about their carbonyl bonds. The motion occurs at a rate of ~2 × 10^6 s^{-1} at room temperature and has an activation energy of 23 ± 2 kJ mol^{-1}. This value may be interpreted as the energy associated with the breaking of four hydrogen bonds. Thus, each individual hydrogen bond experiences a barrier of about 6 kJ mol^{-1}, a rather low value which probably reflects the inefficiency of the oxygen atoms in supporting four hydrogen bonds.

A quadrupole coupling constant, $e^2qQ/h = 212 \pm 2$ kHz and asymmetry parameter, $\eta = 0.145 \pm 0.005$ were determined for the deuterons in pure urea-d_4, while the same parameters in UIC were found to be 208 ± 3 kHz and 0.155 ± 0.005, respectively. In UIC, the 180° jump motion distinguishes those deuterons for which the N–D bond makes an angle of approximately 60° with the jump axis (i.e., the C=O bond) from those for which the N–D bond is virtually parallel with this axis. Values of 59.0 ± 0.5° and 177 ± 3°, respectively, were determined for the angles made by the principal components of the electric field gradient tensors of the two types of deuterons with the jump axis, in good agreement with values found by neutron diffraction for the angles which the N–D vectors make with C=O bond in pure urea. For the D′ deuterons it was found that the X component (i.e., the component with the smallest absolute value assuming $\eta = (V_{xx} - V_{yy})/V_{zz} \geq 0$) of the principal electric field gradient tensor lies in the urea plane.

While the 180° jump model for the urea motion is able to reproduce the deuterium line shape for short pulse spacings over a range of temperatures, it does not account for the pulse spacing dependence of the line shape. This inability to explain the spectra obtained with long pulse spacings results not from any major flaw in the model proposed for the urea motion, but instead arises from a significant anisotropic contribution to the deuterium transverse relaxation rate from unresolved D–D and especially N–D dipolar couplings. Such dipolar interactions will, in general, cause dephasing of the transverse magnetization in quadrupole echo experiments and may be expected to complicate the line shape analysis at long pulse spacings. In addition, comparison of the pulse spacing dependence of the echo amplitude for pure urea-d_4 with that for UIC indicates some degree of self-decoupling of the N–D interaction in UIC. This effect, due to transitions between the ^{14}N spin states occurring at frequencies comparable to or higher than the N–D dipolar coupling, can be shown to provide an anisotropic contribution to the deuterium T_2. Although we have not attempted a detailed quantitative analysis of the pulse spacing dependence of the UIC deuterium line shapes, the expected contribution from these mechanisms is consistent with the observed discrepancies between experimental and simulated line shapes. Their relative importance is currently under evaluation in a relaxation study on single crystals of UIC.

Having identified the nature and rate of urea motion in the $C_{19}H_{40}$ complex, it is natural to consider what implications this type of motion might have on the stability and other properties of the complex. In view of the dimensions of the channels, it is conceivable that there is some relationship between the urea motion and the character and dynamics of guest molecules. It is known that the correlation times for the $C_{19}H_{40}$ motion are short, typically about 10^{-12} s,[17,45] compared with the lifetime for the urea flipping process (~10^{-6} s), suggesting that the guest and host dynamics are essentially independent. Nonetheless, there remains the possibility that there is some connection between the length of the guest molecules and the rate of urea motion. Accordingly, we are investigating the effect of the alkane by performing relaxation measurements on $C_{36}H_{74}$ and C_8H_{18} urea adducts. It would be of interest to explore this possibility further by investigating the behavior of urea complexes with other types of guest such as fatty acids, for instance, which contain chemically more diverse groups and whose motion is considerably slower[15] than that of the alkanes.

