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Concerning the Proton Affinity of Hydrazoic Acid and Methyl Nitrate

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The proton affinity (PA) of hydrazoic acid has been reevaluated with experimental and *ab initio* methods in order to resolve the disturbing discrepancy between experiment and theory introduced by a recent computational study performed at the CISD (fc)/6-311G(df,p)//MP2(full)/6-31G* + ΔZPVE (MP2(full)/6-31G*) level of theory, giving a value, 186.4 kcal mol^{-1} at 0 K, corresponding to ca 187.9 kcal mol^{-1} at 298 K, much higher than our earlier experimental value of 176.6 kcal mol^{-1} at 298 K. Additional experimental measurements have been performed by ICR mass spectrometry, using the equilibrium and the bracketing methods and reference bases including propene, methanol, and benzene, whose PA is firmly established. From the results of these experiments, the PA of HN_3 is estimated to be 180 ± 2 kcal mol^{-1} at 298 K, a value independently supported by additional mass spectrometric evidence obtained with the kinetic method based on the metastable decomposition of the $[MeOH–H–N_3H]^+$ proton-bound dimer. The results of an *ab initio* study of the HN_3 molecule and the $H_2N-N_2^+$ ion performed with the Gaussian-1 method give a PA of 177.9 kcal mol^{-1} at 0 K, corresponding to ca. 179.4 kcal mol^{-1} at 298 K, in excellent agreement with the experimental measurements. The overall conclusion is that all presently available evidence from high-level *ab initio* methods, as well as from different experimental techniques, suggests that the PA of HN_3 calculated at the CISD (fc)/6-311G(df,p)/MP2 (full)/6-31G* + ΔZPVE (MP2 (full)/6-31G*) was overestimated.

Recently, a theoretical estimate of the gas-phase proton affinities (PA) of HN_3 and $MeONO_2$ was reported.[1] The PA of HN_3 at 0 K, computed at the CISD (fc,ssc)/6-311G-(df,p)//MP2 (full)/6-31G* + ΔVZPE (MP2(full)/6-31G*) level of theory, amounts to 186.4 kcal mol^{-1}, corresponding to ca. 187.9 kcal mol^{-1} at 298 K, a value which is well in excess of the uncertainty range associated with the 176.6 ± 2 kcal mol^{-1} experimental value determined from our ICR equilibrium measurements at 298 K.[2,3] A similar discrepancy is found between the 186.4 kcal mol^{-1} value and previous theoretical estimates, 181.6 kcal mol^{-1} [4] and 176.2 kcal mol^{-1}, the latter computed by us at the MP2/6-31G*//6-31G* + ZPVE (6-31G*) level of theory.[2] Discussing the source of the discrepancy of their theoretical PA with experiment, the authors rule out errors affecting our ICR study of the prototropic equilibrium

$$(HN_3)H^+ + MeONO_2 \rightleftharpoons HN_3 + (MeONO_2)H^+ \quad (1)$$

whose results happen to agree with their theoretically derived ΔE_1 value. Instead, they suggest that the experimental PA of HN_3 reported by us is too low as a consequence of an underestimated PA of $MeONO_2$, the reference base in eq. 1. Their contention, based on the results of calculations performed at the CISD (fc, ssc)/6-311G** level of theory, giving a PA ($MeONO_2$) = 184.65 kcal mol^{-1} at 0 K, corresponding to 186.1 kcal mol^{-1} at 298 K, marks a second discrepancy from our experimental value of 176.0 kcal mol^{-1} deduced from ICR equilibrium measurements.[3]

In this work we address the problems raised by Glaser and Choy,[1] attempting to resolve the above disturbing discrepancies in the light of new, relevant evidence from both theoretical and experimental approaches.

Experimental Results. Considering HN_3 first, we note that Glaser and Choy[1] focus attention exclusively on eq. 1, as the source of experimental information on the PA of hydrazoic acid. As a matter of fact, published[2] results of ICR bracketing experiments show that $H_2N_3^+$ ions efficiently protonate benzene, PA = 181.3 kcal mol^{-1}.[5] These experiments, totally unrelated to $MeONO_2$, set an upper limit of ca. 180 kcal mol^{-1} to the PA of HN_3.

