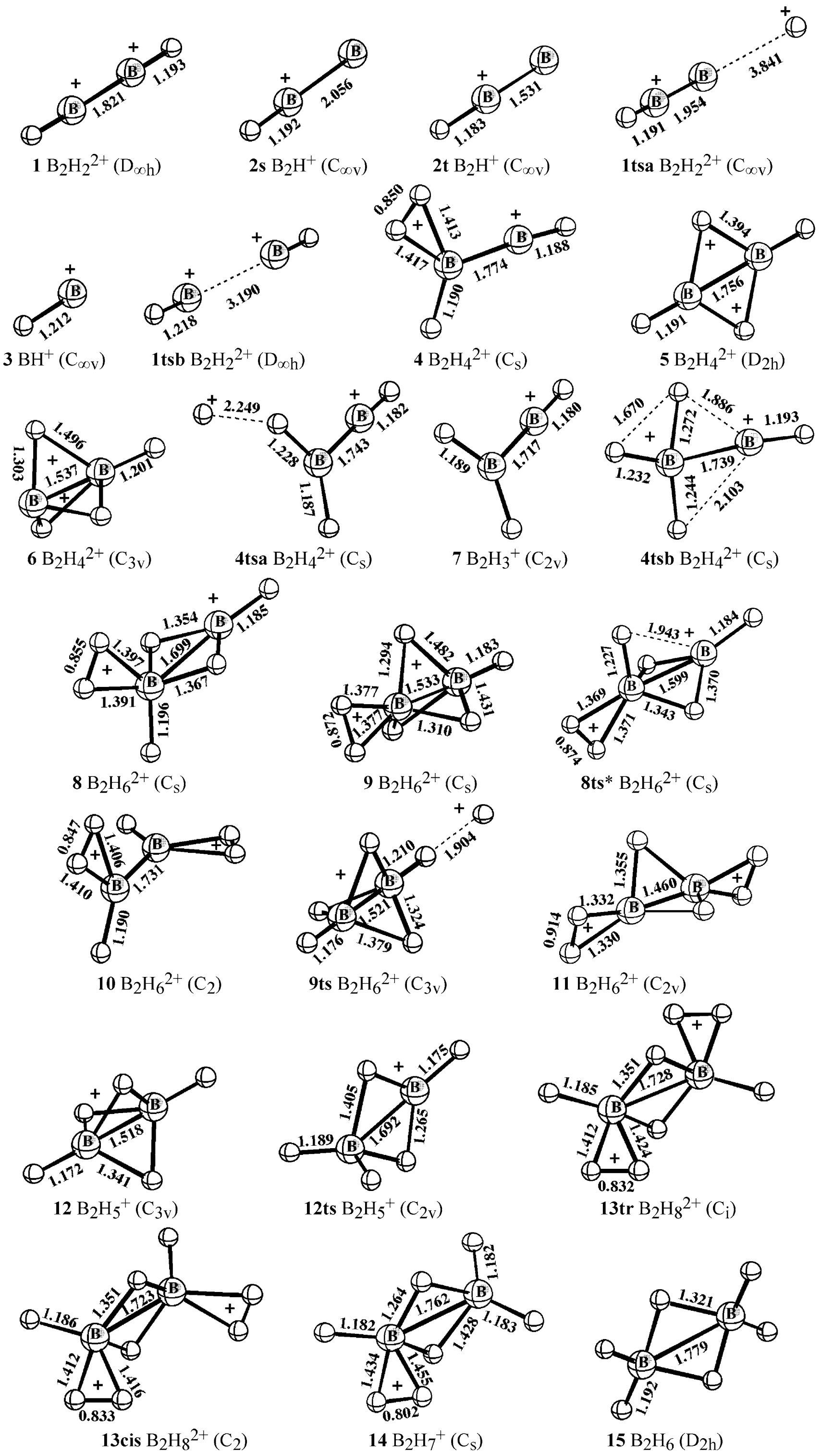
[†] Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California.

[‡] Departamento de Química - Instituto Militar de Engenharia.

[§] Instituto de Química - Universidade Federal Fluminense.

[||] E-mail: gprakash@usc.edu.