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Anisotropy of the ^1H and ^{13}C Chemical Shifts and of the ^{13}C–^{14}N Spin–Spin Couplings of Methyl Isocyanide As Determined by NMR in Nematic Mesogens

Y. Hiltunen, J. Jokisaari,* J. Lounila, and A. Pulkkinen

Contribution from the Department of Physics, University of Oulu, SF-90570 Oulu, Finland.
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Abstract: Proton and carbon-13 chemical shift anisotropies have been determined for methyl isocyanide by applying the NMR method which utilizes a proper mixture of nematic liquid crystals with opposite diamagnetic anisotropies. The resulting anisotropies, $\Delta\sigma$, are the following: 4.26 ± 0.01 ppm for proton, 52.4 ± 0.3 ppm for the CH_3 carbon, and 359 ± 5 ppm for the NC carbon. The agreement between the experimental and recently published theoretical anisotropies for carbon-13 nuclei is very good. The anisotropies of the indirect ^{13}C–^{14}N spin–spin coupling tensors, ΔJ, were determined by applying a new approach which takes into consideration the deformational contributions both in the direct dipolar couplings and in the corresponding anisotropic indirect couplings. The analysis yielded the values of 8.7 ± 1.7 and 42.8 ± 2.8 Hz for the couplings over the single and triple CN bonds, respectively.

I. Introduction

The NMR spectroscopy of molecules partially oriented in liquid crystals (LCNMR) has been applied to the determination of chemical shift as well as spin–spin coupling anisotropies almost since the invention of the technique in 1963.[1] The early experiments were, however, in most cases carried out in only one liquid crystal solvent, which prevented researchers from becoming aware of the remarkable solvent dependence of these quantities. Furthermore, chemical shift anisotropies were derived by methods which today are known to lead to large errors. The various techniques proposed and applied until recently are described in the review of Lounila and Jokisaari.[2]

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Table I. Liquid Crystals Used To Orient Methyl Isocyanide in the Determination of Shielding and Spin-Spin Coupling Anisotropies

no.	liquid crystal composition[a]
1	ZLI 1167
2	ZLI 1167 (80.0) + phase IV (20.0)
3	ZLI 1167 (58.0) + phase IV (42.0)
4	ZLI 1167 (30.0) + phase IV (70.0)
5	phase IV

[a] The ZLI 1167 and phase IV are commercial products from Merck. ZLI 1167 is a mixture of bicyclohexylcarbonitriles, and its anisotropy of diamagnetic susceptibility is negative. Phase IV is an eutectic mixture of *p*-methoxy-*p′*-*n*-butylazoxybenzenes with positive anisotropy of diamagnetic susceptibility. The figures in parentheses stand for the concentrations (in weight per cent) of the components in the liquid crystal mixture. Each sample contained 5 wt % of methyl isocyanide and about 1 atm of $^{13}CH_4$ gas serving as a chemical shift standard.

Table II. Experimental Anisotropic Couplings (in Hz and Referenced to the Liquid Crystal Director), $D^{D}_{C_1N}$ and $D^{D}_{C_2N}$, of Methyl Isocyanide in Various Liquid Crystals

liquid crystal[a]	$D^{D}_{C_1N}$[b]	$D^{D}_{C_2N}$[b]
1	−122.66 (16)	−222.50 (36)
2	−103.96 (18)	−188.40 (39)
3	−87.60 (11)	−159.67 (20)
4	−71.03 (7)	−129.27 (19)
5	−56.25 (8)	−102.91 (21)

[a] For the composition of the liquid crystal, see Table I. In samples 1 and 2, the liquid crystal director is perpendicular to the external magnetic field, and thus $D^{D}_{ij} = -2D^{exp}_{ij}$. In the other samples, the director lies along the magnetic field, and $D^{D}_{ij} = D^{exp}_{ij}$. [b] Uncertainties in parentheses are one standard deviation in the last figure quoted. In the spectral analyses, the J_{C_1N} and J_{C_2N} couplings were fixed to the values of 7.63 and 6.30 Hz, respectively.[9]

In the light of recent theories,[3-6] it is obvious that the apparent deformation of molecular structures, when determined in various liquid crystal solvents, is a consequence of the orienting forces acting on the molecule in its anisotropic environment. The true orientation-dependent deformation is apparently enhanced by a low degree of orientational order. The deformational contributions to the spectral parameters due to these forces can be minimized by performing measurements in proper liquid crystal mixtures,[7-9] i.e., in mixtures in which the methane-^{13}C ($^{13}CH_4$) molecules do not display any dipolar $^{13}C-^{1}H$ splitting. These contributions can also be incorporated into the theoretical expressions for the spectral parameters by a method developed by Lounila and Diehl;[3-5] then the analysis should result in undistorted structural parameters (and accurate description of the orienting forces) in any liquid crystal.