In the following sections we report the results of a careful reinvestigation of the problem, based both on ICR experiments performed by the equilibrium and/or the bracketing technique, and by the kinetic method, involving MIKE spectrometry of the proton-bound dimers formed by HN_3 with suitable reference bases.

Equilibrium Experiments. The method based on proton-transfer equilibrium constants is not particularly suitable in the case of HN_3, whose high reactivity prevents using otherwise valuable reference bases, and whose facile thermal decomposition when the inlet system and the ion source are heated above room temperature allows, in practice, only single-temperature equilibrium constant measurements. An additional restraint arises from the specific purpose of the present study, which requires using reference bases whose PA is firmly established. Two such

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(1) Glaser, R.; Choy, G. S.-C. *J. Org. Chem.* **1992,** *57,* 4976.

(2) Cacace, F.; Attinà, M.; de Petris, G.; Grandinetti, F.; Speranza, M. *Gazz. Chim. Ital.* **1990,** *120,* 691.

(3) Attinà, M.; Cacace, F.; Yañez, M. *J. Am. Chem. Soc.* **1987,** *109,* 5092.

(4) Glaser, R.; Choy, G. S.-C. *J. Phys. Chem.* **1991,** *95,* 7682.

(5) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988,** *17* (suppl. 1).

0022-3263/93/1958-3639$04.00/0

bases exist in the PA range of interest, namely propene, PA = 179.5 kcal mol^{-1}, a standard used in the construction of relative basicity scales, and methanol, whose PA = 181.9 kcal mol^{-1} has been established by at least five different measurements involving four different reference bases.[5]

Ionization of premixed HN_3/C_3H_6 mixtures of known composition yields both $H_2N_3^+$ and $C_3H_7^+$ ions, each of whom had been isolated with the multiple-resonance technique and allowed to react with the neutrals. It is worth noting that isolation of $C_3H_7^+$ (m/z = 43.0548) requires working at high resolution, since HN_3^+ (m/z = 43.0170) is also formed. The proton-transfer reaction

$$C_3H_7^+ + HN_3 \rightleftharpoons C_3H_6 + H_2N_3^+ \quad (2)$$

is observed to occur in both directions, and measurable intensities of the protonated species are simultaneously detectable over long observation periods. However, true equilibrium cannot be achieved owing to reactions other than eq 2, yielding CH_4N^+, $C_3H_6N^+$, etc. which gradually become predominant. The only firm conclusion from these experiments is that the difference between the GPB of HN_3 and of C_3H_6, and hence between their PA, is very unlikely to exceed 1-2 kcal mol^{-1}.

Although CH_3OH is more basic than HN_3, analogous experiments have shown that measurable intensities of $H_2N_3^+$ and $CH_3OH_2^+$ ions can be detected over long observation times following introduction of $CH_3OH_2^+$ or $H_2N_3^+$ ions, isolated by the multiple-resonance technique, into premixed gaseous mixtures containing an excess of HN_3. Again, attainment of the true prototropic equilibrium

$$CH_3OH_2^+ + NH_3 \rightleftharpoons CH_3OH + H_2N_3^+ \quad (3)$$

is prevented by the incursion of other reactions in particular the process

$$CH_3OH_2^+ + CH_3OH \rightleftharpoons (CH_3)_2OH^+ + H_2O \quad (4)$$

leading to the accumulation of protonated dimethyl ether. From the initial trends of the $H_2N_3^+$ and $CH_3OH_2^+$ intensities one can obtain an approximate estimate of K_3, indicating that the GPB of CH_3OH exceeds that of HN_3 by ca. 1.2 kcal mol^{-1}. Under the customary assumption that $\Delta(GPB) \cong \Delta(PA)$, the PA of HN_3 would amount to 180.7 kcal mol^{-1}, with an estimated uncertainty of ±2 kcal mol^{-1}.

