Nitro $\rightleftharpoons$ *aci*-Nitro Tautomerism

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Abstract: The nitromethane $\rightleftharpoons$ *aci*-nitromethane tautomerism is studied by high-level ab initio methods. The MP2/6-31G* geometry of nitromethane compares well with that determined experimentally. The G1 energy difference between the two tautomers amounts to 14.1 kcal/mol in favor of nitromethane. The calculated heat of atomization of −570.7 kcal/mol for nitromethane differs by only 2.4 kcal/mol from the experimental value. The nitromethide anion has C_s symmetry with the 6-311+G* basis set. Its G1 proton affinity is 355.2 kcal/mol, which differs from the gas-phase value by 1.4 kcal/mol. The anion does not display Y-aromaticity.

Nitronic acids play an important role in thermal and redox reactions, in photochemical processes, in pyrolysis, as well as in the toxicity of nitro compounds.[1] They are intermediates, for example, in the Nef reaction,[1b] which converts nitroalkanes to ketones. Kinetic studies show similar pK_a values for nitronic acids and their carbon counterparts, the carboxylic acids.[1] The nitronic acids have received by far the lesser attention, undoubtedly in part due to their tautomeric equilibria with nitroalkanes. However, processes like the keto $\rightleftharpoons$ enol tautomerism are receiving renewed interest largely because of their biochemical importance. Also in the case of nitro compounds, experimental[2] and theoretical studies[3] suggest a more prominent place for nitronic acids. In light of the recent gas-phase observation of *aci*-nitromethane,[4] it is surprising that the parent tautomeric process, nitromethane $\rightleftharpoons$ *aci*-nitromethane, has not been studied in greater detail. Instead, most studies concern the C–N and C–O bond strengths in the related nitromethane $\rightleftharpoons$ methyl nitrite equilibrium.[5] In a comprehensive study on the potential energy hypersurface of nitromethane, McKee[6] included the nitro $\rightleftharpoons$ *aci*-nitro equilibrium and reported nitromethane to be 21.8 kcal/mol (MP2/6-31G*) more stable with a barrier of 75.0 kcal/mol for the thermally forbidden [1,3]-H transfer. However, recent studies on nitro compounds have illustrated that larger basis sets and extensive electron correlation treatments are required for reliable energy evaluations.[5a,g,7] This has also been demonstrated by Wiberg et al.[8a] and Radom and co-workers[8b] in an evaluation of the keto $\rightleftharpoons$ enol equilibrium in acetaldehyde. For example, the 16.5 kcal/mol energy difference at MP2/6-31G in favor of acetaldehyde reduces to 10.4 kcal/mol at MP3/6-31++G**[8,9] and to 11.2 kcal/mol at Gaussian (G1) theory. Hence, we decided to evaluate the nitromethane $\rightleftharpoons$ *aci*-nitromethane tautomerism using Pople's G1 theory.[10]

Computational Methods

All ab initio molecular orbital calculations[11] were carried out using the GAUSSIAN 90 suite of programs.[12] The nitromethane (**1**, **2**, C_s symmetry), *aci*-nitromethane (**3**, **4**, C_s symmetry), and nitromethane anion (**5**, C_1 symmetry) structures were optimized at the SCF level with the split-valence 3-21G and the d-polarized 6-31G* basis sets and with inclusion of the effects of all electron correlation by using Møller–Plesset (MP) perturbation theory at second order, i.e., MP2/6-31G*. The latter geometries, which are shown in Figure 1 (see also Table I for nitromethane), were used for energy evaluation at the G1 level.[10a] In this approach additive energy corrections are made to those obtained with frozen core MP full fourth-order (including singles, doubles, triples, and quadruples) calculations using an essentially triply split valence basis set that includes d- and for hydrogen p-polarization functions, i.e., MP4/6-311G**. The corrections include additional diffuse (+) functions, and extra d- and f-functions (2df) for nonhydrogen atoms, quadratic configuration interaction (QCI or QCISD(T)), an empirical higher level correlation (HLC) based on the number of electrons (HLC = $-0.19n_\alpha - 5.95n_\beta$), and 0.95 scaled[13] zero-point vibrational MP2/6-31G* energy corrections (instead of the 0.9 scaled HF energies)[10a] and is shown in the equation:

$$\mathrm{G1} = \mathrm{MP4/6\text{-}311G^{**}} + \Delta E(+) + \Delta E(\mathrm{2df}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{HCL}) + \text{scaled ZPE} \quad (1)$$

