15N magnetic shielding anisotropies in 15N15NO

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The ^{15}N magnetic shielding anisotropies in nitrous oxide (^{15}N^{15}NO) have been determined using a pulsed FT NMR spectrometer. The shielding anisotropies obtained from the temperature dependence of the nematic phase chemical shifts are 512 ± 10 ppm (central ^{15}N) and 369 ± 15 ppm (end ^{15}N). The values obtained from the nematic–isotropic phase difference method are 505 ± 10 ppm (central ^{15}N) and 366 ± 10 ppm (end ^{15}N). Theoretical estimates of the anisotropies from the so-called atom dipole method are also reported. The indirect scalar coupling constant has been assigned to be negative. The signs of the ^{15}N spin–rotation constants are predicted to be positive.

I. THEORY

The liquid crystal NMR technique has not proved very useful in the determination of the ^{14}N-chemical shift anisotropies[1] due to the disadvantages associated with the presence of the quadrupole moment of the ^{14}N nucleus and the poor natural sensitivity to detection of this nucleus. These drawbacks may be overcome by using ^{15}N-enriched molecules and pulsed NMR techniques. In this work, the results of ^{15}N magnetic resonance studies in a liquid crystal solution of doubly ^{15}N-substituted nitrous oxide (^{15}N^{15}NO) are reported. The NMR spectrum of either ^{15}N nucleus is expected to consist of a doublet in both the isotropic and nematic phases. In the isotropic phase the spectral splitting in each doublet is given by the indirect scalar coupling constant $J_{^{15}N^{15}N}$, while in the nematic phase this splitting would be

$$\Delta \nu_{^{15}N^{15}N} = J_{^{15}N^{15}N} + 2 D_{^{15}N^{15}N} , \qquad (1)$$

where $D_{^{15}N^{15}N}$ is the direct dipole–dipole coupling constant

$$D_{^{15}N^{15}N} = (-h \gamma^2_{^{15}N} / 4\pi^2 r^3_{NN}) S_{zz} , \qquad (2)$$

$\gamma_{^{15}N}$ is the gyromagnetic ratio of the ^{15}N nucleus. r_{NN} is the internuclear distance between the nitrogen nuclei which is taken to be 1.1286 Å from microwave studies.[2] S_{zz} is the ordering parameter which describes the average degree of partial orientation of the C_∞ axes of the solute molecules with respect to the Zeeman field. The anisotropy in the indirect spin–spin coupling tensor has been assumed to be negligible in Eq. (1).

The nematic phase ^{15}N nuclear shielding constant of either nucleus is given by the equation

$$\sigma_n = \sigma_i + \tfrac{2}{3} S_{zz} \Delta \sigma , \qquad (3)$$

where $\sigma_i = \tfrac{1}{3} \mathrm{Tr}(\sigma)$ is the isotropic phase shift and

$$\Delta \sigma = \sigma_{||} - \sigma_{\perp}$$

($||$ direction corresponds to the C_∞ axis of the molecule: $\sigma_{||} = \sigma_{zz}$).

II. EXPERIMENTS

The ^{15}N experiments were performed on a JNM-PFT-100 pulsed NMR spectrometer equipped with a variable temperature controller and a 1085 Nicolet computer. A ^{19}F field/frequency lock was used. (C_6F_6 was the lock sample contained in an 8 mm o.d. tube.) The sample of nitrous oxide enriched to contain doubly substituted 99 at.% ^{15}N was purchased from Prochem Ltd. The following liquid crystal preparation was contained in a 504-pp Wilmad NMR tube: ^{15}N^{15}NO gas (~23 atm. pressure) dissolved in approximately 0.22 g of properly degassed N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA). A sealed capillary containing an aqueous solution of approximately 7M HNO$_3$ enriched to contain ~50 at.% ^{15}N was used as the reference sample. At the beginning of the exper-
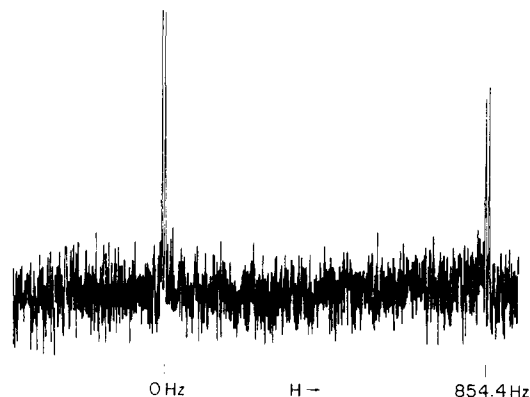
FIG. 1. Fourier transform absorption mode ^{15}N NMR spectrum of ^{15}N^{15}NO in CCl$_4$ solution at 30 °C obtained from 11 600 sweeps (pulse width: 5μs; repetition: 3 s). The central-^{15}N nucleus gives rise to the low field doublet and the end-^{15}N nucleus to the high field doublet.

