Gas-Phase Ion Chemistry of Nitramide. A Mass Spectrometric and ab Initio Study of H_2N-NO_2 and the $H_2N-NO_2^{\bullet+}$, $[H_2N-NO_2]H^+$, and $[HN-NO_2]^-$ Ions

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Abstract: The gas-phase ion chemistry of H_2N-NO_2 (**1**) has been studied with mass spectrometric and *ab initio* theoretical methods. The $H_2N_2O_2^{\bullet+}$ molecular ion is formed upon electron-impact ionization of **1**, whose photoelectron (PE) spectra have been recorded. From the onset of the PE bands the ionization energy of **1** has been estimated to be 11.02 ± 0.06 eV. Reaction of **1** with gaseous Brønsted acid such as H_3^+, CH_5^+, H_3O^+, and $i\text{-}C_3H_7^+$, etc., gives protonated adducts $[H_2N-NO_2]H^+$. Evaluation of prototropic equilibria involving C_6H_6 and CH_3OH as the reference bases gives a gas-phase basicity and a proton affinity (PA) of nitramide of 174.4 ± 2 and 182.1 ± 2 kcal mol⁻¹ at 300 K, respectively. Comparison of the metastable ion kinetic energy and collisionally activated dissociation spectra of the $[H_2N-NO_2]H^+$ populations from the protonation of **1** with those of $H_3N-NO_2^+$ model ions suggests that O-protonated protomers are more stable and represent the predominant $[H_2N-NO_2]H^+$ species at the time of structural analysis, *i.e.*, ca. 10 μs after the protonation event. These conclusions are consistent with *ab initio* results at the G1 level of theory that identify the O atoms of the nitro group as the thermodynamically preferred protonation site of **1** and give a value of the PA of nitramide, 180.2 kcal mol⁻¹ at 298 K, in satisfactory agreement with the experimental value. In addition, on the basis of the G1 value of the $H_3N-NO_2^+$ binding energy, one can estimate the experimentally unknown heat of formation of **1**, 0 ± 4 kcal mol⁻¹. The higher stability of the O-protonated $[H_2N-NO_2]H^+$ isomer that emerges from this study represents the first departure from the general trend previously observed in the protonation of other simple $X-NO_2$ molecules, giving the $HX-NO_2^+$ adduct as the most stable isomer. The $[HN-NO_2]^-$ anion has been obtained by negative-ion chemical ionization of **1** either by dissociative electron attachment or *via* proton transfer to gaseous anions. The evaluation of the prototropic equilibrium of **1** with HCOO⁻ leads to a gas-phase acidity of **1** and a PA of its anion amounting to 338.3 ± 2 and 345.3 ± 2 kcal mol⁻¹, respectively, at 300 K. The latter value is consistent with the results of G1 theoretical calculations giving a PA of the $[HN-NO_2]^-$ anion of 339.8 kcal mol⁻¹ at 298 K.

Simple reactive species (radicals, neutral molecules, and ions) containing the NO_2 group are currently the subject of considerable interest. Both fundamental problems related to their structure, stability, and reactivity and their role in the chemistry of propellants and explosives, in atmospheric and environmental chemistry, etc., are extensively investigated.[1]

We have carried out a systematic study, based on the joint application of mass spectrometric and theoretical methods, of the gas-phase ion chemistry of simple $X-NO_2$ molecules. Particular attention has been devoted to their protonated adducts, whose most stable isomeric form, $HX-NO_2^+$, is best described as a nitronium ion solvated by a HX ligand.

Having examined oxygenated species, X = OH,[2] OCH_3,[3] OCH_2CF_3, and $OCH(CF_3)_2$,[4] we have undertaken the study of

species whose X group contains a nitrogen atom, examining first nitramide, H_2N-NO_2 (**1**), the most simple among the molecules of interest.

Nitramide, the prototypal nitramine, first prepared in 1895 by Thiele and Lachmann,[5] has been since the focus of sustained interest, despite the problems arising from its difficult preparation[6] and its pronounced instability[7] with respect to the decomposition

$$H_2N-NO_2 \rightarrow H_2O + N_2O \qquad (1)$$
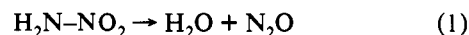
As a matter of fact, nitramide owes its place in the history of chemistry precisely to reaction (1), whose kinetic study has been the foundation of the Brønsted generalized theory of basic catalysis.[8] The structure of nitramide has been established by X-ray crystallography,[9] complemented by microwave,[10] IR,[11] and Raman[12] spectroscopy, although the body of available experimental data is relatively restricted, due to the instability of **1**,

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(2) (a) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. *J. Am. Chem. Soc.* **1989**, *111*, 5481. (b) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. *J. Am. Chem. Soc.* **1990**, *112*, 1014.
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(4) Attinà, M.; Cacace, F.; Ricci, A. *Tetrahedron* **1988**, *44*, 2015.

(5) Thiele, J.; Lachmann, A. *Lieb. Ann.* **1895**, *288*, 298.
(6) Several preparative methods have been reported, none of whose fully satisfactory and/or reproducible. (a) Marlies, C. A.; La Mer, V. K. *J. Am. Chem. Soc.* **1935**, *57*, 2008. (b) Marlies, C. A.; La Mer, V. K.; Greenspan, J. *Inorg. Synth.* **1939**, *1*, 68. (c) Canis, C. *Rev. Chim. Miner.* **1964**, *1*, 521. (d) Tellier-Pollon, S.; Heubel, J. *Rev. Chim. Miner.* **1967**, *4*, 413. (e) Vast, P.; Heubel, J. *Compt. Rend.* **1967**, *264*, 1697.
(7) Marlies, C. A.; La Mer, V. K. *J. Am. Chem. Soc.* **1935**, *57*, 1812.
(8) (a) Brønsted, J. N. *Recl. Trav. Chim.* **1923**, *42*, 718. (b) Brøsted, J. N.; Guggenheim, E. A. *J. Am. Chem. Soc.* **1927**, *49*, 2554.
(9) Beevers, C. A.; Trotman-Dickinson, A. F. *Acta Crystallogr.* **1957**, *10*, 34.
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(11) Davies, M.; Jonathan, N. *Trans. Faraday Soc.* **1958**, *54*, 469.
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Gas-Phase Ion Chemistry of Nitramide