The magnitude of these corrections is illustrated by comparison of the energies with those at MP4/6-311++G** in which diffuse and polarization functions were added to both hydrogen and nonhydrogen atoms. Absolute energies are given in Table II and those at G1 theory in Table III; all relative energies are summarized in Table IV. Ionization energies

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Table I. Experimental and Calculated Geometrical Parameters of Nitromethane

geometrical parameters[a]	X-ray, single crystal, 228 K[b]	neutron, single crystal, 15 K[c]	microwave[d]	MP2/6-31G*, this work
C–N	1.449(6)	1.4855(9)	1.489(5)	1.485
N–O	1.231(4)	1.2270(9)	1.224(5)	1.240
	1.214(3)	1.2225(9)		
$\mathrm{C{-}H_4}$			1.088(1)	1.090
$\mathrm{C{-}H_5}$				1.087
∠ONO	123.4(4)	123.7(1)	125.3	125.7
$\angle\mathrm{NCH_4}$		106.4	107.2	107.1

[a] Distances are in Å, angles in deg. [b] Reference 17. The C–H distances range from 0.7 to 0.95 Å, and the NCH angles from 105 to 111°. [c] Reference 18. The crystal structure of deuterionitromethane was determined. The other NCD angles are 107.7 and 108.5°. The C–D distances are 1.0751(13), 1.0736(14), and 1.0739(13). [d] Reference 19.

Table II. Absolute Energies (in hartrees) of Nitromethane, *aci*-Nitromethane, and the Nitromethide Anion[a]

compound	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*[a]	MP4/6-311++G**[b]	ZPED[c]
1 C_s	−242.255 86 (0)	−243.661 99 (0)	−244.345 33 (0)	−244.374 27	−244.528 59	30.63
2 C_s	−242.255 85 (1)	−243.661 98 (1)	−244.345 31 (1)	−244.374 25	−244.528 55	30.58
3 C_s	−242.255 41 (0)	−243.629 63 (0)	−244.308 87 (0)	−244.339 06	−244.497 82	29.39
4 C_s	−242.231 61 (1)	−243.613 50 (0)	−244.296 32 (1)	−244.326 36	−244.487 22	28.75
5 C_{2v}	−241.663 32 (0)	−243.057 73 (0)	−243.737 22 (0)	−243.762 96	−243.937 06	21.56

[a] Number of imaginary frequencies is given in parentheses. [b] MP4(SDTQ) energies using MP2/6-31G* geometries. [c] Scaled to 0.95 in kcal/mol.

Table III. Total Energies (in hartrees) and Corrections (in millihartrees) at the G1 Level for Nitromethane, *aci*-Nitromethane, and the Nitromethide Anion

compound	MP4/6-311G**	Δ*E*(+)	Δ*E*(2df)	Δ*E*(QCI)	Δ*E*(HLC)	ZPE[a]	G1
1	−244.513 04	−15.28	−132.29	+9.55	−73.68	48.82	−244.675 93
2	−244.513 03	−15.26	−132.34	+9.55	−73.68	48.73	−244.676 03
3	−244.481 76	−15.73	−135.03	+5.96	−73.68	46.84	−244.653 40
4	−244.470 85	−16.05	−134.87	+7.04	−73.68	45.82	−244.642 60
5	−243.900 08	−36.72	−140.94	+7.19	−73.68	34.35	−244.109 88

[a] Scaled to 0.95 mhartrees.

Table IV. Relative Energies (in kcal/mol) for Nitromethane, *aci*-Nitromethane, and the Nitromethide Anion

compound	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP4/ 6-31G*	MP4/ 6-311++G**	MP4/(+ZPE) 6-311++G**	G1
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.01	0.01	0.01	0.01	0.03	−0.02	−0.06
3	0.27	20.31	22.88	22.09	19.31	18.07	14.14
4	15.21	30.43	30.76	30.05	25.96	24.08	20.91

Table V. Ionization Energies (in kcal/mol) for Nitromethane and *aci*-Nitromethane

reaction	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP4/ 6-31G*	MP4/ 6-311++G**	MP4/(+ZPE) 6-311++G**	G1	expt[a]
2 → **5**	371.8	379.2	381.6	383.6	371.2	362.1	355.2	356.4
3 → **5**	371.6	388.9	358.7	361.5	351.9	344.1	341.1	

[a] Reference 28.