The solvent dependence of chemical shift anisotropies, $\Delta\sigma$, is a more complicated question than geometrical variation because of many possible disturbing contributions. In particular, when $\Delta\sigma$ is expected to be small, say of the order of −20 to +20 ppm as is general for protons, one has to be careful in choosing the method and the reference compound.[2,7] Theoretical calculations of the deformational contributions to nuclear shielding tensors can be done in principle, but additional complications arise from, for example, the local and bulk effects which should be separated from the experimental chemical shifts.[2,7] However, the experimental method called ENEMIX[7] has given promising results. This method is based on mixing two nematic liquid crystals with opposite anisotropies of diamagnetic susceptibility. The particular mixture in which the ^{1}H or ^{13}C NMR spectrum of dissolved methane-^{13}C does not display any dipolar $^{13}C-^{1}H$ splitting, i.e., the experimental dipole-dipole coupling $D_{CH}(CH_4) = 0$, is used to measure the necessary chemical shifts and order parameters for the calculation of $\Delta\sigma$. Methane is also used as an internal chemical shift standard.

The elimination of the solvent dependence of spin-spin coupling anisotropy, ΔJ, can be done in a corresponding way as the elimination of the solvent dependence of geometry. Then, however, one has to consider the deformational contributions not only to the dipole-dipole coupling tensor but also to the indirect spin-spin coupling tensor.[3-5] This approach was successfully applied to the ΔJ_{CF} in methyl-^{13}C fluoride.[8] A large range of ΔJ_{CF} values, from −4955 to +689.8 Hz, was obtained in various liquid crystals when only harmonic vibrational corrections to the experimental dipolar couplings were allowed for. After also applying the deformation corrections to the dipolar as well as indirect couplings, an umambigious value of 404 ± 31 Hz was obtained.[8]

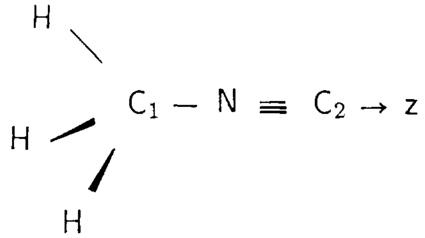

Figure 1. Numbering of the carbon atoms and definition of the coordinate system used for methyl isocyanide.

In the present paper, we report the results for the $\Delta\sigma_H$ and $\Delta\sigma_C$'s and the ΔJ_{CN}'s in methyl isocyanide. The theoretical treatment of the deformation of the $^{13}C-^{14}N$ spin-spin coupling tensors is partly based on our earlier study of the geometrical deformation of methyl isocyanide.[9]

II. Experimental Section

Methyl isocyanide was prepared by the method described in ref 10. It was dissolved in the liquid crystals listed in Table I. Each sample also contained carbon-13 enriched methane (from Merck Sharp & Dohme) relative to which both ^{1}H and ^{13}C chemical shifts were measured. The ^{1}H (with natural abundance ^{13}C satellites) and ^{13}C NMR spectra were recorded on a JNM-GX400 spectrometer from coaxial double tubes (outer diameter 5 mm) with $CDCl_3$ as lock substance in the interwall volume. The latter spectra yield the anisotropic $^{13}C-^{14}N$ couplings for the determination of the ΔJ_{CN}'s. Their values are shown in Table II. The slight change of the molecular orientation in the ^{1}H and ^{13}C spectra was taken into account by scaling the D^{exp}_{CN}'s with the aid of the dipolar $^{13}C-^{1}H$ couplings. In order to distinguish between the two carbon atoms in methyl isocyanide, the numbering given in Figure 1 is used.

III. Theoretical Section

The nuclear chemical shift, δ, measurable for a molecule with C_3 or higher symmetry in a uniaxial environment can be represented in the form

$$\delta = \delta^{iso} + 2/3P_2(\cos\alpha)S^{D}\langle\Delta\sigma\rangle \qquad (1)$$

where δ^{iso} is the isotropic chemical shift, S^{D} is the orientational order parameter of the molecular symmetry axis (z axis) referenced to the liquid crystal director, $P_2(\cos\alpha)$ is the Legendre polynomial with α being the angle between the liquid crystal director and the external magnetic field ($P_2(\cos\alpha)S^{D} \equiv S$ is the order parameter referenced to the magnetic field), and the vibrationally averaged shielding anisotropy $\langle\Delta\sigma\rangle = \langle\sigma_{zz}\rangle - 1/2(\langle\sigma_{xx}\rangle + \langle\sigma_{yy}\rangle)$. The chemical shift scale is chosen positive to low frequency.