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TABLE I. Spectral splittings and the ^{15}N chemical shifts of ^{15}N^{15}NO in nematic and isotropic phases of EBBA.

Phase	Temp. (°C)	$\Delta\nu_{15N15N}$ (Hz)	S_{zz}	Observed chemical shifts[a] (ppm)		Corrected chemical shifts[b] σ_n (ppm)	
				Central-^{15}N	End-^{15}N	Central-^{15}N	End-^{15}N
Nematic	30	−166.32	0.09157	166.88	242.65	165.63	241.15
	40	−151.06	0.08268	163.42	240.02	162.67	239.12
	50	−129.70	0.07023	158.61	236.22	158.36	235.92
Isotropic	55	−9.16	0	134.80	218.84	134.80	218.84
	65	−9.16	0	134.30	218.22	134.80	218.84
	75	−9.16	0	133.78	217.60	134.78	218.84

[a]Relative to H^{15}NO$_3$ (~7M aqueous solution) (1 ppm = 10.14 Hz).
[b]Corrected for the temperature dependence of the isotropic phase shift by referencing the chemical shifts relative to the shift at 55 °C.

iments, the sample was heated to the isotropic phase to obtain a homogeneous solution and subsequently the temperature was lowered to obtain the nematic phase. The sample was kept for at least half an hour at each temperature so that an equilibrium temperature was obtained over the effective sample volume.

III. RESULTS

The doublet splittings, values of the ordering parameter and the corresponding ^{15}N chemical shifts in ^{15}N^{15}NO (relative to H^{15}NO$_3$) in the isotropic and nematic phases of EBBA are given in Table I. Typical ^{15}N spectra are shown in Figs. 1 and 2. Errors in frequency difference measurements are estimated to be less than ± 0.4 Hz (errors in chemical shifts ~± 0.04 ppm; 1 ppm = 10.14 Hz). Both the ^{15}N resonances in nitrous oxide are situated at higher magnetic fields than the resonance in H^{15}NO$_3$. Assignment of the end-^{15}N peak to a higher field than the central-^{15}N peak leads to an excellent agreement between the experimental and theoretical ^{15}N shielding anisotropies (see Sec. IV). This identification of the peaks which are separated by ~84 ppm is suggested from a consideration of the following arguments. As the electronegativity of the atoms or groups directly bonded to a nitrogen atom increases there is a gradual decrease in the ionic character of the nitrogen atom and, therefore, a progressive increase of covalency resulting in paramagnetic shifts toward lower magnetic fields. Electronic asymmetry may also arise from unshared electron pairs which cause an upfield shift in contrast to the asymmetry due to electronegativity substituents causing a downfield shift. Therefore, the central-^{15}N resonance is expected to be at a lower field strength than the end-^{15}N resonance in nitrous oxide. The isotropic phase ^{15}N chemical shifts in this compound are found to be slightly tempera-

ture dependent with a negative linear variation. The chemical shifts measured relative to an external reference are expected to be dependent on both temperature and concentration (or solubility in the case of gases in solution) in the isotropic phase because of the variation of the diamagnetic susceptibilities with concentration as well as temperature due to density changes. The shifts of the central- and end-nitrogen nuclei in the isotropic phase of EBBA decreases linearly with the approximate gradients of 0.05 ppm/°C (~0.5 Hz/°C) and 0.06 ppm/°C (~0.6 Hz/°C), respectively. Hence it is necessary to correct for the temperature dependence of the isotropic term σ_i so that varia-