Table VI. Vibrational Frequencies of Nitromethane and *aci*-Nitromethane

1, calc[a]	a′	522 (3)	640 (29)	898 (7)	1114 (2)	1365 (64)	1392 (2)
	a′	1459 (20)	2994 (6)	3095 (4)			
	a″	33 (>0)	402 (<1)	1094 (2)	1454 (21)	1726 (85)	3122 (>0)
1, exp[b]	a′	607 (+*35*)	655 (+*15*)	917 (−*19*)	1103 (−*11*)	1402 (+*37*)	1379 (−*13*)
	a′	1426 (−*33*)	2967 (−*27*)	3065 (−*30*)			
	a″		480 (+*18*)	1103 (−9)	1426 (−*28*)	1561 (−*165*)	3045 (−77)
3, calc[a]	a′	469 (2)	543 (10)	777 (144)	1069 (16)	1240 (145)	1309 (67)
	a′	1414 (24)	1722 (265)	3120 (12)	3259 (3)	3489 (96)	
	a″	314 (131)	553 (75)	616 (24)	665 (14)		

[a] Calculated at MP2/6-31G*, scaled by 0.95. Values in parentheses indicate intensities. [b] Reference 23. Italic values in parentheses indicate the difference with those calculated.

of nitromethane and *aci*-nitromethane to anion **5** are given in Table V. MP2/6-31G* vibrational harmonic frequencies for **1** and **3** are given in Table VI.

The bonding properties of all structures were investigated with Bader's topological one-electron density analysis[14–16] using optimized MP2/6-31G* wave functions for **1–5**. For each the one-electron density distribution $\rho(\mathrm{r})$ was analyzed with the aid of the gradient vector field $\nabla\rho(\mathrm{r})$ and the Laplacian $\nabla^2\rho(\mathrm{r})$, which also determines the regions in space wherein electronic charge is concentrated or depleted. Bond critical points are characterized by having a minimum value in $\rho(\mathrm{r})$ along the maximum electron density path connecting two nuclei and are maxima in all other directions. The ellipticity ϵ at such a critical point describes the spatial symmetry of a bond, whereas the total energy density indicates a bond to be covalent ($H(\mathrm{r}) < 0$) or ionic ($H(\mathrm{r}) > 0$). The properties of the bond critical points of **1–5** are listed in Table VII. The electron

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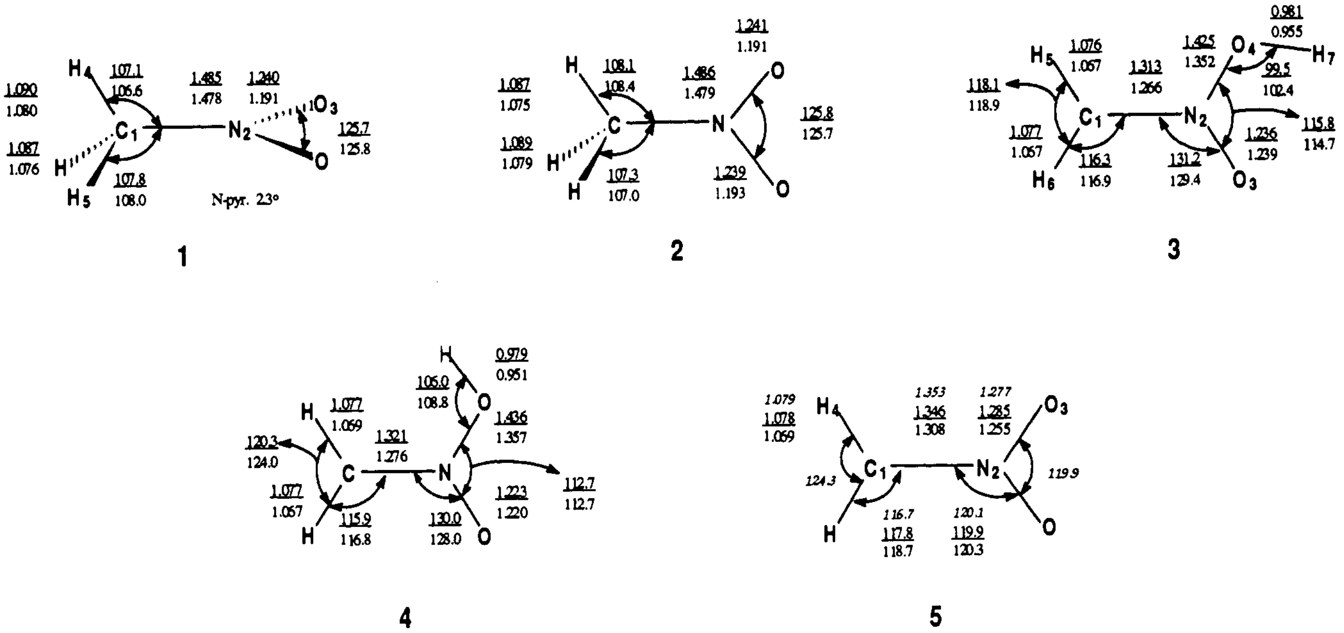