In the present case the ENEMIX method[7] with internal $^{13}CH_4$ reference was applied. In this method the chemical shifts as well as order parameters are measured when the liquid crystal director is parallel to the magnetic field, i.e., $\alpha = 0°$, and when the director is perpendicular to the field, i.e., $\alpha = 90°$. The superscripts $\parallel$ and

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Table III. The Coefficients a^{kl}_{ij} and b^{kl}_{ij} (in 10^{22} Hz J^{-1}) of Methyl Isocyanide Applied in the Calculation of the Deformational Contributions to the Experimental ^{13}C–^{14}N Dipolar Couplings

i	j	a^{CH}_{ij}	b^{CH}_{ij}	a^{CN}_{ij}	b^{CN}_{ij}	a^{NC}_{ij}	b^{NC}_{ij}
C_1	N	0.0662	0.0436	–0.0747	–0.0533	0.1192	0.0851
N	C_2	–0.2258	–0.1618	0.2180	0.1557	–0.3538	–0.2527

Table IV. Proton and Carbon-13 Chemical Shift Anisotropies (in ppm) of Methyl Isocyanide Determined at 293 K by the ENEMIX Method[a]

chemical shift anisotropy[b]	this work int $^{13}CH_4$ ref	 ext $CHCl_3/CDCl_3$ ref	other works
$\langle\Delta\sigma_H\rangle$	4.26 (1)	–0.58 (9)	–0.76 (50)[c]
$\langle\Delta\sigma_{C_1}\rangle$	52.4 (3)	42.8 (10)	43,[d] 5.94[e]
$\langle\Delta\sigma_{C_2}\rangle$	359 (5)	350 (5)	387,[d] 339.1[e]

[a] For comparison, other experimental and theoretical results are also given. Uncertainties in parentheses are one standard deviation in the last figure quoted. Theoretical values do not include vibrational contributions. [b] For the assignment of the nuclei, see Figure 1. [c] Experimental LCNMR result from ref 18. Chemical shift reference: internal Me_4Si. Method: nematic-isotropic phase transition with solvent correction. [d] Theoretical result from ref 16. [e] Theoretical result from ref 17.

⊥ are used to indicate the parallel and perpendicular orientation. Then the chemical shift anisotropy is obtained from equation

$$\langle\Delta\sigma\rangle = \frac{3}{2}\frac{\delta^{\parallel} - \delta^{\perp}}{S^{\parallel} - S^{\perp}} \tag{2}$$

Theoretically $S^{\parallel}/S^{\perp}$ equals –2 exactly, but experimentally small deviation from this may appear because of measurement uncertainty due to, for instance, extrapolation needed to get the parameters at the perpendicular orientation.[7]

The experimentally observable anisotropic coupling between two magnetic nuclei can be written in the form (neglecting anharmonicity in vibrations)

$$D^{exp}_{ij} = D^{e}_{ij} + D^{h}_{ij} + D^{d}_{ij} + D^{ind}_{ij} \tag{3}$$

where the various terms on the right-hand side correspond to the following contributions: D^{e}_{ij}, equilibrium; D^{h}_{ij}, harmonic vibration, D^{d}_{ij}, deformation; and D^{ind}_{ij}, indirect spin–spin coupling anisotropy. The determination of molecular geometries has to be based on the couplings between nuclei for which D^{ind}_{ij} is negligible. Such nuclear pairs are, for example, ^1H–^nX (^nX being almost any magnetic nucleus).[2] The most commonly used anisotropic couplings in geometrical studies are the ^1H–^1H and ^1H–^{13}C ones. The details of the geometrical analysis of methyl isocyanide have been reported elsewhere.[9]

The harmonic correction factors, $p^{h}_{ij} = D^{h}_{ij}/D^{e}_{ij}$, were calculated by the program VIBR[11] using the force field of Duncan et al.[12] Results for the ^{13}C–^{14}N couplings are the following (at 300 K): $p^{h}_{C_1N} = -0.0180$ and $p^{h}_{NC_2} = -0.0552$. The corresponding factors of the other couplings in methyl isocyanide are given in ref 9.

