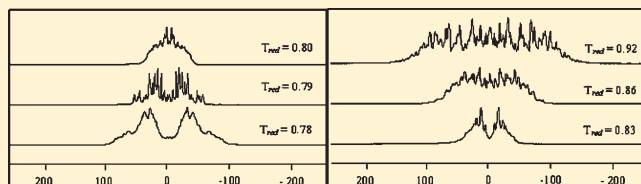


Experimental Assessment of the Vibration-Reorientation Contribution to Liquid Crystal NMR Dipolar Couplings: The Case of Tetramethylallene Dissolved in a Nematic Mesophase

Giorgio Celebre,* Giuseppina De Luca, and Maria Enrica Di Pietro

Dipartimento di Chimica, Università della Calabria, v. P. Bucci, I-87036 Rende (CS), Italy

ABSTRACT: In the present paper, the peculiar orientational behavior, studied by liquid crystal NMR (LXNMR) spectroscopy, of the D_{2d} symmetry quasi-spherical molecule of tetramethylallene (TMA) dissolved in the nematic solvent IS2 is exploited to attempt a quantitative experimental assessment of the correlation between molecular vibrations and overall rotations in weakly oriented molecules. The analysis of the very small D_{HH} and ${}^1D_{13C-H}$ dipolar couplings, available from the natural abundance LXNMR spectra of TMA at different temperatures, allows for a derivation leading (by making a few approximations) to the quantification of the vibration–reorientation (also called *nonrigid*) contribution affecting the observed direct ${}^1D_{13C-H}$ dipolar coupling. The obtained results show that, under the particular conditions of the studied system (very weak orientational ordering of a highly symmetric molecule), this contribution is particularly important, in order to reproduce the whole value of the “observed” dipolar coupling. This issue is discussed and commented on at length in the work, also, by making reference to the analogy with perfectly symmetric molecules (such as methane and analogues) dissolved in liquid crystalline phases.



1. INTRODUCTION

Since the seminal work of Saupe and Englert¹ (the 1H NMR spectrum of benzene in a nematic solution), the liquid crystal NMR spectroscopy (LXNMR) of molecules dissolved in uniaxial liquid crystalline solvents (typically nematics, but also smectic A mesophases) has been recognized as a very powerful tool to investigate molecular interactions in condensed phases. In particular, the observed dipolar couplings D_{ij}^{obs} between the i -th and j -th magnetically active nuclei present in the probe molecule potentially bring a significant amount of invaluable information. In a uniaxial anisotropic medium where the mesophase director \hat{n} aligns along the external Z -applied magnetic field (i.e., $\hat{n} \parallel Z$, as for the nematic solvent IS2 used in this work; see below), the expression giving the D_{ij}^{obs} has to be strictly written in the following way:²

$$\forall i, j, D_{ij}^{obs} = -\mu_0 \gamma_i \gamma_j \frac{\hbar}{16\pi^2} \sum_{(a,b) \in \{x,y,z\}^2} \langle s_{ab} d_{ij}^{ab} \rangle \quad (1)$$

where $\hbar = h/2\pi$ (being, of course, h the Planck's constant), γ is the nuclear magnetogyric ratio, and μ_0 is the vacuum magnetic permeability. Moreover,

$$d_{ij}^{ab} = \frac{\cos \theta_{ij}^a \cos \theta_{ij}^b}{r_{ij}^3} \quad (2)$$

with r_{ij} as the i – j internuclear distance and θ_{ij}^a as the angle between the a -axis of the molecular frame and the ij direction. Finally,

$$s_{ab} = \frac{3 \cos \omega_n^a \cos \omega_n^b - \delta_{ab}}{2} \quad (3)$$

where δ_{ab} is the Kronecker delta function and ω_n^a represents the instantaneous angle between \hat{n} and the a -axis of a Cartesian coordinate system (a, b, c) fixed on the solute molecule. The angular brackets of eq 1 denote averaging over all the relevant molecular motions, namely, the vibrational and reorientational motions (the latter are also called “overall rotations” or “molecular tumbling”) of the molecule. The calculations of the dipolar couplings are, of course, made easier by assuming the internal and reorientational motions of the molecule are independent. So, for convenience, the average of eq 1 is often “conventionally”^{3h} decoupled to give