Benzene, PA = 181.3 kcal mol^{-1}, has also been considered as a possible reference base. By allowing $C_6H_7^+$ ions, isolated by multiple resonance, to react in a premixed C_6H_6/HN_3 mixture containing a large excess of HN_3, well-measurable amounts of $C_6H_7^+$ and $H_2N_3^+$ can be detected over long observation times, but again true equilibrium cannot be attained, owing to the incursion of other reactions, yielding $C_6H_8N^+$ and especially $C_6H_6^{\bullet+}$, that gradually becomes the predominant ion. Although no quantitative data could be obtained, these experiments are significant, in that they support previous results showing that benzene is more basic than hydrazoic acid.[2]

Bracketing Experiments. In view of the problems associated with the application of the equilibrium method, the bracketing technique seems to represent the most suitable approach to the experimental determination of the PA of HN_3. Earlier experiments showed that the latter is intermediate between the PA of CH_2O and of C_6H_6, 171.7 and 181.3 kcal mol^{-1}, respectively.[5] In order to reduce the uncertainty range additional ICR bracketing experiments have been performed, where $H_2N_3^+$ ions isolated with the multiple-resonance technique have been allowed to react with suitable bases, B, observing whether or not proton transfer occurs and studying as well the inverse proton transfer from isolated BH^+ ions to HN_3. In order to minimize instrumental effects, two different ICR spectrometers have been used, equipped with an internal ion-source (FTMS 1000 model from Nicolet) and with both internal and external ion sources (Apex TM 47e from Bruker Spectrospin). The results show that HN_3 is more basic than CF_3COOCH_3, PA = 178.8 kcal mol^{-1} and CH_3NO_2, PA = 179.2 kcal mol^{-1},[5] although formation of $(CH_3NO_2)H^+$ ions in low, but detectable amounts, shows that the PA of hydrazoic acid and nitromethane cannot differ by more that 2 kcal mol^{-1}. Since HN_3 is less basic than C_6H_6, PA = 181.3 kcal mol^{-1},[2] the uncertainty range of the PA of HN_3 from the bracketing experiments is now restricted to the span from 179.2 to 181.3 kcal mol^{-1}, whose middle point, 180.2 kcal mol^{-1}, is consistent with the results of the equilibrium measurements reported in the previous section, which can be regarded in this context as bracketing experiments involving bases of comparable strength.

Summing up the results from all ICR experiments, we conclude that the PA of HN_3 can be assigned a value of 180 kcal mol^{-1}, with an estimated uncertainty of ±2 kcal mol^{-1}.

MIKE Spectrometry. In order to widen the scope of the experimental approach, we have resorted to a technique other than ICR spectrometry, namely the kinetic method based on the metastable dissociation of dimeric $(B_1\text{–}H\text{–}B_2)^+$ ions, where B_1 and B_2 are the two bases whose PA is being compared.[6] The method is a limiting-case procedure, based on simplified assumptions regarding the factors which control dissociation kinetics. Its results need to be used with great care,[7] especially when the proton is bound to two different functional groups, and hence the force constants of the two bounds involved are also different. In spite of these limitations, the kinetic method has been used successfully in a large number of cases, especially where alternative methods are not applicable,[6] and appears particularly suitable in the problem of interest, where the mere demonstration that HN_3 is less basic than a suitably chosen reference base may prove crucial. We have used methanol, whose PA is well established and falls in the range of interest, as discussed in the previous sections.

The proton-bound dimer formed by methanol and hydrazoic acid under chemical ionization conditions is found to undergo predominant metastable dissociation into protonated methanol, as illustrated by the typical MIKE spectrum reported in Figure 1. This provides additional evidence, entirely independent of ICR experiments, that the PA of HN_3 *is significantly lower* than that of MeOH, 181.9 kcal mol^{-1}, and hence that the 186.4 kcal mol^{-1} value at 0 K calculated by Glaser and Choy,[4] corresponding to 187.9 kcal mol^{-1} at 298 K, is overestimated. It is interesting that the ΔH_3 value calculated from the relative abundances of the $CH_3OH_2^+$ and $H_2N_3^+$ fragments from the metastable decomposition of the $(CH_3OH\text{–}H\text{–}HN_3)^+$ adduct amounts to 1.8 kcal mol^{-1}, which gives PA (HN_3) = 180.1 kcal mol^{-1}, in excellent

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(6) Majumdar, T. K.; Clairet, F.; Tabet, F.-C.; Cooks, R. G. *J. Am. Chem. Soc.*, **1992**, *114*, 2897 and ref. therein.