The deformational contribution, D^{d}_{ij}, can be written as

$$D^{d}_{ij}/P_2(\cos\alpha) = (a^{CH}_{ij} + b^{CH}_{ij}S^D)\Delta A_{CH} + (a^{CN}_{ij} + b^{CN}_{ij}S^D)\Delta A_{CN} + (a^{NC}_{ij} + b^{NC}_{ij}S^D)\Delta A_{NC} \tag{4}$$

where the ΔA_{CH}, ΔA_{CN} ($=\Delta A_{C_1N}$), and ΔA_{NC} ($=\Delta A_{C_2N}$) are the so-called interaction parameters of the CH, CN single, and NC triple bonds, respectively. The ΔA's, which specify the torques acting on the bonds, are defined by equation

$$U_{ext} = -\Delta A P_2(\cos\Theta) \tag{5}$$

where U_{ext} is the orienting potential energy of a bond (assumed to be axially symmetric) and Θ is the angle between the bond axis and the director.[5] S^D can be calculated from the ΔA's by classical Boltzmann statistics. Consequently, in the present method S^D is not a fundamental parameter. The coefficients a^{kl}_{ij} and b^{kl}_{ij} can be calculated using the geometry and harmonic force field of the molecule.[3-5] Their numerical values for the ^{13}C–^{14}N couplings are collected in Table III, while for the other couplings they are given in ref 9.

The determination of the vibrationally averaged spin–spin coupling anisotropy, $\langle\Delta J_{ij}\rangle$, is based on the contribution D^{ind}_{ij} in eq 3. In the conventional method (neglecting the deformational contributions)

$$D^{ind}_{ij}/P_2(\cos\alpha) = (D^{exp}_{ij} - D^{calc}_{ij})/P_2(\cos\alpha) = 1/3S^D\langle\Delta J_{ij}\rangle \tag{6}$$

and thus

$$\langle\Delta J_{ij}\rangle = 3\frac{D^{exp}_{ij} - D^{calc}_{ij}}{P_2(\cos\alpha)S^D} \tag{7}$$

where $D^{calc}_{ij} = D^{e}_{ij} + D^{h}_{ij}$ is calculated from the molecular geometry and order parameter (derived from the anisotropic couplings where D^{ind}_{ij} is negligible). In some cases this kind of approach leads to strongly solvent-dependent ΔJ's. For example, in the present case the ΔJ_{CN} varies from –35 to 30 Hz and the ΔJ_{NC} from 10 to 70 Hz depending upon the liquid crystal solvent. In the next step, one may also apply deformational corrections to the dipolar couplings. This diminishes the range of variation of ΔJ's but does not remove it totally. Obviously the orienting torques that deform the molecular geometry also deform the spin–spin coupling tensors. To correct D^{ind}_{ij} for deformational effects, the equations should be supplemented by the deformational contributions to D^{ind}_{ij}. These are similar in form to those for the dipolar couplings, eq 4.[3-5] However, the values of the coefficients a^{kl}_{ij} and b^{kl}_{ij} can be calculated only if the derivatives of the indirect coupling tensors with respect to the vibrational normal coordinates are known. These are not available. Thus the coefficients should be determined experimentally, by treating them as free parameters in the least-squares fits of sufficiently overdetermined systems.[8] The number of adjustable parameters can be reduced by making use of the observed approximately linear relations between the interaction parameters ΔA_{CH}, ΔA_{CN}, and ΔA_{NC}:[9]

$$\Delta A_{CN} \approx a_1\Delta A_{CH} + b_1 \tag{8}$$

$$\Delta A_{NC} \approx a_2\Delta A_{CH} + b_2 \tag{9}$$

Here $a_1 = 1.727$, $b_1 = 8.77 \times 10^{-22}$ J (correlation coefficient 0.999), and $a_2 = 0.195$, $b_2 = 13.8 \times 10^{-22}$ J (correlation coefficient 0.881). Further, neglecting the terms linear in S^D, the deformational contribution to D^{ind}_{ij} reduces to

$$D^{(ind)d}_{ij}/P_2(\cos\alpha) = a_{ij}\Delta A_{CH} + b_{ij} \tag{10}$$

where $a_{ij} = a^{CH}_{ij} + a_1a^{CN}_{ij} + a_2a^{NC}_{ij}$ and $b_{ij} = b_1a^{CN}_{ij} + b_2a^{NC}_{ij}$. Actually it turned out that the refinement of the parameters b_{ij} resulted in very small and poorly determined values for them. Therefore, in the final analysis b_{C_1N} and b_{C_2N} were constrained to zero and only the coefficients a_{C_1N} and a_{C_2N} were treated as free parameters.