Figure 1. Geometries of **1–5**. The top underlined values are the MP2/6-31G* structural parameters, and the lower values are those at the HF level. The top values in italics for **5** are the parameters at MP2/6-311+G*.

Table VII. Summary of Critical Point Data for Nitromethane **1**, *aci*-Nitromethane **3**, and the Nitromethide Anion **5**

struct	bond	ϵ	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$H(\mathbf{r})$
1	C_1–N_2	0.053	1.530	–0.117	-1.473
	N_2–O_3	0.069	2.887	-9.569	-3.001
	C_1–H_4	0.042	1.751	-18.126	-1.592
	C_1–H_5	0.040	1.775	-18.761	-1.633
3	C_1–N_2	0.607	2.177	3.956	-3.521
	C_1–H_5	0.055	1.886	-24.930	-2.004
	C_1–H_6	0.055	1.891	-25.084	-2.016
	N_2–O_4	0.143	2.068	-7.894	-1.916
	N_2–O_3	0.073	3.187	-19.287	-3.969
	O_4–H_7	0.029	2.220	-41.544	-3.351
5	C_1–N_2	0.855	2.128	-5.925	-3.489
	N_2–O_3	0.101	1.835	-22.278	-1.886
	C_1–H_4	0.106	2.862	-15.946	-3.311

[a] $\rho(\mathbf{r})$ is in e A^{-3}; $\nabla^2\rho(\mathbf{r})$ is in e A^{-5}; $H(\mathbf{r})$ is in hartree A^{-3}.

Table VIII. Atomic Properties of Nitromethane **1**, *aci*-Nitromethane **3**, and the Nitromethide Anion **5**[a]

struct	atom	charge	scaled energy
1	C	+0.207	-37.942 38
	N	+0.396	-54.293 97
	O	–0.448	-75.189 48
	H_1	+0.095	–0.575 53
	H_2	+0.098	–0.577 01
	sum	–0.002	-244.344 86
			(–244.345 33)
3	C	+0.394	-37.714 32
	N	–0.003	-54.611 90
	O(H)	–0.736	-75.331 85
	O	–0.523	-75.177 94
	H_1	+0.131	–0.557 95
	H_2	+0.135	–0.557 99
	H(O)	+0.600	–0.341 17
	sum	–0.002	-244.293 12
			(–244.308 87)
5	C	+0.220	-37.745 91
	N	+0.105	-54.439 90
	O	–0.692	-75.171 21
	H	+0.025	–0.598 97
	sum	-1.009	-243.726 18
			(–243.737 22)

[a] The kinetic energies are corrected for the small virial defect found in the calculations by multiplying them by $-V/T - 1$. The values in parentheses are the total MP2/6-31G* energies.

population for each element (charges, listed in Table VIII) were obtained by integration of the charge density within their respective basin as defined by the zero-flux surfaces.

Results and Discussion

The organization is to discuss first the geometries and energies for nitromethane and *aci*-nitromethane, followed by sections on the tautomeric process and ionizations. MP2/6-31G* geometrical parameters and G1 energies will be used unless noted otherwise.