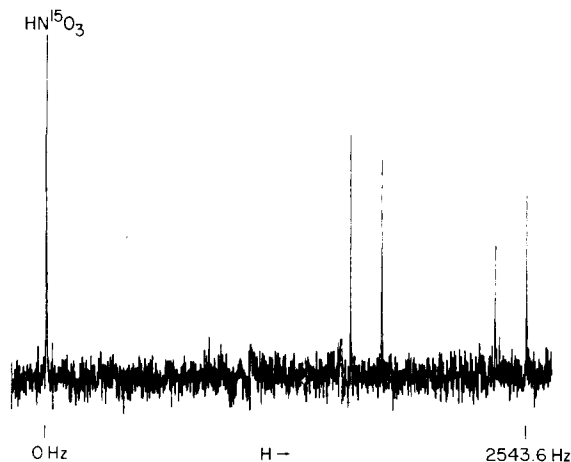FIG. 2. Fourier transform ^{15}N magnetic resonance spectrum (absorption mode) of ^{15}N^{15}NO in the nematic phase of EBBA at 30 °C obtained from an accumulation of 21 200 scans. Pulse width: 5μs; repetition: 3 s. Computer dwell time setting: 160 μs (sweep width: 3125 Hz). 16K interferogram. The middle and the outermost doublets arise from the central- and the end-^{15}N nuclei, respectively.

tions in the nematic phase chemical shift due to changes in S_{zz} only are considered in the evaluation of shielding anisotropies. This has been accomplished through the elimination of the relative temperature dependent term $(d\sigma_i/dt)(t - t_0)$ by referencing the chemical shifts with respect to the isotropic shift at 55 °C (which is close to the nematic–isotropic transition point). The σ_i in Eq. (3) is then expected to be the isotropic shift (at 55 °C). Similar temperature dependence of the isotropic shift in $^{15}N^{15}NQ$ has also been observed in CCl_4 solution (~10 atm pressure of N_2O dissolved in ~0.3 g of CCl_4) where, for example, the central- and end-^{15}N shifts are 135.40 and 219.66 ppm, respectively, at 30 °C, and 134.30 and 218.72 ppm, respectively, at 50 °C.

The sign of the ordering parameter S_{zz} has been assigned to be positive from polarizability measurements[3] which show the direction of the greatest electrical polarizability to be along the axis of the molecule. The magnitudes of the partial orientation parameter are rather large ($S_{zz} \sim 0.1$), which contributes to an increased accuracy in the determination of shielding anisotropies. The absolute value of the indirect spin–spin coupling constant $J_{15_N15_N}$ is rather small and has been determined to be 9.16 ± 0.30 Hz in the isotropic phase of EBBA as well as in CCl_4. Its sign has been assigned to be negative from the following considerations. The intercept of the plot of σ_n vs S_{zz} is in agreement with the isotropic phase chemical shift within the limits of experimental errors for both the ^{15}N nuclei when J is assumed to be negative (see Table II). When J is taken to be positive, the intercept does not agree with the value of σ_i for either nucleus.

Table III lists the ^{15}N shielding anisotropies obtained from the slope of the plot of σ_n vs S_{zz} by the least squares procedure (Method 1) which are found to be in excellent agreement with the anisotropies obtained from the nematic–isotropic phase chemical shift differences (Method 2) which are of considerable magnitudes (~20 to 30 ppm). In the nematic–isotropic subtraction method where an average of the anisotropies obtained at the different temperatures are given, the corrections due to the anisotropy of the bulk magnetic susceptibility of the nematic medium[4] have been taken into account in the estimation of errors.

IV. THEORETICAL CALCULATIONS

Theoretical estimations of the ^{15}N shielding anisotropies in nitrous oxide may be made using the atom dipole method.[5] The parallel element of the paramagnetic shielding tensor vanishes for a linear molecule ($\sigma_{\parallel}^p = 0$) since the electronic distribution is cylindrically symmetric. The parallel

TABLE II. Assignment of the sign of $J_{15_N15_N}$.

Values of S_{zz}		Corrected σ_n (ppm)		Isotropic chemical shift σ_i at 55 °C (in ppm)							Sign of $J_{15_N15_N}$ (assigned)
				Central-^{15}N			End-^{15}N				
J_{NN} positive	J_{NN} negative	Central-^{15}N	End-^{15}N	From experiment	From plot[a] $J, +ve$	$J, -ve$	From experiment	From plot[a] $J, +ve$	$J, -ve$		
0.10224	0.09157	165.63	241.15								
0.09335	0.08268	162.67	239.12	134.80 ±0.04	130.79 ±0.34	134.43 ±0.30	218.84 ±0.04	216.07 ±0.74	218.70 ±0.65		negative
0.08090	0.07023	158.36	235.92								

[a]This is the intercept of the plot of σ_n vs S_{zz}.

TABLE III. Values of the ^{15}N magnetic shielding anisotropies in ^{15}N^{15}NO.