IV. Results and Discussion

1. Chemical Shift Anisotropies. The ^1H and ^{13}C chemical shifts of methyl isocyanide were measured with respect to internal methane and external chloroform standard at 293 K in the liquid crystal solvents shown in Table I. In the latter case no susceptibility corrections were applied. The chemical shift anisotropies, $\Delta\sigma$, were determined by the ENEMIX method using eq 2. The results are collected in Table IV where results from other studies are also shown for comparison.

Table IV shows that the proton and carbon chemical shift anisotropies differ by ca. 5 and 10 ppm, respectively, when internal methane and external chloroform references are used. This difference arises mostly from the anisotropy of the local contributions which an external reference cannot take into account at all. It has been observed that the local contributions affect the

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^1H and ^{13}C chemical shifts of methane by ca. −0.5 and −1.0 ppm, respectively, when the liquid crystal director rotates from the parallel to the perpendicular orientation with respect to the external magnetic field.[7,13] The effect of this phenomenon on the chemical shift anisotropies can be evaluated from equation

$$\Delta(\Delta\sigma_i) = -\frac{3}{2}\frac{\Delta\delta_i}{S^{\parallel} - S^{\perp}} \tag{11}$$

where $\Delta\delta_i = \delta_i^{\parallel} - \delta_i^{\perp}$ is the above-mentioned ^1H or ^{13}C shift in methane and $\Delta(\Delta\sigma_i) = \Delta\sigma_i^{int} - \Delta\sigma_i^{ext}$. In the present case this leads to the $\Delta(\Delta\sigma_H)$ of +4.2 ppm and to the $\Delta(\Delta\sigma_C)$ of +8.3 ppm which fit very well with the experimental values and thus confirm the conclusion that $\Delta(\Delta\sigma_i)$ indeed arises from the local contributions to chemical shifts of the reference molecule. On the other hand, the molecule under investigation, e.g., methyl isocyanide in this work, may experience a local contribution that slightly differs from the one of the reference molecule. This, however, can only be revealed by comparing the final experimental LCNMR results to the corresponding ones derived by other means. It has been argued that the method called NEMIX,[14,15] without any reference and the simultaneous observation of the spectra corresponding to the parallel and perpendicular orientations of the liquid crystal director, would be an applicable way to derive chemical shift anisotropies.[14] The fact, however, is that this kind of an experiment corresponds to the one with external reference and, consequently, is not at all able to allow for the local effects on chemical shifts.

The experimental ^{13}C chemical shift anisotropies determined in the present work and the recent theoretical results calculated by Schindler[16] (see Table IV) by means of the IGLO method are in good accord. On the contrary, the earlier value for $\Delta\sigma_{C_1}$ calculated by Ebraheem and Webb[17] is much too small.

The determination of the proton chemical shift anisotropies is in general a difficult task because of the fact that they are small, usually within ±10 ppm and always within ±20 ppm.[2] Thus the variation of proton chemical shifts, δ_H^{exp}, as a function of the molecular degree of order is only slight and the contributions from other effects than shielding anisotropy may become even dominating. For methyl isocyanide, no reliable $\Delta\sigma_H$ value could be found for comparison. The only available value ($\Delta\sigma_H$ = −0.76 ppm) is the one determined by Silverman and Dailey[18] by applying the LCNMR technique which is based on the nematic-isotropic phase transition with solvent shift correction. The $\Delta\sigma_H$ of 4.26 ppm of this work differs from the one in ref 18 both in sign and magnitude.

The experimental results of some methyl compounds from this laboratory[8,15,19] indicate that the $\Delta\sigma_H$ increases when the methyl angle (∠HCH) opens. The present $\Delta\sigma_H$ of 4.26 ppm of methyl isocyanide fits nicely to this trend. This fact may be taken as an indication of the reliability of the value.