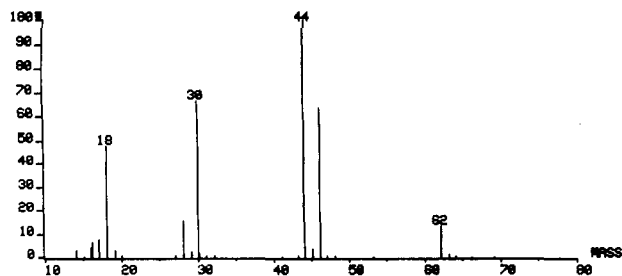J. Am. Chem. Soc., Vol. 115, No. 26, 1993   12399

Figure 1. 70-eV EI mass spectrum of nitramide.

whose decomposition, already appreciable at room temperature, becomes fast in the presence of traces of water and on metallic surfaces and explosive above 175 °C.[13]

By contrast, the theoretical interest in the stability and bonding of nitramide and in its nitro–nitrite rearrangement is truly exceptional, as witnessed by the unordinarily large number of studies performed at different levels of theory in the past few years.[14]

Despite its importance as a link between theory and experiment, the gas-phase ion chemistry of nitramide has so far been neglected, and in particular, to the best of our knowledge, no mass spectra of 1 have been reported. In the following section we shall illustrate the results of measurements carried out with different mass spectrometric techniques and of ab initio calculations at the G1 level of theory, on nitramide, its $H_2N-NO_2^{\bullet+}$ molecular ion, its isomeric conjugate acids $[H_2N-NO_2]H^+$, and its $[HN-NO_2]^-$ anion.

Mass Spectrometric Results

The $H_2N_2O_2^{\bullet+}$ Molecular Ion. A typical electron-impact (EI) mass spectrum of 1, recorded at a nominal 70-eV electron energy, is shown in Figure 1. The base peak is the N_2O^+ ion at $m/z = 44$, accompanied by NO_2^+, $m/z = 46$, NO^+, $m/z = 30$, and H_2O^+, $m/z = 18$, whereas the relative intensity of the $H_2N_2O_2^{\bullet+}$ molecular ion, $m/z = 62$, is rather low, ca. 15%. It should be noted that the H_2O^+ and the N_2O^+ ions are likely to arise, at least in part, from the ionization of neutral H_2O and N_2O formed from the decomposition of 1 in the ion source according to eq 1. This view is supported by the results of photoelectron (PE) spectroscopic measurements performed in the gas phase to evaluate the ionization energies (IE) of 1. As shown in Figure 2, the PE spectrum of nitramide shows evidence of two broad band systems and indeed bands due to its decomposition products, N_2O and H_2O, appear in the expected spectral region.

The ionization energies associated with the various PE features are listed in Table I. Consistent with the results of ab initio calculations (vide infra), the molecular geometry of 1 is assumed to have C_s symmetry even though the two constituent subunits NO_2 and NH_2 can be described within a local C_{2v} symmetry.

The assignment of the bands can qualitatively be proposed by comparison with the well-known energy sequence of the isoelectronic CH_3NO_2 molecule.[15] In particular, the PE spectrum of

(13) Vast, P. *Bull. Soc. Chim. Fr.* **1970**, 2136.

(14) (a) Duke, B. J. *J. Mol. Struct.* **1978**, *50*, 109. (b) Kleier, D. A.; Lipton, M. A. *J. Mol. Struct. (Theochem)* **1984**, *109*, 39. (c) Ritchie, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1829. (d) Marynick, D. S.; Ray, A. K.; Fry, J. L. *Chem. Phys. Lett.* **1985**, *116*, 429. (e) Nonella, M.; Mueller, R. P.; Huber, J. R. *J. Mol. Spectrosc.* **1985**, *112*, 142. (f) Palmer, M. H. *Z. Naturforsch.* **1986**, *41 A*, 147. (g) Picard, M.; Blain, M.; Odiot, S.; Lechercq, J. M. *J. Mol. Struct. (Theochem)* **1986**, *139*, 221. (h) Leroy, G.; Sana, M.; Wilante, C.; Peters, D.; Dogimont, C. *J. Mol. Struct. (Theochem)* **1987**, *153*, 249. (i) Politzer, P.; Sukumar, N.; Jayasuriya, K.; Ranganathan, S. *J. Am. Chem. Soc.* **1988**, *110*, 3425. (l) Saxon, R. P.; Yoshimine, M. *J. Chem. Phys.* **1989**, *93*, 3130. (m) Ritchie, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 2517. (n) Roszak, S.; Kaufman, J. *J. Chem. Phys.* **1992**, *160*, 1.

(15) (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press, Halsted Press: Tokyo, 1981. (b) Lloyd, D. R.; Roberts, P. J.; Hillier, J. H. *Faraday Trans. II* **1975**, 496.
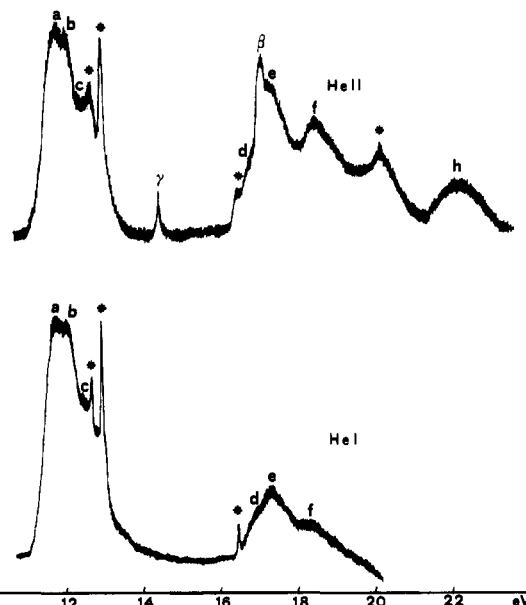

Figure 2. PE spectra of nitramide. The band labels correspond to those of Table I. The peaks marked with an asterisk arise from N_2O and H_2O impurities. The peaks β and γ refer to He self-ionizations induced by He II β and γ satellites.

