Calculation of ^{15}N NMR Parameters of Azides and Some Related Compounds. Revisiting the Methylation of Nitrous Oxide N$_2$O

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The results of a calculation of ^{15}N NMR parameters (chemical shifts and coupling constants) of azides and related compounds are in reasonably good agreement with experimental data, even for triazadienyl fluoride, F-N$_3$. The reaction between [CH$_3$]$^+$ and nitrous oxide, N$_2$O, can yield either an *O*- or an *N*-methylated cation, [Me(N$_2$O)]$^+$. The calculated ^{15}N NMR parameters clearly indicate that under the experimental conditions *N*-methylation to give [MeNNO]$^+$ is preferred instead of the methoxydiazonium ion [MeONN]$^+$ previously proposed.

Key words: ^{15}N NMR, Chemical Shifts, Nitrous Oxide, Methylation

Much effort has been made to elucidate the reactivity and structure of azides depending on substituents R or X (Scheme 1) [1]. This includes tedious procedures for selective single or multiple ^{15}N labeling to apply suitable analytical techniques [2 – 6], in particular ^{15}N NMR spectroscopy [7, 8]. Calculations carried out at a fairly high level of theory [*e. g.* B3LYP/6-311+G(d,p)] for optimizing molecular structures and estimating relative energies of reasonably sized molecules can provide valuable contributions [9, 10]. Using these calculated geometries, NMR parameters (*e. g.* nuclear shielding or chemical shifts and spin-spin coupling constants) can be calculated and compared with experimental data. In the present Note it is shown that this approach confirms numerous assignments of ^{15}N chemical shifts (δ^{15}N) and reveals the likely (experimentally undetermined) signs of various spin-spin coupling constants and the respective contributions from the spin-spin coupling mechanisms (Table 1). Furthermore, a classical problem can
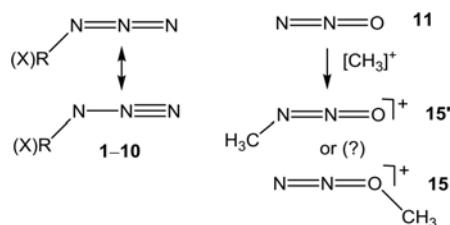
Scheme 1. Important canonic structures of azides, and the methylation of nitrous oxide.

be solved with regard to the site of methylation of nitrous oxide N$_2$O (Scheme 1), to give [Me(N$_2$O)]$^+$, for which experimental NMR data [6] have been waiting for the correct interpretation (Table 2).

Considering the influence of different solvents on polar molecules, the respective method of referencing and conversion of all experimental data to the MeNO$_2$ scale of δ^{15}N, as well as the shortcomings of the theoretical methods used, the agreement between experimental and calculated δ^{15}N data of the azides listed in Table 1 is satisfactory, at least for assignment purposes. It should be mentioned that even δ^{15}N data of an "extreme" example such as FN$_3$, **8**, [4b] are fairly well reproduced. This is also true for the *Z/E*-isomers of [O=N(F)-N$_3$]$^+$, for which the δN values have been measured and compared with the calculated data [11]. The pronounced differences in the calculated δ^{15}N data for H-N$_3$, **2**, known to possess the typical bent structure of covalent azides, and an assumed linear H-N$_3$ molecule shows the great sensitivity with respect to changes in geometry. This is also born out by the calculated signs and magnitudes of coupling constants for bent and linear H-N$_3$, **2**.

As for chemical shift data, all calculated coupling constants also fit for the bent structure of H-N$_3$. Expectedly, the one-bond ^{15}N-^{15}N coupling constants are dominated by the Fermi contact term, and the calculated negative sign can be traced to the presence of a lone pair of electrons at the terminal nitrogen atoms. This is seen in the case of **16**, where the sign of $^1J(^{15}$N(1),^{15}N(2)) is now positive, since protonation of the terminal N(1) reduces the negative contributions.

The results obtained in the calculation of the NMR parameters of azides (Table 1) prompted us to apply the same approach to related species, some of which are listed in Table 2. The calculated data for N$_2$O, **11**, as well as for **12 – 14**, and **16** are similarly accurate as for the azides.

Table 1. $^{14/15}$N NMR parameters[a,b] of some representative azides.