$$\forall i, j, D_{ij}^{obs} \equiv -\mu_0 \gamma_i \gamma_j \frac{\hbar}{16\pi^2} \sum_{(a,b) \in \{x,y,z\}^2} \langle d_{ij}^{ab} \rangle_{\text{vibrations}} \langle s_{ab} \rangle_{\text{overall rotations}} \quad (4)$$

where $\langle s_{ab} \rangle_{\text{overall rotations}} = S_{ab}$ represents the familiar Saupe matrix, made up of the solute order parameters (the symbol “ \equiv ” stands for “assumed equal to”). The assumption of eq 4 would be strictly valid only in the very particular case where the ordering process is completely independent of the internal state of the molecule;^{3a,c,g} if this is not so (as in the overwhelming majority of cases), the correlation between molecular vibrations and reorientational motions should be, in principle, taken into account (for a wide selection of works treating the problem, see the long list reported in ref 3). In our opinion, a very effective way to express the approximated D_{ij}^{obs}

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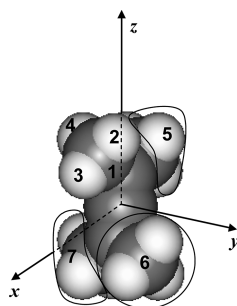


Figure 1. Structure of the D_{2d} symmetry tetramethylallene (TMA), numbering of atoms (^{13}C 1, H2, H3, and H4), groups of equivalent methyl protons (5, 6, and 7), and the molecular frame.

term is that suggested by a formulation developed in the past within a perturbation approach, taking as zero-order wave functions the products of electronic, harmonic vibrational, and rigid rotor rotational wave functions (for more theoretical details, see refs 3a–3g and 3m–3o):

$$D_{ij}^{\text{obs}} \approx D_{ij}^{\text{eq}} + D_{ij}^{\text{a}} + D_{ij}^{\text{h}} + D_{ij}^{\text{nonrigid}} \quad (5)$$

where D_{ij}^w (with $w = \text{eq, a, or h}$) represents the “equilibrium”, “anharmonic”, and “harmonic” contributions, whereas the last D_{ij}^{nonrigid} is a correction term accounting for the coupling between vibrational and reorientational motions. An important feature of eq 5 is that the first three terms all scale with the usual Saupe solute orientation parameters S_{ab} , according to the following generalized formula:

$$D_{ij}^w = -K_{ij} \sum_{a,b} S_{ab} ({}^w\Phi_{ij}^{ab}); w = \text{eq, a, h} \quad (6)$$

where, as usual, $K_{ij} = \mu_0 \gamma_i \gamma_j / (\hbar / 16\pi^2)$ and the generic ${}^w\Phi_{ij}^{ab}$ terms (whose form is dependent on the chosen model) can be, in principle, determined following the existing and widely used methods.^{2c,3b–3o,4} On the contrary, the nonrigid contribution shows a different, more complex orientational dependence of the kind $\langle s_{ab} s_{kl} \rangle_{\text{overall rotations}}$ where the k and l subscripts run over the components of some second-rank tensorial property β_{kl} of the solute molecule.^{3m} The assessment of the relative weights of the different contributions D_{ij}^w (and, in particular, of D_{ij}^{nonrigid}) in reproducing the sum D_{ij}^{obs} is a debated question.³ⁿ As a matter of fact, D_{ij}^{eq} , D_{ij}^{a} , and D_{ij}^{h} could be estimated, as said above (at least in principle), by theoretical calculations and/or experimental procedures,^{2c,3b–o,4} whereas the term D_{ij}^{nonrigid} is rather subtle and elusive and it is usually considered as an adjustable parameter^{3n,o} or its value is taken from that (calculated by least-squares fits) of similar groups in different, simpler molecules,^{3l} claiming a certain degree of transferability.^{3m} It is indeed very difficult to assess experimentally the single nonrigid contribution because, of course, only the whole sum giving the observed D_{ij}^{obs} is known from the experiment. Anyway, there are cases (in particular, when the orientational ordering of the molecule is very small and some of the other D_{ij}^w contributions can be safely neglected) where we will show it is possible to appreciate the “experimental” value of the D_{ij}^{nonrigid} term; this is the case of the quasi-spherical D_{2d} symmetry tetramethylallene molecule (TMA; see Figure 1 for structure, molecular frame, and atom numbering) dissolved in the nematic solvent IS2, whose chemical structure is reported in ref 5. Of course, the symmetry of the molecule is such that only one order parameter (namely, S_{zz}) is required to describe the orientational ordering of the solute.