Table I. Ionization Energies of Nitramide from PE Spectroscopy

experimental IE (eV)	bond label[a]	orbital character[b]
11.75	a	$a_2\pi^-$ NO_2
12.06	b	a^1O n^+ NO_2
		b_1 n NH_2
12.47	c	b_1O n^- NO_2
(12.61)	*	(H_2O)
(12.89)	*	(N_2O)
16.38	*	(N_2O)
16.70	d	
17.23	e	
18.33	f	
19.58	g	
20.04	*	(N_2O)
22.04	h	

[a] Identification refs to band labels in Figure 2. [b] Symmetry representations refer to a local C_{2v} symmetry (zx in NO_2 plane).
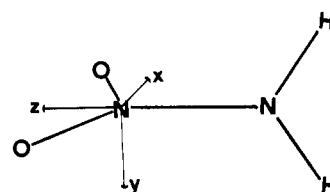
nitromethane consists of two bands below 13 eV, which are centered at 11.28 and 11.69 eV. They represent ionizations from the π^- and σ n^+ + σ n^- MOs localized on the NO_2 subunit, respectively. The π orbital (a_2 in C_{2v}) is the out-of-phase combination of O $2p_y$ orbitals. The σ n^+ (a_1) and σ n (b_1) orbitals represent an accidentally degenerate pair of MOs in the xz plane. Moreover, the ionization from the N $2p$ (NH_2) lone pair is expected in the same region since it was reported at 9.91 eV for methylamine, 9.91 eV for hydrazine, and 10.85 eV for ammonia,[15,16] and because of the strong electron-withdrawing effect[17] of the NO_2 group, an higher IE shift up to 12 eV must be expected. In addition, due to overlap arguments, the N $2p$ lone pair may interact with the σ n^- MO which, in turn, might be stabilized relative to that found in CH_3NO_2.

Within this context, a tentative assignment becomes possible on a pure experimental basis. Accordingly we can assign band

(16) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 2392.
(17) Rabelais, J. W. *J. Chem. Phys.* **1972**, *57*, 960.

Figure 3. CH$_4$/CI spectrum of nitramide.
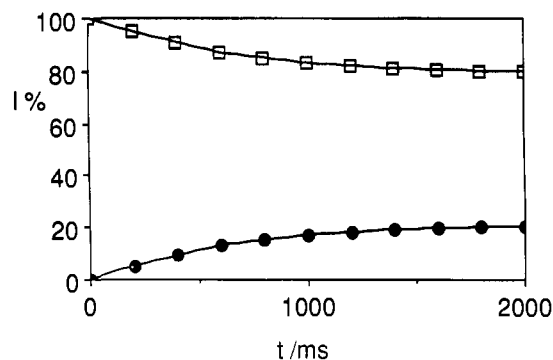
Figure 4. Time dependence of the relative intensity of [H$_2$N–NO$_2$]H$^+$ ions (squares) and C$_6$H$_7$$^+$ ions (circles) in a gaseous mixture of C$_6$H$_6$ and H$_2$N–NO$_2$ (see text).

a to the π^- orbital and band b to the accidentally degenerate σ^+ and N 2p (NH$_2$) lone-pair ionizations. Finally, the shoulder c is left to represent the remaining σ^+ MO. The other broad bands, necessarily more evident in the He II spectrum, are related to deeper π orbitals, as well as to the σ framework of 1.

From the onset of the PE bands, obtained with a standard curve-fitting procedure, we estimate the adiabatic ionization energy of nitramide to be 11.02 ± 0.06 eV, the relatively large uncertainty arising from the broad envelope typical of the band of interest.

Protonation of Nitramide. The [H$_2$N–NO$_2$]H$^+$ Ions. Protonation of 1 readily occurs under chemical ionization (CI) conditions, according to the general reaction

$$BH^+ + H_2N–NO_2 \rightarrow B + [H_2N–NO_2]H^+ \qquad (2)$$

where B = H$_2$, CH$_4$, C$_2$H$_4$, H$_2$O, C$_6$H$_6$, CH$_3$OH, etc., yielding adduct(s) at m/z = 63, as shown in the typical CH$_4$/CI spectrum of Figure 3. Decomposition (1) of 1 occurs in the ion source, as shown by the presence of H$_3$O$^+$, m/z = 19, and N$_2$OH$^+$, m/z = 45, namely the ions arising from the protonation of H$_2$O and N$_2$O, the neutral products from (1). Their presence introduces a serious complication when strong BH$^+$ acids such as H$_3$$^+$ and CH$_5$$^+$ are used, since H$_3$O$^+$ and N$_2$OH$^+$ are unavoidably formed, and therefore proton transfer to nitramide does not occur exclusively from the BH$^+$ acid chosen but from H$_3$O$^+$ and N$_2$-OH$^+$ ions as well.

When the strength of the base B is comparable to that of 1, proton transfer (2) reaches equilibrium, which allows one to estimate the gas-phase basicity (GPB) and hence the proton affinity (PA) of nitramide. The best results have been obtained using benzene and methanol as the reference bases, in equilibrium measurements performed by ion cyclotron resonance (ICR) mass spectrometry. A typical example is shown in Figure 4, which refers to the equilibration of [H$_2$N–NO$_2$]H$^+$ ions isolated by multiple resonance in a gaseous mixture containing C$_6$H$_6$ and 1 in the 3:2 molar ratio at 300 K and a total pressure of 1.3 × 10^{-6} Torr. From the equilibrium constants deduced from experiments involving benzene, GPB = 174.6 kcal mol^{-1}, and CH$_3$OH, GPB

Table II. CAD Spectra of H$_3$N$_2$O$_2$$^+$ Ions from Different Reactions

charged fragment, m/z	formation process of H$_3$N$_2$O$_2$$^+$ ions (relative intensity, %)[a]			
	Reaction 2			reaction 3
	B = H$_2$	B = H$_2$O	B = C$_3$H$_6$	
47	5.4	6.7	5.6	3.4
45	23.2	23.4	25.1	5.0
33	0.7	1.0	0.6	16.3
32	0.6	0.6	0.6	7.8
30	63.4	62.7	62.2	47.3
18	0.7	0.5	0.6	1.7
17	2.6	3.1	2.2	15.2
16	2.8	1.9	3.0	3.3

[a] The fragment at m/z = 46, formed by the metastable decomposition of H$_3$N$_2$O$_2$$^+$, is not taken into account.