Compound	δ^{15}N(1) calcd. [found]	δ^{15}N(2) calcd. [found]	δ^{15}N(3) calcd. [found]	$J(^{15}$N,^{15}N) [Hz] calcd. [found] {FC, SD, PSO} [Hz] calcd.[c]
1 [N$_3$]$^-$	−293.7 [−280.9]	−117.0 [−130.4]	−293.7 [−280.9]	−10.4 [11.35] (1-2), −10.4 [11.35] (2-3) {−9.3, +0.8, −2.2} +2.8 (1-3)
2 H-N$_3$	−334.9 [−324.9]	−128.9 [−134.5]	−161.3 [−179.0]	−12.0 [13.95] (1-2), −2.6 [7.2] (2-3) {−8.9, −0.4, −2.6}{−4.9, +3.0, −0.8} +1.6 (1-3)
H-N$_3$ (asumed as linear)	−387.6	−180.4	−250.2	+23.0 (1-2), −4.3 (2-3) {+25.2, −0.4, −1.8}{−6.9, +2.8, 0.0} +3.3 (1-3)
3 Me-N$_3$	−325.4 [−321.2]	−125.6 [−129.7]	−162.9 [−171.0]	−12.2 (1-2), −4.3 (2-3) {−9.5, −0.2, −2.6}{−5.9, +2.6, −1.2} +1.8 (1-3)
4 CF$_3$-N$_3$	−289.3 [−286.2]	−143.2 [−147.8]	−135.7 [−144.7]	−12.9 (1-2), −2.6 (2-3) {−10.0, −0.5, −2.4}{−5.5, +3.3, −0.4} +0.6 (1-3)
5 ^{t}Bu-N$_3$	−290.7 [282]	−129.9 [130.5]	−157.1 [159]	−13.0 (1-2), −4.7 (2-3) {−10.2, −0.2, −2.5}{−6.0, +2.5, −1.1} +1.6 (1-3)
6 Ph-N$_3$	−293.1 [−287.9]	−133.5 [−136.2]	−132.1 [−146.9]	−10.8 (1-2), −4.7 (2-3) {−8.3, −0.2, −2.4}[−6.3, +2.8, −1.2] +1.4 (1-3)
7 fc(N$_3$)$_2$ fc = Fe(η^5-C$_5$H$_4$)$_2$	−307.4 [−303.1][d]	−130.4 [−134.7][d]	−140.7 [−150.2][d]	−11.2 (1-2), −5.2 (2-3) {−8.6, −0.3, −2.3}{−6.8, +2.6. −1.2} +1.5 (1-3)
8 F-N$_3$[e,f]	−86.2 [−87.7]	−101.3 [−113.5]	+28.1 [−1.6]	−25.5 [26.5] (1-2), −6.0 [9.3] (2-3) [−23.1, +0.4, −2.8]{−7.2, +3.8, −1.6} −5.6 (1-3)
9 Cl-N$_3$	−249.5 [−273.5]	−116.4 [−124.1]	−89.9 [−114.5]	−24.0 [24.0] (1-2), −5.3 [7.8] (2-3) {−21.5, +0.2, −2.5}{−7.1, +2.9, −1.2} −3.3 (1-3)
10 Me$_3$Si-N$_3$	−328.6 [−324.3]	−138.7 [−149.7]	−201.6 [−219.0]	−8.1 (1-2), −3.7 (2-3) {−5.1, −0.4, −2.5}{−5.9. +2.7, −0.8} +1.8 (1-3)

[a] Experimental data are taken from refs. [7, 8] if not noted otherwise, and all δN values were converted to the MeNO$_2$ (neat) scale; [b] calcd. σ(N) data are converted to δN values by $\delta N = \sigma(N)[NH_3] - \sigma(N) - 399.3$, with $\sigma(N)$ [NH$_3$] = 259.4 ppm, δN [NH$_3$] = −399.3 ppm and δN [neat MeNO$_2$] = 0 ppm; [c] FC, SD and PSO are the mechanisms for spin-spin coupling, referring to the Fermi contact, spin-dipole and paramagnetic spin-orbital terms; [d] this work; [e] $J(^{19}$F,^{15}N) +79.1 [58.2] Hz (^1J), −14.3 [4.7] Hz (^2J), +86.2 [58.6] Hz (^3J); [f] since $\gamma(^{15}$N) < 0, the sign of $^1J(^{19}$F,^{15}N) is opposite to that of the reduced coupling constant $^1K(^{19}$F,^{15}N).

An interesting question arises in the case of [Me(N$_2$O)]$^+$ (Scheme 1), for which on the basis of experimental data the methoxydiazonium structure **15**, [MeO-NN]$^+$, has been proposed [6] rather than the *N*-methylated structure **15′** [Me-NNO]$^+$. Although this problem has been addressed several times by experimental and numerous theoretical methods [6, 12, 13], the answer has remained open. All advanced theoretical methods seem to favor **15′** as the species of somewhat lower energy than **15** [13]. However, this appears to be in contrast with the experimental NMR spectro-scopic evidence, collected in an elegant study by Olah *et al.* [6]. To the best of our knowledge, the calculation of NMR parameters has not been used so far to gain further insight. The entries for calculated δ^{15}N data for **15** and **15′** in Table 2 show that reasonable agreement with experimental data is found only for **15′**, [Me-NNO]$^+$. A difference of > 150 ppm between calculated and experimental data for one of the ^{15}N nuclei in **15** is far beyond the error of the calculations. The authors claim the absence of ^{15}N-^{13}C spin-spin coupling as another proof of **15** [6]. However, the N–Me

Table 2. Experimental[a] and calcd.[b] NMR parameters of nitrous oxide and other species containing the N_2 moiety.