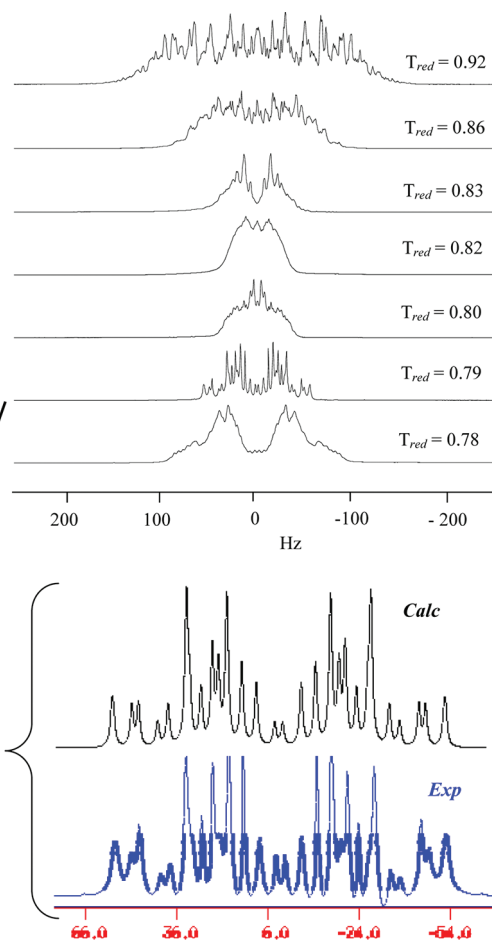


Figure 2. 500 MHz experimental ^1H spectra of TMA dissolved in IS2 at different values of T_{red} (top). The comparison between the experimental spectrum and the fitted spectrum for the best case ($T_{\text{red}} = 0.79$) is also shown. The dipolar couplings used to obtain the calculated spectrum are those reported in Table 1; moreover, only J_{25} has been set slightly different from 0 ($J_{25} = -0.2$ Hz) to reproduce some fine features of the spectrum.

2. NMR EXPERIMENTS

A dilute solution (~ 3 wt %) was prepared by dissolving the TMA (commercially available from Aldrich) in the nematic liquid crystal solvent IS2 (purchased from Merck Ltd.). The sample was heated a few times up to its nematic–isotropic transition temperature (T_{NI}); then, it was strongly shaken to give a very homogeneous solution; and finally, it was left to cool slowly in the magnetic field of the NMR spectrometer. The ^1H and ^{13}C (^1H coupled) spectra were recorded at various temperatures on a Bruker Avance 500 MHz instrument (11.74 T) within 40–50 min intervals of thermostatzation for each T value. The proton spectra were recorded upon cooling from the isotropic phase, ranging from 363 to 260 K (so covering, in practice, the whole range of the nematic phase; in terms of reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$; this corresponds to the range 0.70–0.99). In Figure 2, the experimental ^1H spectra at different values of T_{red} are shown. Unfortunately, as a result of the low ordering of the solute and the high number of lines, we were not able to obtain always “very good” spectra with well separated and sharp lines. Some spectra appear crowded with quite broad lines due to the many transitions of the twelve-spin system, so that an extremely thorough analysis is not always possible. The best case (shown at

the bottom of Figure 2) is at $T_{\text{red}} = 0.79$, where the D_{26} is zero (see below) and the proton NMR spectrum is simply described by two coupled methyl groups (i.e. it is the same six-spin system as that of acetone); this explains the relatively simple spectrum obtained. On the other hand, the quality of the spectra is good enough to appreciate the following two main features, which deserve to be immediately emphasized: (1) all the spectra are characterized by a whole spectral width of only a few tens of hertz (which is indicative, as said above, of a very weak orientational order of the molecule); (2) it is possible to observe the peculiar phenomenon that, on cooling, the spectral width initially decreases until it reaches its minimum value at $T_{\text{red}} = 0.82$ (where the narrowest spectrum is recorded), then it starts to increase again on going to lower temperatures. The just mentioned points were revealed to be crucial in this work. The second point, in particular, suggested to us intuitively the possibility that S_{zz} changes its sign along T_{red} (in this case, the molecular order parameter should cross through 0 at about $T_{\text{red}} = 0.82$, as said above). As we will explain, even though the hypothesis of the change of sign is immediate and, probably, the more physically sensible, it is not fully satisfactory because it conflicts with other reasonable considerations that can be made about our system. Thanks to the small orientational ordering of the molecule in IS2, it was possible to record also the natural abundance ^{13}C spectra. Each ^{13}C NMR spectrum, recorded averaging over 5000 free induction decays, resulted to be basically composed by the lines resulting from the C1 carbon coupled with the three equivalent protons H2, H3, and H4 (see Figure 1), so producing a quadruplet from which the D_{12} dipolar coupling constant was extracted by fixing $J_{12} = 127$ Hz (value obtained from the isotropic spectrum of TMA in CDCl_3). Unfortunately, the ^{13}C spectra showed a satisfactory signal-to-noise ratio only at the following three reduced temperatures, in common with the ^1H spectra: $T_{\text{red}} = 0.79$; $T_{\text{red}} = 0.83$; and $T_{\text{red}} = 0.86$. Nonetheless, the information from the carbon LXNMR resulted to be of fundamental importance for the whole development of this study; as a matter of fact, it is the only D_{ij}^{obs} for which the magnitude and absolute sign can be attributed unambiguously.