= 174.1 kcal mol^{-1},[18] we estimate the GPB of (H$_2$N–NO$_2$) to be 174.4 ± 2 kcal mol^{-1} at 300 K, the error limits largely reflecting the estimated uncertainity in the p (H$_2$N–NO$_2$) measurement. The thermal instability of 1 prevents the evaluation of equilibrium constants in a temperature range sufficiently extended to allow the construction of meaningful van't Hoff plots. With the customary assumption that $\Delta H°_2 \simeq \Delta G°_2$, the PA of nitramide can be estimated to be 182.1 ± 2 kcal mol^{-1} at 300 K.

Structural Study of [H$_2$N–NO$_2$]H$^+$ Ions. Protonation of 1 can occur at different sites, in particular the N atom of the amino group and the O atoms of the nitro group, yielding protomers that in principle can be discriminated by structurally diagnostic mass spectrometric techniques.
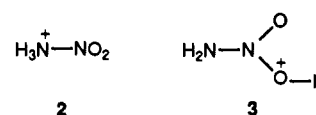
As generally in gas-phase ion chemistry, the term structure is used here to denote connectivity, without taking into account bond angles and distances.

Since the selectivity of the protonation can be affected by the exothermicity of reaction 2, metastable ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) mass spectrometry have been used to detect possible structural differences among the populations of [H$_2$N–NO$_2$]H$^+$ ions from reaction 2 carried out with BH$^+$ acids of different strength. To this end, we have used H$_3$$^+$, H$_3O^+$, and i-C$_3H_7$$^+$, whose conjugate bases B have PA ranging from 101.2 to 179.5 kcal mol^{-1}.[18]

For the reasons outlined in a previous section, the protonation occurring in the H$_2$/CI and CH$_4$/CI of 1 involves, in addition to H$_3$$^+$ and CH$_5$$^+$, respectively, H$_3O^+$ and N$_2$OH$^+$ ions.

The MIKE spectra invariably display a single, Gaussian-shaped peak, NO$_2$$^+$ at m/z = 46. The CAD spectra of the [H$_2$N–NO$_2$]-H$^+$ ions from the protonation of 1 with acids of various strength, reported in Table II, show the same fragmentation pattern, dominated by the NO$^+$ ion at m/z = 30. The relatively high intensity of the N$_2$OH$^+$ fragment at m/z = 45, which contrasts with the remarkably low intensity of the NH$_3$$^+$ fragment at m/z = 17, accord much better with structure 3 of the [H$_2$N–NO$_2$]H$^+$ ion, although evidence of this kind is far from conclusive.

A more definite assignment requires the availability of model ions of well-established structure. The search for such models has been successful in the case of protomer 2, a viable route to which is the ligand exchange reaction

(18) All thermochemical data are taken form (a) 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. The heat of formation of NO$_2$$^+$ is taken from (b) Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1992**, *97*, 2459. The PA of the gaseous N(NO$_2$)$_2$$^-$ anion is taken from (c) Schmitt, R. J.; Krempp, M.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 621.

$$H_3C-\overset{+}{\underset{O_2N}{O}}-NO_2 + NH_3 \longrightarrow CH_3ONO_2 + H_3N-NO_2^+ \qquad (3)$$

2
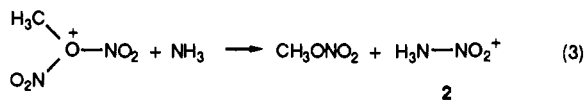
whose occurrence has been demonstrated as follows by ICR experiments. $CH_3O^+(NO_2)_2$ ions have been obtained, together with other cations, from the CH_4/CI of CH_3ONO_2 in the external source of an ICR spectrometer. The ions have been introduced into the resonance cell, isolated by multiple resonance, and allowed to react with NH_3, yielding $H_3N_2O_2^+$ ions, whose composition has unequivocally been established by exact mass measurements.

Given the nature of its formation process, a ligand exchange whereby the more nucleophilic NH_3 molecule displaces CH_3ONO_2 forming an ion–molecule adduct with the nitronium ion, it is legitimate to regard the ion from reaction 3 as the required model of structure **2**.

Accordingly, reaction 3 has been used to generate a population of $H_3N-NO_2^+$ ions whose structure has been probed by CAD spectrometry. The spectrum (last column of Table II) is indeed considerably different from those of isomeric ions from the protonation (**2**) of nitramide, especially as regards the much higher intensity of the NH_3^+ fragment, $m/z = 17$, and the much lower intensity of the N_2OH^+ fragment, $m/z = 45$.

These distinctive CAD spectral features of model ion **2** are fully consistent with its structure and allow a reasonable interpretation of the results summarized in Table II. To make the conclusions absolutely rigorous, it would be necessary to know the CAD spectral features of the unavailable model ion **3**. It appears that at the time of their structural assay, the populations of $[H_2N-NO_2]H^+$ ions from reaction 2 consist predominantly of protomer **3**, as suggested by the low intensity in their spectra of the CAD NH_3^+ fragment, typical of protomer **2**.

The situation can reflect operation of the following factors: (i) Protonation occurs selectively at the O atoms of nitramide, which however seems unlikely in the case of strong, indiscriminate acids such as H_3^+. (ii) The ions **2** initially formed undergo fragmentation and/or isomerization into the more stable ions **3** in the time interval before structural assay, namely some 10 μs after their formation.

The [HN–NO₂]⁻ Anion. Dissociative electron attachment to **1** yields the $HN_2O_2^-$ anion, $m/z = 61$, as shown in the typical negative-ion CH_4/CI mass spectrum of Figure 5. If the spectrum is recorded using sufficiently high concentrations of nitramide, the $[HN_2O_2^-\cdot H_2N-NO_2]$ and $[HN_2O_2^-\cdot 2H_2N-NO_2]$ cluster ions are detectable as well at $m/z = 123$ and 185.

The anion can be obtained also from the general process

$$H_2N - NO_2 + A^- \rightleftharpoons [HN-NO_2]^- + AH \qquad (4)$$

where AH is a sufficiently weak acid. In particular, equilibrium 4 between the formate anion and nitramide has been exploited to evaluate the gas-phase acidity (GPA) of the latter. From the value of K_4 measured in ICR equilibrium experiments and the known GPA of HCOOH,[18] we obtain GPA (H_2N-NO_2) = 338.3 ± 2 kcal mol⁻¹ at 300 K, corresponding, under the usual assumption that $\Delta S_4^\circ \simeq 0$, to a PA of the $[HN-NO_2]^-$ anion of 345.3 ± 2 kcal mol⁻¹.