(7) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 698.

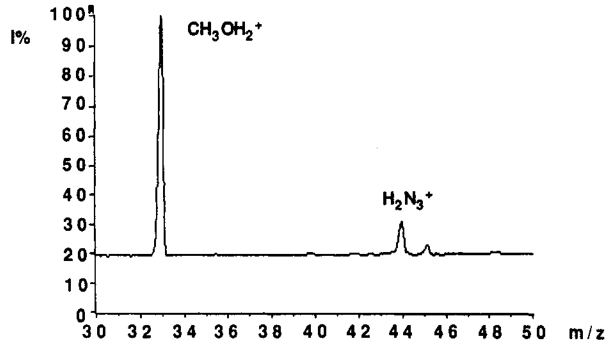

Figure 1. Metastable decomposition of the $(MeOH-H-HN_3)^+$ proton-bound dimer, $m/z = 76$, characterized by the predominant formation of protonated methanol, $m/z = 33$.

agreement with the value of 180 ± 2 kcal mol^{-1} from the ICR measurements.

Theoretical Calculation of the PA of Hydrazoic Acid. We have employed the Gaussian-1 theoretical procedure, designed recently by Pople and co-workers[8,9] with the aim of being able to predict thermochemical data to the so-called chemical accuracy, typically 2 kcal mol^{-1}, and whose usefulness in gas-phase ion chemistry has already been demonstrated.[10] The Gaussian-1 computed absolute energies of HN_3 and of the $H_2N-N_2^+$ ion are compared in Table I with those from earlier calculations at different levels of theory, whereas Table II summarizes the energies and the corrections required for the evaluation of the Gaussian-1 energies of the species of interest. Table III reports the PA at the temperature of 0 K of the HN_3 molecule calculated at various levels of theory. Inspection of Table III shows that the PA computed at the Gaussian-1 level of theory is significantly lower than the most recent value computed by Glaser and Choy,[1] and, more important, is in excellent agreement with our experimental value of 180 ± 2 kcal mol^{-1}, which refers to 298 K.[2] Curiously, the Gaussian-1 result is much closer to the earlier estimate of Glaser and Choy.[4]

The PA of Methyl Nitrate. The PA of $MeONO_2$ is relevant to the main problem addressed in the present discussion. In fact, the PA of HN_3 and that of $MeONO_2$ are strictly interdependent in the study of Glaser and Choy,[1] being linked by their computed ΔE_1 value, 2.9 kcal mol^{-1}. It follows that any new item of evidence pointing to a decrease of the PA of $MeONO_2$, estimated by Glaser and Choy[1] to be 184.65 kcal mol^{-1} at 0 K, reinforces the view that also their PA of HN_3 is overestimated.

In this connection, the theoretical results recently published by Lee and Rice[11] appear particularly significant, in that they are derived from a state-of-the-art computational approach. Their *ab initio* method includes self-consistent field (SCF), second-order Møller-Plesset (MP2) perturbation theory, single and double excitation coupled cluster (CCSD) theory, and the CCSD(CT) method, which incorporates a perturbational estimate of the effects of connected triple excitations. At such high level of theory the PA of $MeONO_2$ is 176.9 ± 5 kcal mol^{-1},[11] considerably lower than the 184.65 kcal mol^{-1} value calculated by Glaser and Choy.[1]

The experimental and theoretical results above outlined support the following conclusions: (i) The PA of HN_3 has been reevaluated using the principal experimental techniques currently available. Two ICR spectrometers of different design have been employed to perform equilibrium and bracketing experiments, using reference compounds of well established basicity. In addition, an entirely independent approach has been followed, namely the kinetic method based on the metastable decomposition of proton-bound dimers. The experimental results are mutually consistent, giving a PA of HN_3 of 180 ± 2 kcal mol^{-1} at 298 K, which represents a limited upward revision of our previous estimate, 176.6 ± 2 kcal mol^{-1}.[2] It should be mentioned that the increment falls in the range defined by the combined uncertainties of the two values, and that the revised PA remains far below the value calculated by Glaser and Choy,[1] 186.4 kcal mol^{-1} at 0 K, corresponding to 187.8 kcal mol^{-1} at 298 K, the temperature of the experimental measurements.