3. RESULTS AND DISCUSSION

The ^1H and ^{13}C (^1H coupled) NMR spectra of TMA in IS2 at different temperatures were analyzed by the homemade iterative computer program ARCAN. About the ^1H spectra, a perfect analysis was not always possible because of the already explained “physiological” low resolution of the spectra. The values reported below for the D_{ij}^{obs} are, anyway, the only ones able to reproduce, at best, our experimental spectra; as a consequence, in this work, we considered these values sufficiently reliable to carry out our study at a semiquantitative level. Moreover, only the magnitudes and relative signs of the three D_{HH} couplings can be determined from the proton spectra, whereas the magnitude and absolute sign of $^1D_{13\text{C-H}}$ (corresponding to D_{12}^{obs}) can be unequivocally assigned, as said in the previous section, from the ^{13}C spectra. The D_{12}^{obs} and the magnitude and relative signs of the remaining three D_{HH} couplings obtained from the analysis (D_{23}^{obs} , D_{25}^{obs} , and D_{26}^{obs}) are reported in Table 1. The just described limitations affecting our observed dipolar couplings hinder a possible unambiguous interpretation of the phenomena; on the contrary, they generate at least a couple of possible scenarios for the explanation of the experimental observations. Even though neither of the two scenarios is fully satisfactory in explaining all the observations, both converge in

Table 1. Observed Dipolar Couplings D_{ij}^{obs} (Hz) of TMA Dissolved in IS2^{a,b}

T/K (T_{red})	283 (0.77)	290 (0.79)	305 (0.83)	315 (0.86)
D_{12}		9.92 ± 0.10	4.82 ± 0.17	2.92 ± 0.47
D_{23}	14.87 ± 0.30	9.70 ± 0.20	9.13 ± 0.11	12.26 ± 0.20
D_{25}	-14.89 ± 0.25	-8.11 ± 0.10	-7.61 ± 0.11	-10.07 ± 0.18
D_{26}	2.61 ± 0.60	0.04 ± 0.15	2.18 ± 0.50	4.29 ± 0.60

^a About the J_{HH} indirect couplings, only J_{25} has been set slightly different from 0 ($J_{25} = -0.2$ Hz) in order to reproduce some fine features of the spectra. ^b Concerning the three D_{HH} couplings, only the magnitudes and relative signs can be obtained from the spectra (see text).

indicating that the contribution to the dipolar couplings accounting for the vibrational–reorientational correlation plays a very important role. In the following, we will try to emphasize the pros and cons of the proposed different interpretations of the experimental observations, and then, we will draw the conclusions.

As already said above, in the NMR Experiments section, our first intuition was that the three D_{HH} couplings change sign at some T_{red} between 0.79 and 0.83 as a consequence of the fact that S_{zz} crosses through 0. According to the literature, the nonrigid contribution for the “long-range” D_{26} and the anharmonic and harmonic contributions for all three interproton couplings are usually considered to be very small or even negligible^{7,4,3m} (less than 1%). Following these assumptions, we can simply write from eq 5

$$\left. \begin{aligned} D_{23}^{\text{obs}} &\approx D_{23}^{\text{eq}} + D_{23}^{\text{nonrigid}} \\ D_{25}^{\text{obs}} &\approx D_{25}^{\text{eq}} + D_{25}^{\text{nonrigid}} \\ D_{26}^{\text{obs}} &\approx D_{26}^{\text{eq}} \end{aligned} \right\} \quad (7)$$