These results characterize nitramide as a relatively strong acid in the gas phase, where its acidity is comparable to that of formic acid. By contrast, in solution the ionization constant of HCOOH exceeds that of **1** by more than 3 orders of magnitude.

Ab Initio Calculations

Calculations up to the G1 level of theory have been performed in order to investigate the structure, the stability, and the interconversion processes of the isomers of protonated nitramide, as well as the structure and the stability of its anion.

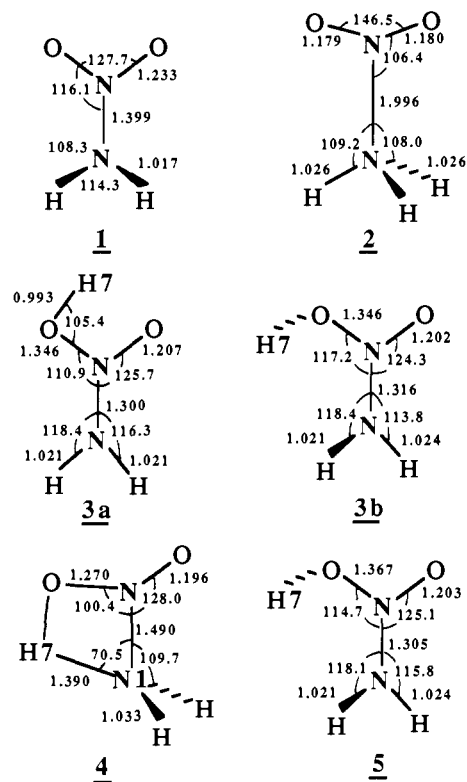**Figure 5.** Negative-ion CH_4/CI spectrum of nitramide.

Figure 6. Computed geometries of nitramide, its protomers, and the $[HN-NO_2]^-$ anion.

At the MP2(FU)/6-31G* post-SCF level of theory three different isomers of protonated nitramide, henceforth indicated as **2**, **3a**, and **3b**, have been located on the $[H_3, N_2, O_2]^+$ potential energy surface. From the relevant vibrational frequencies, all of these species were found to correspond to absolute minima on the surface. The transition structures **4** and **5**, which connect with ion **3b** ion **2** and ion **3a**, respectively, have been also located at the same computational level. The computed post-SCF geometries of all of these species are reported in Figure 6, together with the previously MP2(FU)/6-31G*-optimized structure of H_2N-NO_2[14] which is also shown for comparison. The total energies of these species, calculated at the various computational levels, are collected in Table III. The energy corrections for the evaluation of the corresponding G1 energies are reported in Table IV, together with the relative stability of the various $[H_3, N_2, O_2]^+$ investigated ions, evaluated with respect to ion **2**.

The protonation at the nitrogen atom of the amino group of H_2N-NO_2 gives the C_s symmetry ion **2**. As shown in Figure 6, the N–N bond distance of this species, 1.996 Å, is significantly elongated with respect to the same parameter of the unprotonated H_2N-NO_2, whereas the nitrogen–oxygen bond distances of **2**, 1.180 and 1.179 Å are quite similar to the MP2(FU)/6-31G*-computed N–O bond length of free nitronium ion, 1.155 Å. Both these findings suggest that ion **2** can be viewed as an ion/dipole complex between NO_2^+ and NH_3, although occurrence of some dative N–N bonding cannot be excluded. Consistently, from

**Table III.** Absolute Energies (hartrees) of the Species of Interest

species	MP2(FU)/6-31G*	MP2(FU)/6-31G* MP4/6-311G**	MP4/6-311+G**	MP4/6-311G**(2df)	QCISD(T)/6-311G**	ZPE(MP2(FU)/6-31G*)
H₂N–NO₂	−260.35192	−260.52087	−260.53715	−260.66334	−260.51000	0.04040
2	−260.65711	−260.84107	−260.84952	−260.97479	−260.81300	0.05032
3a	−260.64581	−260.82416	−260.83275	−260.96398	−260.81609	0.05135
3b	−260.62725	−260.80813	−260.81720	−260.94742	−260.80096	0.05094
4	−260.57626	−260.76133	−260.76993	−260.89927	−260.75167	0.04699
5	−260.62651	−260.80744	−260.81646	−260.94636	−260.80041	0.05016
NH₃	−56.35738					0.03531
NO₂⁺	−204.24841	−204.37158	−204.37682	−204.47464	−204.33835	0.01147
6	−259.78103	−259.93899	−259.97712	−260.08732	−259.92980	0.02711

Table IV. MP4/6-311G** Absolute Energies (hartrees) and Corrections (mhartrees) for the Evaluation of the G1 Energies of the Species of Interest

species	MP4/6311G**	ΔE(+)	ΔE(2df)	ΔE(QCI)	ΔE(HLC)	ΔE(ZPE)	G1
H₂N–NO₂	−260.52087	−16.28	−142.47	+10.87	−73.68	40.40	−260.70203
2	−260.84107	−8.45	−133.72	+28.07	−73.68	50.32	−260.97853 (0)
3a	−260.82416	−8.59	−139.82	+8.07	−73.68	51.35	−260.98683 (−5.2)
3b	−260.80813	−9.07	−139.29	+7.17	−73.68	50.94	−260.97206 (+4.1)
4	−260.76133	−8.60	−137.94	+9.66	−73.68	46.99	−260.92490 (+33.6)
5	−260.80744	−9.02	−138.92	+7.03	−73.68	50.16	−260.97187 (+4.2)
NH₃						35.31	−56.45477
NO₂⁺	−204.37158	−5.24	−103.06	+33.23	−49.12	11.47	−204.48430
6	−259.93899	−38.13	−148.33	+9.19	−73.68	27.11	−260.16283