10.1021/jp0307405 CCC: $25.00



1 $B_2H_2^{2+}$ ($D_{\infty h}$) **2s** B_2H^+ ($C_{\infty v}$) **2t** B_2H^+ ($C_{\infty v}$) **1tsa** $B_2H_2^{2+}$ ($C_{\infty v}$)

3 BH^+ ($C_{\infty v}$) **1tsb** $B_2H_2^{2+}$ ($D_{\infty h}$) **4** $B_2H_4^{2+}$ (C_s) **5** $B_2H_4^{2+}$ (D_{2h})

6 $B_2H_4^{2+}$ (C_{3v}) **4tsa** $B_2H_4^{2+}$ (C_s) **7** $B_2H_3^+$ (C_{2v}) **4tsb** $B_2H_4^{2+}$ (C_s)

8 $B_2H_6^{2+}$ (C_s) **9** $B_2H_6^{2+}$ (C_s) **8ts*** $B_2H_6^{2+}$ (C_s)

10 $B_2H_6^{2+}$ (C_2) **9ts** $B_2H_6^{2+}$ (C_{3v}) **11** $B_2H_6^{2+}$ (C_{2v})

12 $B_2H_5^+$ (C_{3v}) **12ts** $B_2H_5^+$ (C_{2v}) **13tr** $B_2H_8^{2+}$ (C_i)

13cis $B_2H_8^{2+}$ (C_2) **14** $B_2H_7^+$ (C_s) **15** B_2H_6 (D_{2h})

Figure 1. QCISD(T)/6-311G** optimized structures of **1**−**15** (* at MP2/6-311G**).

program.[12] GIAO-DFT were done at B3LYP/6-311G** level using the Gaussian 98 program system.[8] The calculated ^{11}B NMR chemical shifts were referenced to B_2H_6 [GIAO-MP2 calculated absolute shift i.e., $\sigma(B) = 97.4$ and GIAO-DFT calculated absolute shift i.e., $\sigma(B) = 83.6$].

Results and Discussion

Linear structure **1** was found to be the only minimum on the potential energy surface (PES) of $B_2H_2^{2+}$ (Figure 1). As reported before by DiLabio and Matusek,[3] it has a relatively long boron−boron bond length of 1.821 Å. Two different dissociation paths for **1** were computed, deprotonation and homolytic cleavage of the boron−boron bond, as shown in Figure 2. The deprotonation process to give singlet B_2H^+ **2s** was found to be endothermic by 48.7 kcal/mol. This process also has a very high kinetic barrier of 105.2 kcal/mol through the transition state **1tsa**. We have also calculated the structure of triplet B_2H^+ **2t**. However, the triplet structure is substantially higher in energy than singlet **2s** by 36.0 kcal/mol. On the other hand, homolytic cleavage of **1** into 2BH$^+$ **3** was calculated to be exothermic by 35.5 kcal/mol. This process has also a high kinetic barrier of 47.7 kcal/mol through the transition state **1tsb**.

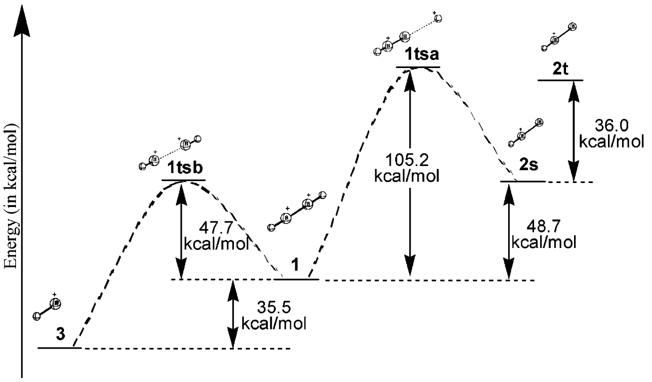


Figure 2. Pictorial representation of the $B_2H_2^{2+}$ PES.

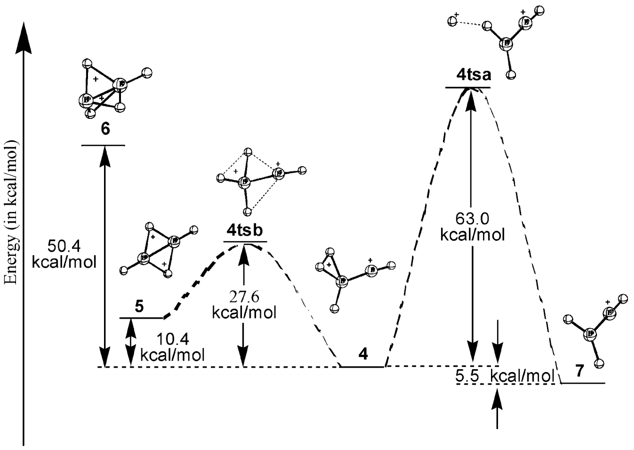
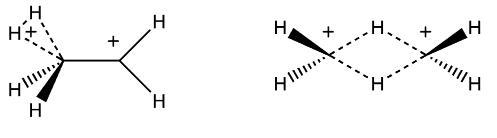


Figure 3. Pictorial representation of the $B_2H_4^{2+}$ PES.