The surviving term D_{26}^{eq} is seen to vanish at T_{red} about 0.79 (see Table 1), and this could be read as a symptom that, at that T_{red} , S_{zz} is ~ 0 . As a consequence of this, also, the contributions D_{23}^{eq} , D_{25}^{eq} , and D_{12}^{eq} should vanish at that temperature, so that, at least for the interproton couplings, the observed values of Table 1 at $T_{\text{red}} = 0.79$ should be due exclusively to the nonrigid contributions (in other words $D_{23}^{\text{obs}} \approx D_{23}^{\text{nonrigid}}$ and $D_{25}^{\text{obs}} \approx D_{25}^{\text{nonrigid}}$ at $T_{\text{red}} = 0.79$). About D_{12}^{obs} , a vibrational contribution (even though probably very small, as a result of the low order of the solute) besides the nonrigid one could be hypothesized. There are, however, a couple of considerations that bring into question this very simple, straightforward, and physically sensible interpretation (which we will call “scenario α ”) of the data. First of all, the values reported in Table 1 are, in our opinion, too large (in particular for the two interproton couplings D_{23}^{obs} and D_{25}^{obs}) to be due exclusively to the nonrigid term. This prompted us to test indirectly the influence of the nonrigid contributions on D_{23}^{obs} and D_{25}^{obs} by plotting the ratio D_{23}/D_{25} vs T_{red} . As a matter of fact, because our D_{2d} molecule requires that all except nonrigid contributions to the D_{ij} to an excellent approximation, be proportional to the sole S_{zz} order parameter, the ratios between the experimental dipolar couplings are expected to be essentially independent of T when the nonrigid contributions are negligible. The ratio D_{23}/D_{25} for the temperatures where the ^{13}C spectra are available is shown in Figure 3.

Immediately, an almost perfect T independence of the D_{23}/D_{25} ratio is observed. Of course, this result could be a coincidence; however, it might be also read as a significant clue that D_{23} and D_{25} both are devoid of nonrigid effects. In this case (because, as said above, the harmonic and anharmonic terms,

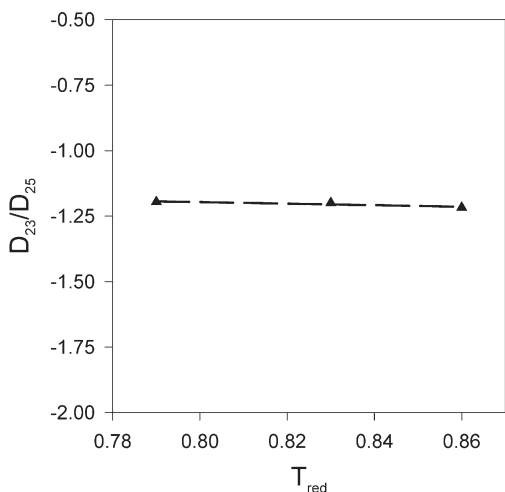


Figure 3. Ratio D_{23}/D_{25} for the temperatures where the ^{13}C NMR spectra are available.

scaling as S_{zz} , typically entail very small corrections to the already small couplings) we should reject what was said above, and on the contrary, we would be allowed to write

$$\left. \begin{aligned} D_{23}^{\text{obs}} &\approx D_{23}^{\text{eq}} \\ D_{25}^{\text{obs}} &\approx D_{25}^{\text{eq}} \end{aligned} \right\} \quad (8)$$