Table IV, the interaction of these two fragments, with formation of **2**, is computed at the G1 level of theory to be 26.9 kcal mol⁻¹ at 298 K. Moreover, from the total energies of nitramide and ion **2**, the G1 PA at the amino group of H₂N–NO₂ is computed as 175.0 kcal mol⁻¹ at 298 K. The search of the oxygen-protonated forms of nitramide has led to the location of the two conformers **3a** and **3b**, the former species being more stable by 9.3 kcal mol⁻¹ at the G1 level of theory, (see Table IV). From Figure 6, it is apparent that the most striking structural difference between the two species is the degree of planarity of the amino group. The N–N bond distance in the fully-planar ion **3a**, 1.300 Å, is shorter than that in ion **3b** and the amino group of the latter species is pyramidal. These findings point to a larger extent of multiple interaction between the two nitrogen atoms in ion **3a** with respect to ion **3b**. The isomerization process of ions **3a** and **3b** has been investigated by locating the relevant conformational transition structure **5**, whose optimized geometry is shown in Figure 6. The value of the dihedral angle which defines the position of the rotating hydrogen (H7) closely resembles the one obtained for ion **3b**; consistently, from Table IV, the conformational barrier for the interconversion of the two isomers is computed at the G1 level of theory as 0.1 kcal mol⁻¹ with respect to ion **3b**, thus suggesting the almost exclusive formation of isomer **3a** by oxygen protonation of H₂N–NO₂. From Table IV, ion **3a** is the absolute minimum among the investigated [H₃, N₂, O₂]⁺ species. In fact, it is more stable than ion **2** by 5.2 kcal mol⁻¹. Moreover assuming the formation of **3a**, the PA at the oxygen atom of nitramide is computed as 178.7 kcal mol⁻¹ at 0 K, corresponding to 180.2 kcal mol⁻¹ at 298 K.

The problem of the interconversion of ion **2** to ions **3a** and/or **3b** has been addressed next. The transition structure **4**, located on the MP2(FU)/6-31G* potential energy surface, possesses only one imaginary frequency (−1858 cm⁻¹). From the examination of the corresponding normal mode of vibration, this species connects ion **2** with ion **3b**, *via* the in-plane motion of the migrating hydrogen (H7). From Figure 6, the N1–H7 bond distance of ion **4** is significantly longer, 1.390 Å, than the same parameter of ion **2**, and, overall, a significant structure rearrangement is required to overcome the activation barrier. Consistently, from Table IV, the **2** → **3b** interconversion process is computed as a high-energy one, the energy difference between **2** and **4** amounting to 33.6 kcal mol⁻¹ at the G1 level of theory. The potential energy profile
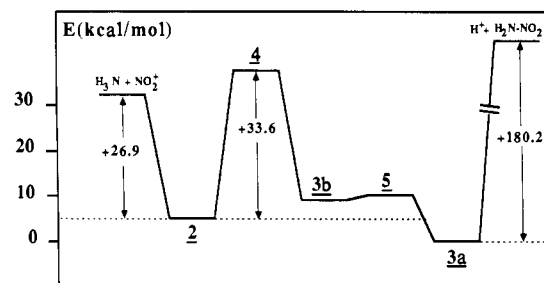

Figure 7. Energy profile of the [H₂N–NO₂]H⁺ system.

for the protonation of H₂N–NO₂, with formation of ion **3a**, and the subsequent isomerization and decomposition patterns, with formation of NH₃ and NO₂⁺ is schematically shown in Figure 7.

We have also evaluated the gas-phase acidity of H₂N–NO₂ by computing the enthalpy change associated with the reaction

$$H_2N-NO_2 \rightarrow [HN-NO_2]^- + H^+ \qquad (5)$$

Also in this case, the G1 level of theory was selected. The preliminary geometry optimization of the [HN–NO₂]⁻ anion (**6**) was performed at the MP2(FU)/6-31G* level and the results are illustrated below

6
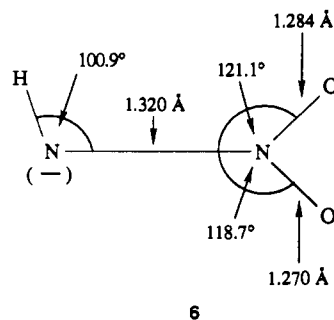
The relevant data for the evaluation of the G1 energy of **6** are collected in Tables III and IV. From these data, the ΔH°₂₉₈ value of the deprotonation of nitramide, corresponding to the PA of its anion, is computed to be 339.8 kcal mol⁻¹.

Discussion

There is a satisfactory agreement between the mass spectro-metric and the theoretical results illustrated in the previous sections, particularly as concerns the stability order of the protomers and important thermochemical quantities; *e.g.*, the computed values of the PA of H_2N-NO_2 and of the $[HN-NO_2]^-$ anion, 180.2 and 339.8 kcal mol^{-1} at 298 K, compare favorably with the corresponding experimental values, 182.1 ± 2 and 345.3 ± 2 kcal mol^{-1} at 300 K, respectively. From the computed $H_3N-NO_2^+$ binding energy and the PA of the NH_2 group of **1**, one can derive the experimentally unknown heat of formation of nitramide, 0 ± 4 kcal mol^{-1}. The only previously reported value is -2.7 kcal mol^{-1}, calculated at the Hf/6-31G* level of theory.[14]

The theoretical evidence outlined in Figure 7 allows satisfactory rationalization of the experimental results concerning the structure of the isomeric ions from the gas-phase protonation of **1** and their interconversion process.
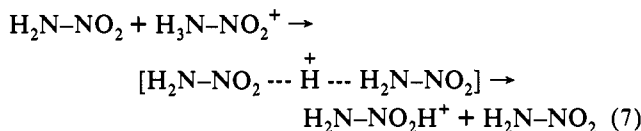
The CAD results suggest that, irrespective of the Brønsted acid employed, the population of $[H_2N-NO_2]H^+$ ions from reaction 2 consists predominantly of O-protonated species of structure **3**.

Since it appears very unlikely that proton transfer from strong, indiscriminate acids such as H_3^+ to **1** occurs exclusively to O atoms, one is left with the problem of explaining the fate of ions **2**, protonated at the amino group. They are likely to be initially formed but are found to be largely, if not entirely depleted at the time of the structural assay.