Compound	$\delta^{15}N(1)$ calcd. [found]	$\delta^{15}N(2)$ calcd. [found]	$\delta^{15}N(3)$ calcd. [found]	$J(^{15}N,^{15}N)$ [Hz] calcd. [found] {FC, SD, PSO} [Hz] calcd.[c]
11 O=N=N	–	−136.8 [−140.0]	−225.1 [−225.0]	−4.9 [−9.2] (2-3) {−8.7, +3.3, +0.5}
12 CH_2-N_2	–	−89.9 [−96]	+43.6 [+7.8]	−4.1 (2-3) {−3.2, +2.1, −3.0}
13 $[Ph$-$N_2]^+$	–	−136.4 [−149.8]	−22.6 [−66.3]	−0.7 (2-3) {−3.7, +3.9, −0.9}
14 $[F$-$N_2]^{+\ d}$	–	−173.7 [−191.2]	−141.2 [−166.1]	−14.9 (2-3) {−24.8, +5.6, +4.3}
15 $[MeO$-$N_2]^+$	–	−152.4 [−158.6][e]	−138.2 [−293.6][e]	−7.1 [12.0][e] (2-3) {−13.5, +4.6, +1.8}
15′ $[O$=N-N-$Me]^+$	–	−152.9 [−158.5] −148.5[f]	−302.3 [−293.6] −299.0[f]	+20.3 (2-3) {+16.6, +2.6, +1.1} +16.0[f] [12.0] (2-3) {+12.4, +2.6, +1.0}
16 $[H_2N$-$N_2]^+$	−321.4 [−316.5]	−165.9 [n. m.]	−60.0 [−115.9]	+3.6 (1-2), −2.1 (2-3) {+6.0, +0.4, −1.9}{−7.2, +4.2, +0.9} −4.0 (1-3) {−4.1, +1.2, −1.0}

[a] See footnote a, Table 1; [b] see footnote b, Table 1, [c] see footnote c, Table 1; [d] $^1J(^{19}F,^{15}N)$: +583.0 [476] Hz; +68.1 [4.7] Hz (^2J); [e] experimental data from ref. [6]; [f] CCSD/6-311+G(d,p) optimized geometry: CNN 152.0°, NNO 173.6° (see also ref. [13]).

bond in **15′** is weak (bond length C–N ≈ 150 pm), and even slow exchange of the methyl group under the experimental conditions ($CH_3F{\rightarrow}SbF_5$ in SO_2F_2 or CH_3O^+SOClF in SO_2ClF) would cancel the ^{15}N-^{13}C spin-spin coupling.

The experimental coupling constant $^1J(^{15}N,^{15}N) =$ 12 Hz in **15/15′** does not allow to distinguish between the isomers, since the agreement with the absolute magnitude of the calculated data is poor. Using the geometry of **15′**, optimized at a higher level of theory [CCSD/6-311+G(d,p)], for the calculation of $^1J(^{15}N,^{15}N)$ improves the agreement, indicating the sensitivity of this parameter to slight geometrical changes. It should be noted that the signs of the calculated $^1J(^{15}N,^{15}N)$ values are opposite for **15** (< 0) and **15′** (> 0). The positive sign for **15′** is expected since negative contributions to the Fermi contact term, arising in **15** (and also still in **11**) from the lone pair of electrons at the nitrogen atom, are reduced as a result of *N*-methylation.

Experimental and computational methods

The 50.7 MHz ^{15}N NMR spectrum of ferrocene-1,1′-diazide **7**, prepared as described [14], was obtained from a saturated solution in CD_2Cl_2 (0.6 mL) at 23 °C, using a Bruker DRX 500 spectrometer, operating in single pulse mode [25° pulses (4.5 µs), acquisition time 2 s, without ^1H decoupling] after 48 h. The assignment (Table 1) was made according to the calculations.

All quantum chemical calculations were done using the GAUSSIAN 09 (revision B.01) program package [15] at the B3LYP/6-311+G(d,p) [16] level of theory. Minima in energy were indicated by the absence of imaginary frequencies. Nuclear shielding constants (GIAO) [17] and spin-spin coupling constants [18] were calculated at the same level of theory.

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