(ii) The experimental PA of HN_3 from this study is in excellent agreement with the value of 179 kal mol^{-1} from a correlation based on core-binding energies.[12]

(iii) The contention by Glaser and Choy[1] that the PA of $MeONO_2$ is as high as 184.65 kcal mol^{-1} is not supported by the independent study of Lee and Rice,[11] performed at a *higher* level of theory, giving a PA of $MeONO_2$ of 176.9 kcal mol^{-1}.

(iv) The PA of HN_3, calculated in this work at the Gaussian-1 level of theory, amounts to 177.9 kcal mol^{-1}, at 0 K, which corresponds to 179.4 kcal mol^{-1} at 298 K, in excellent agreement with the experimental value of 180 ± 2 kcal mol^{-1}.

It seems fair to conclude that in the specific system of interest, the calculations of Glaser and Choy,[1] even if performed at a rather high level, are apparently not adequate to give proton affinities of "chemical accuracy", and a higher level of theory is apparently required to obtain results reliable within a few kilocalories.

Experimental Section

Mass Spectrometric Measurements. The $(MeOH-H-HN_3)^+$ proton-bound dimer was obtained introducing vapors of HN_3 and of MeOH into the CI ion source of a ZAB-2F reversed-geometry mass spectrometer from VG-Micromass Ltd. The operating conditions were as follows: total pressure 0.2 torr, source temperature 150 °C, emission current 1 mA, repeller voltage 0 V. The metastable decomposition of the adduct was studied at a typical resolution of 4000 fwhm. The ICR measurements were carried out using both a FTMS 1000 spectrometer from Nicolet, or an APEX TM 47e spectrometer from Bruker Spectrospin, the latter equipped with an external CI ion source in addition to the standard internal source. The measurements were performed employing gaseous mixtures of known composition, premixed in pyrex bulbs by standard vacuum techniques. The ICR spectrometers were operated at room temperature, in the pressure range from 5×10^{-8} to 5×10^{-7} torr, with observation times up to 5×10^2 s.

Computational Details. *Ab initio* quantum-mechanical calculations were performed using a IBM RISC/6000 version of

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(8) Pople, J. A.; Head-Gordon, M.; Fox, D.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 522.

(9) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(10) See for instance Radom, J. *Int. J. Mass Spectrom. Ion Processes*, **1992**, special issue: Advances in Mass Spectrometry, Proceedings of the 12th International Mass Spectrometry Conference, Amsterdam, 1991, p 339.

(11) Lee, T. J.; Rice, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 8247.

(12) Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 536.

Table I. Absolute Energies (Atomic Units) of the HN_3 Molecule and the $H_2N{-}N_2^+$ Ion

		MP2(FU)/6-31G*			
species	MP2(FU)/6-31G*	MP4/6-311G**	MP4/6-311+G**	MP4/6-311G**(2df)	QCISD(T)/6-311G**
HN_3	−164.35125	−164.44608	−164.45353	−164.53491	−164.43420
$H_2N{-}N_2^+$	−164.643299	−164.74792	−164.75108	−164.83002	−164.74115

Table II. Energies[a] and Corrections[b] for the Evaluation of the Gaussian-1 Energies of the HN_3 Molecule and the $H_2N{-}N_2^+$ Ion

species	MP4/6-311G**	ΔE(+)	ΔE(2df)	ΔE(QCI)	ΔE(HLC)	ΔE(ZPE)[c]	Gaussian-1
HN_3	−164.44608	−7.45	−88.83	+11.88	−49.12	21.52	−164.55808
$H_2N{-}N_2^+$	−164.74792	−3.16	−82.10	+6.77	−49.12	33.98	−164.84155

[a] Energies in hartrees. [b] Corrections in millihartrees calculated as reported in the Experimental Section. [c] MP2(FU)/6-31G*.