On the basis of the scheme of Figure 7, their extensive dissociation

$$H_3N-NO_2^+ \rightarrow NH_3 + NO_2^+ \qquad (6)$$
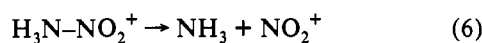
seems unlikely, owing to appreciable endothermicity, calculated to be *ca.* 27 kcal mol^{-1}. Intramolecular **2** → **3** isomerization is even more unlikely, owing to the large barrier, calculated to be 33.6 kcal mol^{-1}. The only plausible route appears to be intermolecular isomerization involving proton transfer between two n-type centers,

$$H_2N-NO_2 + H_3N-NO_2^+ \rightarrow$$
$$[H_2N-NO_2 \cdots \overset{+}{H} \cdots H_2N-NO_2] \rightarrow$$
$$H_2N-NO_2H^+ + H_2N-NO_2 \quad (7)$$

a process generally very fast in the gas phase whenever ener-getically allowed,[19] as in the case of reaction 7, calculated to be exothermic by *ca.* 5 kcal mol^{-1}. In favor of this hypothesis one can mention that low, but well detectable abundances of proton-bound dimers of **1** have been detected under appropriate conditions in the CH$_4$/CI spectra of nitramide. They are the type of ion-molecule complexes whose intermediacy is required in the intermolecular isomerization (7).

The theoretical results help explain why the unimolecular dissociation of O-protonated ions **3** fails to impart appreciable kinetic energy to the fragments, as apparent from the narrow, Gaussian-shaped peak in the MIKE spectra. Consistent with the diagram of Figure 7, conversion of O-protonated species **3** into **2** is characterized by a high barrier, and hence only those ions that contain a large excess of internal energy can reach the transition state **4**. Evolution of the latter into **2** does indeed release a large amount of energy, calculated to exceed 30 kcal mol^{-1}, most of which however is required to promote the highly endothermic dissociation (6) and hence is largely unavailable to impart excess kinetic energy to the NO_2^+ and the NH_3 fragments.

As to the central problem addressed in this study, namely the dependence of the relative stability of the isomeric protonated forms of simple $X-NO_2$ molecules on the nature of the X ligand, the results reveal an interesting trend. In all cases previously

examined, the most stable protomer has been characterized as a complex between the nitronium ion and a neutral HX molecule, *e.g.*, in the case of nitric acid (X = OH) the protomer **7** has been identified as the most stable one.[2] Its stability has been calculated to exceed that of the $HO-NO_2H^+$ isomer by 21.4 kcal mol^{-1}.[20,21] The same trend prevails, if by a narrower margin in related

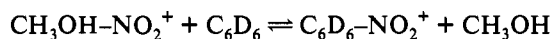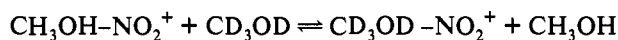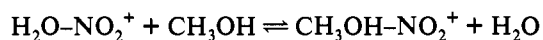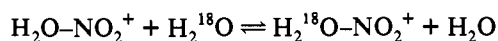**7**   **8**   **9**
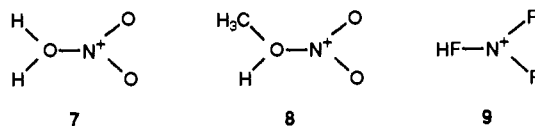
systems, *e.g.*, in the case of the protonated methyl nitrate (X = OCH$_3$) the most stable isomer is found to be the complex **8**,[21] whereas the most stable isomer of protonated nitrogen trifluoride is again the complex **9** of HF with the NF_2^+ cation.[22]

Nitramide (X = NH$_2$) represents the first departure from the above trend. The mutually supporting mass spectrometric and theoretical results convincingly show that ion **2**, in essence a complex between ammonia and the nitronium ion, is *less* stable than the ion **3a**, protonated at the nitro group. Apparently, increasing the electron-donating ability of the X group along the series OH < OCH$_3$ < NH$_2$ gradually enhances the basicity of the oxygen atoms of the nitro group relative to that of the X moiety, as shown by the following comparison of the local PAs in $X-NO_2$ molecules

$$PA(X) - PA(NO_2), \text{ kcal mol}^{-1}$$

X = OH	X = OCH$_3$	X = NH$_2$
21.3	4.9	−5.2

The reversal of the stability order of the protonated isomers has important consequences on their reactivity. Thus, the most stable protomers of nitric acid and methyl nitrate react predomi-nantly as nitronium ion donors and hence as efficient nitrating agents, as illustrated by the typical gas-phase reactions[2b,23] observed under ICR conditions

$$H_2O-NO_2^+ + H_2^{18}O \rightleftharpoons H_2^{18}O-NO_2^+ + H_2O$$

$$H_2O-NO_2^+ + CH_3OH \rightleftharpoons CH_3OH-NO_2^+ + H_2O$$

$$CH_3OH-NO_2^+ + CD_3OD \rightleftharpoons CD_3OD-NO_2^+ + CH_3OH$$

$$CH_3OH-NO_2^+ + C_6D_6 \rightleftharpoons C_6D_6-NO_2^+ + CH_3OH$$

On the other hand, the most stable isomer of protonated nitramide is expected to be devoid of nitrating properties, behaving instead as a Brønsted acid, as observed in the present study in its reaction (2) with methanol and benzene.

Finally, it is worth noting that the IP of the XNO_2 molecules, *i.e.*, 11.95 eV (X = OH), 11.53 eV (X = OCH$_3$),[18] and 11.02 eV (X = NH$_2$, this work), correlate remarkably well with their PA *referred to the protonation of the O atom of the nitro group, i.e.*, 182.1 ± 2 kcal mol^{-1} of H_2N-NO_2 (experimental value from this work), and 161.2 ± 2 and 172.0 ± 3 kcal mol^{-1} of HNO_3 and CH_3ONO_2, respectively, computed with high-level *ab initio* methods.[21] The PA of the nitro group is found to decrease linearly (correlation coefficient 0.997) as the IP of XNO_2 increases, whereas there is no obvious correlation between the IP and the PA of the XNO_2 molecules referred to protonation of their X group, namely 182.5 ± 4, 176.9 ± 5, and 176.9 ± 2 kcal mol^{-1} of HNO_3,[21] CH_3ONO_2,[21] and NH_2-NO_2 (this work), respectively. These experimental trends can be rationalized if one considers

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that ionization of the above XNO$_2$ molecules is known to involve electron removal from orbitals of 2p character formally localized on the O atoms of nitro group and therefore can be expected to be directly related to the PA of the O atoms of the NO$_2$ group rather than to that of the X ligand. As an aside, the above trend provides additional evidence to the conclusion that the experimentally measured PA of **1** refers to O protonation of its nitro group.