Method	$\sigma_\parallel - \sigma_\perp$ (ppm)	
	Central-^{15}N	End-^{15}N
Method 1	512 ± 10	369 ± 15
Method 2	505 ± 10	366 ± 10
Theory (atom dipole)	516	368

component of the diamagnetic shielding tensor is given by

$$\sigma_\parallel^d(N) = \sigma_{atom}^d(N) + (e^2/3mc^2){\sum_n}' (\langle \rho^2 \rangle_n / r_n^3) , \qquad (4)$$

where e, m, c are the electronic charge, electronic mass, and speed of light, respectively. σ_{atom}^d (N) is the free-atom diamagnetic shielding of nitrogen whose value is well known.[6] The prime on the summation excludes the particular ^{15}N nucleus under consideration. The internuclear distances are taken from microwave studies.[2] Values of the atom electronic second moments $\langle \rho^2 \rangle$ are given in Ref. 7. Thus $\sigma_\parallel^d(N)$ is computed to be 364 ppm for the central ^{15}N and 349 ppm for the end ^{15}N. The values of σ_{av} are obtained as follows. The chemical shifts of the middle- and the end-^{15}N nuclei (in CCl$_4$ solution, at 30 °C) are, respectively, ~135 and ~220 ppm relative to H^{15}NO$_3$ (~7M aqueous solution). It was previously observed that the ^{14}N peak in a 70% HNO$_3$ solution (aqueous) showed an upfield shift of 28.3 ppm with respect to the resonance in the NO$_3^-$ ion but as the concentration was decreased, gradually shifted to the NO$_3^-$ position.[8] For example, the resonance of HNO$_3$ (8.57M, aqueous solution) was found to coincide with the NO$_3^-$ ion position within the limits of experimental errors.[9] Neglecting the isotope effect,[10] the ^{15}N resonance of H^{15}NO$_3$ solution used in this study has been assumed to lie at the NO$_3^-$ ion position. The nitrogen shielding constant in NO$_3^-$ is −115 ppm.[11] Therefore the absolute values of the central- and end-^{15}N shielding constants are, respectively, ~20 and ~104 ppm. The shielding anisotropies obtained empirically from a knowledge

of the values of $\sigma_\parallel^d$ and σ_{av} are listed in Table III. The magnitudes of the empirical estimates seem to be in excellent agreement with the experimental results.

It is interesting to note that the sign of the ^{15}N spin−rotation constants M in nitrous oxide molecule may be predicted using the following expression[5]:

$$\sigma_{av} = \sigma_{av}^d (\text{free atom}) + |e| \, MI/3m \, \hbar c \mu_n g_N ,$$

where μ_n is the nuclear magneton, $\hbar$ is Planck's constant divided by 2π, g_N is the g value of the ^{15}N nucleus, and I is the moment of inertia. Expressing M in kilohertz, we obtain

$$\sigma_{av} \cong 326 \times 10^{-6} - 89 \times M \times 10^{-6}.$$

Hence the values of the spin−rotation constants are estimated to be ~3.4 kHz (central-^{15}N) and ~2.5 kHz (end-^{15}N), respectively.

[1]The only instance so far seems to be the following work: C. S. Yannoni, J. Chem. Phys. **52**, 2005 (1970).

[2]C. C. Costain, J. Chem. Phys. **29**, 864 (1968).

[3]*Landolt−Bornstein Zahlenwerte und Funktionen* (Springer−Verlag, Berlin, 1951), Vol. 1, Pt. 3, p. 511.

[4]A. D. Buckingham and E. E. Burnell, J. Am. Chem. Soc. **89**, 3341 (1967).

[5]T. D. Gierke and W. H. Flygare, J. Am. Chem. Soc. **94**, 7277 (1972).

[6]R. A. Bonham and T. G. Strand, J. Chem. Phys. **40**, 3447 (1964).

[7]T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, J. Am. Chem. Soc. **94**, 330 (1972).

[8]B. M. Schmidt, L. C. Brown, and D. Williams, J. Mol. Spectrosc. **2**, 551 (1958).

[9]J. B. Lambert, G. Binsch, and J. D. Roberts, Proc. Natl. Acad. Sci. USA **51**, 735 (1964).

[10]R. L. Lichter, in *Determination of Organic Structures by Physical Methods*, edited by F. C. Nachod and J. J. Zuckermann (Academic, New York, 1971), Vol. 4.

[11]See, for example, A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper and Row, New York, 1967), p. 62. The absolute reference scale for nitrogen shielding was first established in the work of M. R. Baker, C. H. Anderson, and N. F. Ramsey, Phys. Rev. **133**, A1533 (1964).