Table III. Proton Affinity (0 K) of HN_3 Calculated at Various Computational Levels

	proton affinity, kcal mol^{-1}		
level of theory	0 K	298 K[a]	source
MP2(FU)/6-31G*// RHF6-31G* + ZPVE (RHF/ 6-31G*)	174.7 ± 4	176.2 ± 4	Cacace et al., ref 2
MP4(FC,SDTQ)/ 6-311G**// MP2(FU)/6-31G* + ZPVE (MP2(FU)/ 6-31G*)	181.6	183.1	Glaser and Choy, ref 4
CISD (FC, SSC)/ 6-311G(df,p)// MP2(FU)/ 6-31G* + ZPVE (MP2(FU)/ 6-31G*)	186.4	187.9	Glaser and Choy, ref 1
Gaussian-1	177.9 ± 2	179.4 ± 2	this work
experimental value		180.2 ± 2	this work

[a] Approximate values calculated from the PA at 0 K corrected for the translational and rotational contributions and for the -*RT* term.

the Gaussian 90 program package.[13] The standard internal 6-31G*,[14a] 6-311G**,[14b] 6-311+G**,[15] and 6-311G**(2df)[15] basis sets were thoroughly employed. Geometry optimizations of HN_3 and $H_2N_3^+$ were performed, in the full space of the coordinates, by analytical-gradient-based techniques,[16] in the framework of the 2nd order Møller-Plesset perturbation theory,[17] with the 6-31G* basis set. The MP2 theory was used with full (FU) electron correlation including inner-shell electrons. The details of these optimized geometries have been already discussed in ref 4. Single-point calculations, at the post-SCF level of theory, were performed within the Møller-Plesset framework up to the fourth order (MP4), by including single, double, triple, and quadruple excitation. The Gaussian-1 procedure[8] was employed to obtain the PA of the HN_3 molecule.

In the framework of the Gaussian-1 approach, which can be considered to be equivalent to a post-MP4 level, the correction for residual electron correlation energy effects, not taken into account at the MP4 (SDTQ) level of theory, is introduced by quadratic configuration interaction, which is known to reproduce full-configuration interaction (FCI) results quite well, particularly near equilibrium geometries.[18] To avoid very extensive calculations at the QCIST(T)/6-311+G** (2df) level of theory, four correction terms are added to the MP4(SDTQ)/6-311G**//MP2-(FU)/6-31G* absolute energies. These correspond to (i) the effects of the diffuse sp basis functions, (ii) the higher polarization functions on non-hydrogen atoms, and (iii) the corrections of residual correlation effects, and further to the so-called higher-level correction, HLC. Three additional calculations, at the MP4/6-311+G**, MP4/6-311G** (2df), and QCISD(T)/6-311G** level of theory, respectively, are required in order to obtain such corrections. If the corresponding absolute energies are denoted E_1, E_2, and E_3, the correction terms to the MP4/6-311G** computed value, designated as E_o, are $\Delta E(+) = E_1 - E_o$, $\Delta E(\text{2df}) = E_2 - E_o$, and $\Delta E(\text{QCISD(T)}) = E_3 - E_o$, respectively. The final value of the Gaussian-1 energy of a species is then given by the following equation:

$$E(\text{G1}) = E_o + \Delta E(+) + \Delta E(\text{2df}) + \Delta E(\text{QCISD(T)}) + \Delta E(\text{HLC}) + \Delta E(\text{ZPVE})$$

The fourth correction term, ΔE(HLC), is introduced in a parametric way,[8] and the fifth correction term, ΔE(ZPVE), takes into account the zero-point vibrational energy correction (at the MP2/6-31G* level of theory). All single point calculations are performed at the MP2(FU)/6-31G* optimized geometries.

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(13) *Gaussian-90*, Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1990.

(14) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *Ibid.* **1980**, *72*, 4244.

(15) Frish, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(16) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(17) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(18) Pople, J. A.; Head-Gordon, M.; Raghavachari, R. *J. Chem. Phys.* **1987**, *87*, 5968.