SCHEME 1



2e-3c bonded

doubly hydrogen bridged

Three structures (**4**−**6**) were located as minima on the PES of $B_2H_4^{2+}$ (Figure 1 and Figure 3). The planar structure **4** is characterized with a 2e−3c bond. Structure **4** resembles a complex between **1** and a hydrogen molecule, resulting in the formation of a 2e−3c bond. **5** is also planar and is characterized as a doubly hydrogen-bridged structure. On the other hand, structure **6** is a triply hydrogen-bridged structure. Structure **4** is the most stable, being 10.4 kcal/mol more stable than **5** and 50.4 kcal/mol more stable than **6**. These differences of energy show the stabilizing role of the 2e−3c bond in **4** compared to the bridged hydrogen bond in **5** and **6**. Structure **4** can also be compared to the carbon analogue of the ethane dication $C_2H_6^{2+}$ previously studied by Olah et al.[13] In the ethane dication, the carbenium−carbonium structure with a 2e−3c bond was found to be more stable than the doubly hydrogen-bridged diborane type structures (Scheme 1).

We have located the transition structure **4tsa** for deprotonation of **4** into **7**. This deprotonation also has a very high kinetic barrier of 63.0 kcal/mol. However, the process is exothermic by only 5.5 kcal/mol. We also located the transition state **4tsb** that connects **4** with **5**. This isomerization path shows a substantial kinetic barrier of 27.6 kcal/mol. The pictorial representation of the PES of $B_2H_4^{2+}$ is depicted in Figure 3.

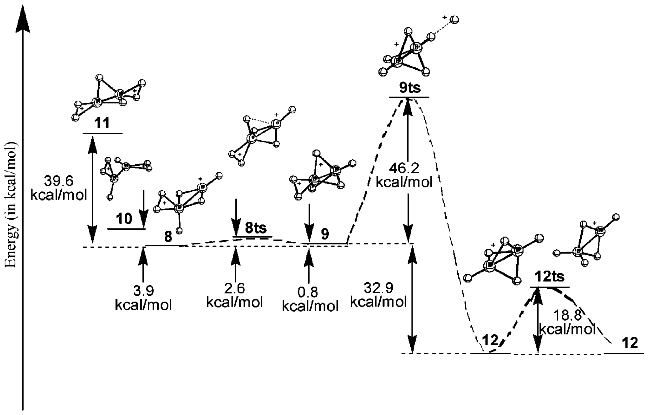


Figure 4. Pictorial representation of the $B_2H_6^{2+}$ PES.

Four minimum (**8**−**11**) structures were located on the PES of diborane dication, $B_2H_6^{2+}$ (Figure 1 and Figure 4). Doubly hydrogen-bridged structure **8** with a 2e−3c bond was found to be the lowest minimum. One of the borons in structure **8** is six-coordinated and the other one is four-coordinated. Structure **9**, on the other hand, is triply hydrogen-bridged with a 2e−3c bond. However, structure **9** is only 0.8 kcal/mol less stable than **8**. We have located the transition state **8ts** connecting the structures **8** and **9**. **8ts** lies above **8** by only 2.6 kcal/mol. We have also located the transition state **9ts** for deprotonation of **9**. Deprotonation of **9** into **12** was found to be exothermic by 32.9 kcal/mol, although it has a significantly high kinetic barrier of 46.2 kcal/mol through the transition state **9ts**. The third minimum corresponds to **10** and is only 3.9 kcal/mol less stable than **8**. Structure **10**, unlike structures **8** and **9**, was characterized to be a non-hydrogen-bridged structure. **10** with two 2e−3c bonds can be considered as a complex between **1** and two hydrogen molecules. The least stable isomer for $B_2H_6^{2+}$ is **11**, which is almost 40 kcal/mol less stable than **8**. This doubly hydrogen-bridged structure also contains two 2e−3c bonds. The energy profile of the PES of $B_2H_6^{2+}$ is displayed in Figure 4.

Two minimum energy structures, **13tr** and **13cis**, were located for $B_2H_8^{2+}$. **13tr** is more stable than **13cis** by only 2.4 kcal/mol, in agreement with the results shown by Jursic.[4] Both structures are doubly hydrogen-bridged with two 2e−3c bonds. The deprotonation of **13tr** into **14** is calculated to be exothermic by 8.5 kcal/mol. No transition state for deprotonation was, however, located.