Nitromethane, CH_3–NO_2. The staggered (**1**) and eclipsed (**2**) conformations of nitromethane were considered. The eclipsed form **2** is a transition structure with an imaginary MP2/6-31G* frequency of 30 cm^{-1}. However, the two orientations are very close in energy at all levels ($\Delta \approx 0.01$ kcal/mol) except when scaled zero-point energy corrections are applied. In this case the eclipsed conformer is slightly favored, suggesting that the correction is not reliable at the applied levels due to, e.g., omission of anharmonicities and inadequate scaling. The results are similar to those obtained by McKee[6] at lower theoretical levels and highlight the essentially free rotation (torsion) within the nitromethane molecule, which is in accord with a microwave study that reports a rotation barrier of only 6 cal/mol.[17]

There is hardly any difference between the geometrical parameters of **1** and **2**, but for both structures the MP2/6-31G* bond lengths are noticeably longer than those at HF/6-31G* with differences as large as 0.051 Å for N–O bonds. The correlated structure is in good agreement with those obtained from microwave spectroscopy[20] (assigned to **2**!) and single-crystal neutron diffraction data[19] at 15 K (assigned to **1**), but deviate from a single-crystal X-ray structure[18] at 228 K, which is just below the melting point (see Table I). The crystal structure analyses show different N–O and different C–H (X-ray[18]) and C–D (neutron[20]) bond distances due to variations in intermolecular hydrogen bonds. Analyses based on neutron powder diffraction data (at 4.2° and 78 K) give similar results.[18] The agreement of the MP2/6-31G* C–N bond length of 1.485 Å with that obtained using single-crystal

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neutron diffraction data is excellent as is the agreement between the 2.3° theoretical and 1.5° experimental N-pyramidalization angle. However, the data do suggest that the N–O bond lengths calculated at MP2/6-31G* are ca. 0.015 Å too long. It is well recognized that MP2 bonds are often slightly too long because MP2 exaggerates the loss of charge density in the bonding region,[21] and this effect is strongest for the NO bonds; i.e., the MP2-HF/6-31G* differences in both lengths are $\Delta d_{NO} = 0.051$ Å and $\Delta d_{CN} = 0.07$ Å.

Comparison of experimental[22] with harmonic vibrational MP2/6-31G* frequencies is very good with a mean deviation of only -11 cm^{-1} (SD 30.1) by excluding the single largest difference of -165 cm^{-1} for the calculated NO_2 (a″) stretch vibration of 3045 cm^{-1} (Table VI).[23] Thus, both structure and frequency analysis suggest that the NO_2 group is the least well described at MP2/6-31G*. The CH_3 torsion frequency of only 33 cm^{-1} and the ellipticity ϵ for the C–N bond of only 0.053, which suggests lack of hyperconjugative stabilization, also support the absence of a rotation barrier.

From the G1 absolute energies of the molecule and its elements, an atomization energy ($\sum D_0$) for nitromethane of -570.69 kcal/mol is calculated. Based on the heats of formation given in the JANAF Tables[24] (0 K) and $\Delta H_f(CH_3NO_2) = -17.8$ kcal/mol,[25] an experimental atomization energy of -573.13 kcal/mol is obtained for nitromethane, which differs from the theoretical value by only 2.44 kcal/mol. This excellent agreement suggests that the theoretical description of nitromethane is adequate.

***aci*-Nitromethane, $CH_2{=}NO_2H$.** Two methanenitronic acid conformers were considered. The cis (**3**) and trans (**4**) forms differ in the orientation of the OH relative to the NO unit. The trans conformer, which also has the larger dipole moment ($\mu = 5.05$ D versus $\mu = 2.16$ D for *cis*-**3**), is a transition structure for N–OH bond rotation at MP2/6-31G* with an imaginary frequency of 141 cm^{-1}. The barrier ΔE for this rotation amounts to 6.8 kcal/mol at G1. The **3** – **4** energy difference is similar at all correlated levels. Because **4** is a SCF minimum, McKee discussed earlier the cis and trans forms in terms of different stabilizations. A contributing factor may be that the MP2/6-31G* geometrical parameters differ significantly from those at SCF. The correlated structures have much longer bond lengths, in particular, the C═N and N—OH bonds, with MP2-SCF differences of ca. 0.045 and 0.075 Å, respectively. Rotation around the N—OH bond from cis to trans lengthens this bond and the C═N bond, which may suggest an in-plane repulsive (electrostatic) interactive between the *aci*-nitro hydrogen and the methylene group. The electron density analysis does not indicate hydrogen bonding between the *aci*-nitro hydrogen and the NO unit ($d_{(O)H..O(N)} = 2.13$ Å) in the cis conformer. The atomic charges indicate a strong polarization in *aci*-nitromethane, but, whereas the CH_2 group of the C═N double bond ($\epsilon = 0.607$) has a positive charge of +0.660e, the nitrogen atom is essentially neutral. Vibrational harmonic frequencies of this species are provided in Table VI to assist its experimental verification.