Passing to negative-ion chemistry, it is interesting to examine the effect of an increasing number of nitro groups on the gas-phase acidity of the unsubstituted NH$_3$ molecule. From the PA of the H$_2$N$^-$, HN–NO$_2^-$, and N(NO$_2$)$_2^-$ anions, that amount to 403.7, 339.8 (this work) and ≤310 kcal mol^{-1},[18] respectively, it is apparent that whereas, not unexpectedly, the first nitro group causes the largest acidity enhancement, the effect of the second nitro group is still considerable.

Experimental Section

Materials. Nitramide was prepared according to the method based on the reaction of 95% nitric acid with sodium sulfamate, in the presence of sodium nitrate, carried out at –50 °C.[6d] Following neutralization with 5 M sodium hydroxide and dilution with a solution of sodium nitrate, the product was extracted with ether at low temperature (–10 to 0 °C), the solvent was evaporated under vacuum, and the nitramide was recovered as a white solid residue, which can be dissolved in dry ether and precipitates upon addition of isopentane. Despite careful control of the purity of the reagents and of the reaction conditions, the yields of nitramide recovered at the end of the entire preparation purpose have been found to be quite variable, and no nitramide could at all be obtained from several runs. Apparently, most of the losses occur in the extraction step. Nitramide was stored over P$_2$O$_5$ in a vacuum desiccator kept at 0 °C and cooled to –78 °C with dry ice whenever samples had to be transported over long distances. The identity and the purity of nitramide were established by IR spectroscopy.

It should be noted that whereas reaction 1 causes a continuous loss of nitramide, its purity is not affected by the volatile decomposition products, which are effectively removed from the solid in the storage condition adopted.

The other chemicals used were obtained from commercial sources, or prepared according to standard procedures. The gases were purchased from Matheson Gas Products and from UCAR Co. with a minimum stated purity in excess of 99.95 mol %.

Warning. Nitramide is potentially hazardous, owing to its recognized explosive properties. Although its detonation has not been observed, deflagration occurs when nitramide is heated above its melting point.

Mass Spectrometric Measurements. EI and CI, as well as MIKE spectra, were recorded using a VG Micromass ZAB-2F instrument, whereas the ICR experiments were performed with a Nicolet FTMS 1000 or a Bruker Spectrospin APEX 47e spectrometer equipped with an external ion source.

The introduction of nitramide into the ion sources of the spectrometers requires great care, owing to its instability toward dissociation (1), whose products, in any case, accompany nitramide, as discussed in a previous section. To minimize decomposition, the sample was introduced into the ion source using a specially built direct-insertion probe thermostated to –60 °C, the temperature being measured with a thermocouple inserted in the metal body of the probe. The source temperature was 100~120 °C in the ZAB-2F spectrometer, whereas the ICR resonance cells where ionization occurs were maintained at room temperature. The EI spectra were recorded using the ZAB-2F instrument at the following operating parameters: electron energy 70 eV, trap current 100 μA, repeller voltage 0 to 5 V, acceleration voltage 8 kV. The CI spectra were recorded using the following typical conditions, that refer to CH$_4$/CI: reactant gas pressure 0.3 Torr, source temperature 100–120 °C, emission current 1 mA, repeller voltage 0 V. The MIKE and the CAD spectra were recorded at a typical resolution of 4000 fwhm, each spectrum representing the average of the least 40 individual consecutive scans. To record CAD spectra, He was introduced into the collisional cell, adjusting its pressure to the value required to reduce the main beam to 30% of its original intensity.

Photoelectron Spectra. Vapor-phase PE spectra were recorded using a Perkin-Elmer PS 18 derived photoelectron spectrometer, modified by addition of a Helectros He I/He II photon source and interfaced to an IBM PC computer as previously described.[24] Spectral resolution measured on the Ar$^+$ ^{2}p$_{3/2}$ peak was always better than 0.030 eV. The PE spectra were run in the 321 to 323 K temperature range. The deconvolution of the peaks was obtained using a DuPont Model 310 analogic curve resolver, equipped with Gaussian function generators.

Computational Details. *Ab initio* quantum-mechanical calculations were performed by using a IBM RISC/6000 version of the GAUSSIAN 90 program package.[25] The standard 6-31G*, 6-31G**, 6-311+G**, and 6-311G**(2df)[26] basis sets were employed throughout. Geometry optimizations were performed in the full space of coordinates by analytical gradient-based techniques;[27] to this end, the 6-31G* basis set was employed in the framework of the second-order Møller–Plesset perturbation theory (MP2).[28] The MP2 theory was used with full (FU) electron correlation (including inner-shell electrons). The geometries obtained in this way are denoted by MP2(FU)/6-31G*. The MP2(FU)/6-31G* vibrational frequencies were computed for all of the investigated species, in order to characterize them as true minima, transition structures, or higher-order saddle points on the corresponding potential energy hypersurfaces, and the zero-point vibrational energies (ZPVE) of the various species were taken into account in this way. 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 (SDTQ) excitations. The G1 procedure[29] was employed to obtain the total energies of the investigated species. This method is generally accepted[30] as a computational procedure which is able to predict or to reproduce thermochemical data to a target accuracy of ±2 kcal mol^{-1} (0.1 eV).

In the framework of the G1 approach, 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. In order to avoid very extensive calculations at the QCISD(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, (iii) the corrections for residual correlation effects, and (iv) the so-called higher-level corrections, HLC. Three additional calculations, at MP4(SDTQ)/6-311+G**, MP4/(SDTQ)/6-311G**(2df), and QCISD(T)/6-311G** levels of theory, respectively, are required in order to obtain such corrections. If the corresponding absolute energies are denoted as E1, E2 and E3, the correction terms to the MP4(SDTQ)/6-311G** computed value, designated as E0 are $\Delta E(+) = E1 - E0$, $\Delta E(2df) = E2 - E0$ and $\Delta E(QCISD-(T)) = E3 - E0$, respectively. The final value of the G1 energy of a species is then given by the following equation:

$$E(G1) = E0 + \Delta E(+) + \Delta E(2df) + \Delta E(QCISD(T)) + \Delta E(HLC) + \Delta E(ZPVE)$$

The fourth correction term, $\Delta E(HLC)$, is introduced in a parametric way,[29] and the fifth correction term, $\Delta E(ZPVE)$, takes into account the zero-point vibrational energy correction. All single-point calculations were performed at the MP2(FU)/6-31G*-optimized geometries.

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