2. ^{13}C–^{14}N Spin–Spin Coupling Anisotropies. The anisotropy of the two ^{13}C–^{14}N spin–spin coupling tensors of methyl isocyanide was determined by allowing for the harmonic vibrational corrections and deformational corrections in the dipole–dipole couplings. Moreover, the deformational corrections to the indirect contribution D_{ij}^{ind} were taken into account by applying eq 10 with $b_{ij} = 0$. The coefficients a_{C_1N} and a_{C_2N} were used as free parameters in the least-squares fit, whereas the interaction parameters (which depend on the liquid crystal solvent) and the molecular geometry were fixed to the values derived from the geometrical analysis.[9] Thus in the joint analysis of the five experiments there were 4 parameters ($\langle\Delta J_{C_1N}\rangle$, $\langle\Delta J_{C_2N}\rangle$, a_{C_1N}, and a_{C_2N}) to be fitted for 10 D_{CN} couplings. The results are given in Table V.

Table V. Spin–Spin Coupling Anisotropies (in Hz), $\langle\Delta J_{C_1N}\rangle$ and $\langle\Delta J_{NC_2}\rangle$, of Methyl Isocyanide Determined by the Joint Analysis of the Couplings given in Table II[a]

parameter	experimental value	computed value
$\langle\Delta J_{C_1N}\rangle$	8.7 (17)	8.2,[b] 7.0[c]
$\langle\Delta J_{NC_2}\rangle$	42.8 (28)	45.8,[b] 22.9[c]
a_{C_1N}	710 (200)	
a_{NC_2}	−1740 (200)	

[a] The meaning of the coefficients a_{C_1N} and a_{NC_2} (given in Hz a J^{-1}) is described in the text. The computed values do not include vibrational contributions. [b] Calculated in this work by the REXNMR program. [c] Reference 22. These values were transformed from the reported $\Delta J_{^{15}N^{13}C}$ values by using the $\gamma(^{14}N)/\gamma(^{15}N) = -0.7129$.

In order to produce values for comparison, the ΔJ_{NC}'s were computed by the noniterative version of the programs REX[20] and REXNMR[21] using the default parameters of the programs. The results (see Table V) are in excellent agreement with the experimental ones. Nakatsuji et al.[22] have calculated for ΔJ_{C_2N} the value of 22.9 Hz which is only one-half of the present experimental and theoretical value obtained by the REX programs. On the contrary, the ΔJ_{C_1N} of Nakatsuji et al.[22] agrees with the results of the present work.

The relative values of the resulting correction parameters for D_{CN}^{ind}, $a_{C_1N}/\langle\Delta J_{C_1N}\rangle = 82$ aJ^{-1} and $a_{C_2N}/\langle\Delta J_{C_2N}\rangle = -41$ aJ^{-1}, are of the same order of magnitude as that for D_{CF}^{ind} of methyl fluoride, $a_{CF}/\langle\Delta J_{CF}\rangle = -\hat{b}_1^{CF}/3 = 21$ aJ^{-1}.[8] As noted in ref 8, the values of this magnitude are considerably larger than those of the corresponding parameters for the dipolar couplings. This suggests that there might be some additional mechanism behind eq 10, besides the perturbations of the indirect coupling tensors originating from deformations of molecular geometry. One contribution could be the direct interaction between the anisotropic forces and the molecular electron system.[3] However, this additional mechanism should result in the contributions to the couplings which are approximately similar in form to eq 10. This is evidenced by the drastic improvement of the fit when eq 10 is used; the weighted root-mean-square error of the fit drops from 0.61 to 0.12 Hz when the parameters a_{C_1N} and a_{C_2N} are introduced (b_{C_1N} and b_{C_2N} are constrained to zero in both fits).

V. Conclusions

From the present results for methyl isocyanide two main conclusions can be drawn. (a) The ENEMIX method leads to proton and carbon chemical shift anisotropies which are consistent with theoretical predictions and/or are in accord with the corresponding values experimentally derived for other methyl compounds. (b) Solvent-independent values for the indirect spin–spin coupling anisotropies can be obtained by considering deformational corrections both to direct and indirect contributions to the anisotropic couplings D_{ij}^{exp}. Further, the resulting values are in good agreement with those computed theoretically.

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Registry No. Methyl isocyanide, 593-75-9.

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