Based on the theoretical atomization energy of -565.55 kcal/mol and the heats of formation given in the JANAF Tables, a heat of formation of -1.17 kcal/mol is calculated for *aci*-nitromethane.

Tautomerism. The energy difference between nitromethane (**1**) and *aci*-nitromethane (**3**) determines the extent of tautomerism. This ΔE amounts to 14.1 kcal/mol at G1 in favor of nitromethane to give an estimated gas-phase equilibrium constant of 4.5×10^{11}. The energy difference is sensitive to the method employed as illustrated by the larger ΔE of 22.9 at MP2/6-31G* (ZPE uncorrected) and 19.1 kcal/mol at MP4/6-311++G** + scaled ZPE. The smaller ΔE at G1 results from contributions due to both the basis set (more polarization (2df) functions) and corrections in the MP treatment by QCI. For comparison, the "best" reported G1 keto ⇌ enol energy difference between the acetaldehyde and vinyl alcohol tautomers amounts to 11.2 kcal/mol.[8] The energy difference between the two tautomeric processes of 3.7 kcal/mol is surprisingly small and may suggest that substitution of nitro compounds can lead to enhanced tautomerism as is the case for many keto derivatives.[1] This is the subject of further study.

Nitromethide Anion. Nitro ⇌ *aci*-nitro tautomerism is likely to proceed via a common anion,[1] because the [1,3]-H shift is a symmetry-forbidden process. The nitromethide anion **5** (also termed methyl nitronate), which has been subject of earlier studies,[26] has a planar (C_{2v}) structure whose geometry is dependent on the theoretical method employed with MP2-HF/6-31G* differences in C–N and N–O bond lengths of 0.038 and 0.03 Å, respectively (see Figure 1). The nitromethide anion is a potentially Y-aromatic system. However, in a recent theoretical study, Wiberg found no evidence for Y-aromaticity in the trimethylenemethyl, acetone, acetate, and carbonate dianions, all of which are isoelectronic with **5**.[27a] Moreover, Gobbi et al.[27b] showed that the trimethylenemethyl dianion has, in fact, a nonplanar geometry (with all methylenes pyramidalized up to 48.5° (MP2/6-31G*)), that is, 4.3 kcal/mol more stable at MP2/6-31++G* than the planar form. Only geometry optimization of the nitromethide anion **5** with a more flexible basis set (MP2/6-311+G*) leads to pyramidalization of the methylene group, but the angle of 15.7° (**5a**) is modest (the pyramidalization angle at nitrogen is only 1°). At the same level of theory the barrier for inversion (**5a** (C_s) – **5b** (C_{2v})) amounts to a small 32 cal/mol. This energy difference is small enough to validate the use of the planar geometry (MP2/6-31G*) for calculating a G1 proton affinity for **5** of 355.2 kcal/mol. This value agrees remarkably well with the experimentally determined ionization energy of 356.4 kcal/mol (gas phase, pulsed ICR) for nitromethane.[28]

The MP2 correlated structure of the nitromethide anion has a short C–N bond length of 1.346 Å using the 6-31G* basis set (1.351 Å with 6-311+G*), which is indicative of significant double-bond character ($\epsilon = 0.855$). Whereas also the N–O bonds of 1.285 Å (1.278, MP2/6-311+G*) are rather short, both molecular orbital and electron density arguments suggest that most (if not all) of the negative charge is located on the oxygens, which are also the more electronegative elements. The Bader electron density analysis shows that the negative charge is not evenly dispersed over the CH_2 group and the oxygens, and that the central nitrogen atom is not strongly positively charged either. In fact, the calculated charges support the contention that the strongly negatively charged oxygens (−0.692e) and not the methylene group (+0.270e) are the most receptive toward protonation and this would render the methylnitronic acid **3**.

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