We have calculated the charge distribution and Wiberg bond indices according to the NBO method. In dication **1,** both positive charges are concentrated only on the boron atoms. In dication **4,** the divalent boron carries a charge of 1.12 and the tetravalent boron carries a charge of only 0.35. Similar charge distributions are also observed for dication **8** with the lower coordinated boron carrying substantially more positive charge than the higher coordinated boron atom. The charge distributions along with the calculated Wiberg bond indices of other ions are given in Figure 5.

We have also calculated the ^{11}B NMR chemical shifts of the boron dications as well as monocations by the GIAO-MP2 method (Figure 5). For comparison ^{11}B NMR chemical shifts were also calculated by the GIAO-DFT method. In most of the dications, the GIAO-MP2 calculated values agree very well with the GIAO-DFT method. The GIAO-MP2-calculated $\delta^{11}B$ of **1** is 65.6, and it agrees very well with the GIAO-DFT value of 64.5. Similarly, GIAO-MP2-calculated $\delta^{11}B$ of divalent and tetravalent borons of **4** are 87.2 and 44.3, respectively, and agree rather well with the GIAO-DFT values of 89.7 and 44.0.

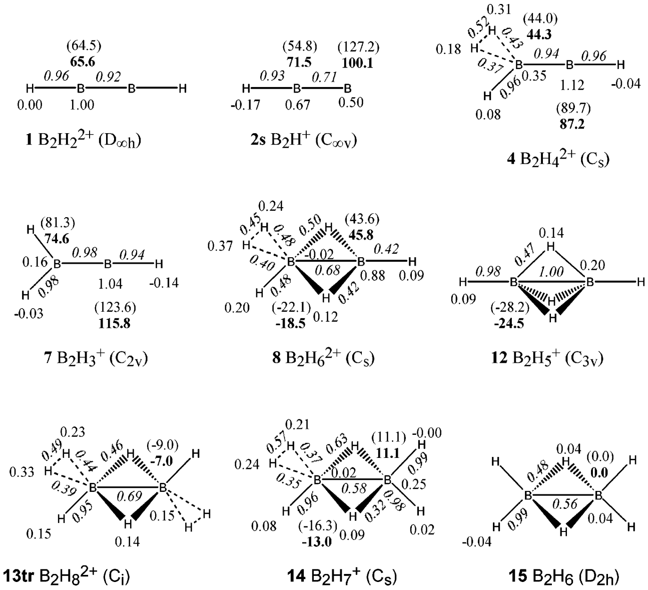


Figure 5. QCISD(T)/6-311G** calculated NBO charges and Wiberg bond index (in italics); GIAO MP2/tzp (in bold) and B3LYP/6-311G** (in parentheses) calculated ^{11}B NMR chemical shifts of structures **1**, **2s**, **4**, **7**, **8**, **12**, **13tr**, **14,** and **15**.

However, in monocations (such as **2s** and **7**), GIAO-MP2-calculated values differ somewhat from those of the GIAO-DFT values.

Conclusions

We have investigated the structures and energetics of $B_2H_{2n}^{2+}$ dications ($n = 1-4$) at the ab initio QCISD(T)/6-311G** level of theory. Deprotonations of most of the dications are calculated to be exothermic although the processes have substantial kinetic barrier. Wiberg bond indices and charge distributions were computed by the NBO method. The ^{11}B NMR chemical shifts were calculated by the GIAO-MP2 method. For comparison, the ^{11}B NMR chemical shifts were also calculated by the GIAO-DFT method.

References and Notes

(1) (a) *Chemistry in Superacids.* Part 63. For Part 62, see: Rasul, G.; Dias, J. F.; Seidl, P. R.; Prakash, G. K. S.; Olah, G. A. *J. Phys. Chem. A* **2003**, *107*, 4731.

(2) Koch, W.; Schwarz, H. *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987; Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321; Lammertsma, K. *Rev. Chem. Intermed.* **1988**, *9*, 141; Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimica* **1985**, *39*, 376; Schleyer, P. v. R.; *Adv. Mass Spectrom.* **1986**, *10*, 287. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

(3) DiLabio, G. A.; Matusek, D. R. *Chem. Phys. Lett.* **2000**, *317*, 597.

(4) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **1999**, *491*, 147.

(5) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, 1996; p 64.

(6) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(7) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Pople, J. A. *Gaussian 98* (Revision A.5); Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) London, F. J. *Phys. Radium* **1937**, *8*, 3974; Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789; Wolinski, K.; Himton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(11) Gauss, J. *J. Chem. Phys. Lett.* **1992**, *191*, 614; Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629; Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1991**, *97*, 2571.

(12) Stanton, J. F., Gauss, J., Watts, J. D., Lauderdale, W. J., Bartlett, R. J., Eds.; *ACES II*; Quantum Theory Project; University of Florida; Gainesville, FL, 1991.

(13) Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851.