Another criticism, based on common physical sense and intuition, can be raised to the hypothesis α . The D_{12}^{obs} is observed to decrease as T_{red} increases, so that the decreased value of this coupling at $T_{\text{red}} = 0.83$ ($D_{12}^{\text{obs}} = 4.82$) with respect to $D_{12}^{\text{obs}} = 9.92$ at $T_{\text{red}} = 0.79$ should be due to an additional contribution opposite in sign to the nonrigid one. Now, if we reasonably admit that $D_{12}^{\text{eq}} \gg D_{12}^{\text{a}}, D_{12}^{\text{h}}$, in order to have a negative additional contribution to D_{12}^{nonrigid} at $T_{\text{red}} = 0.83$, we should have an order parameter that, from being ~ 0 at $T_{\text{red}} = 0.79$, becomes positive at $T_{\text{red}} = 0.83$ (this is because D_{12}^{eq} is negative when S_{zz} is positive). This is in principle possible, of course, but if we consider this situation within our scenario α , where S_{zz} changes its sign crossing through 0 at $T_{\text{red}} \approx 0.79$, this means that the order parameter is negative at temperatures lower than $T_{\text{red}} = 0.79$ and becomes positive for higher temperatures. This result is, in our opinion, quite counterintuitive, because the solute seems to prefer the parallel alignment for higher temperatures (where the orientational thermal disorder is higher) whereas it “opts” for the more hampered perpendicular orientation when the temperature is lower and the thermal disorder is less important. If we invert the sequence of the signs of S_{zz} , assuming the more reasonable one (positive for $T_{\text{red}} < 0.79$, 0 for $T_{\text{red}} = 0.79$, and negative for $T_{\text{red}} > 0.79$), the behavior of D_{12} vs T_{red} becomes inexplicable, because after $T_{\text{red}} = 0.79$ the significant additional term to D_{12}^{nonrigid} (i.e., D_{12}^{eq}) is positive, so that an increase of D_{12} with the increase in temperature should be expected, contrary to what we observe. In the light of the arguments expounded above, the scenario α (i.e., the immediate and intuitive qualitative explanation that the observed phenomenon is due to the change of sign of the order parameter) is, in our opinion, not completely satisfactory because it conflicts with the reasonable considerations carried out above about our system. If the change of sign of S_{zz} does not occur, the order parameter has to be necessarily negative (as a result of the D_{12} couplings trend), and the dipolar

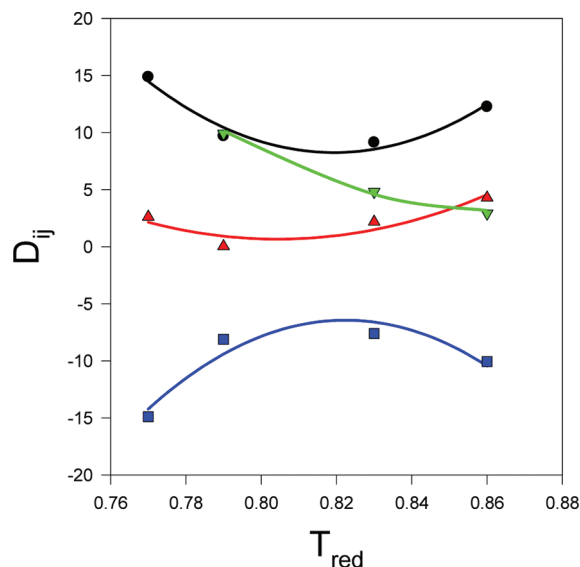


Figure 4. Behaviors of interproton dipolar couplings (D_{23} , black circle; D_{26} , red triangle; and D_{25} , blue square) and of the ^{13}C –H coupling (D_{12} , green inverted triangle) as a function of T_{red} when $S_{zz} < 0$ is assumed (see text for explanation). The local quadratic fittings of the curves are drawn just as eye-guides.

couplings pass through a minimum (maximum) when S_{zz} reaches its smallest possible magnitude (see Figure 4). This originates another possible scenario (called β), which is undoubtedly less intuitive. Looking at Figure 4, it is immediately realized that the three interproton dipolar couplings share their minimum magnitude at the same $(T_{\text{red}})_{\text{min}}$ of about 0.82 (that is, of course, exactly the temperature where the experimental ^1H – ^{13}C NMR spectra show their narrowest whole spectral width); on the contrary, the extrapolated minimum of the ^{13}C –H dipolar coupling D_{12} falls at $T_{\text{red}} > 0.86$. Now, keeping the approximation of neglecting the vibrational contributions and accepting eq 8, as suggested by Figure 3, we are allowed to write $D_{23}^{\text{obs}} \approx D_{23}^{\text{eq}}$; $D_{25}^{\text{obs}} \approx D_{25}^{\text{eq}}$; and $D_{26}^{\text{obs}} \approx D_{26}^{\text{eq}}$. Following this assumption, it is very simple, by adopting standard regular geometries for the molecule,⁸ to calculate the values of S_{zz} (reported in Table 2 and shown in Figure 5) from the interproton dipolar couplings D_{23} and D_{25} at the different temperatures.

Note that the observed D_{26} couplings have been excluded in this case from the calculation of the order parameter because they are too small and affected by large relative errors. If we include it, the results concerning S_{zz} are in practice the same (even though affected by quite high relative errors) but the D_{26} observed values at the different temperatures are very badly reproduced.

In Figure 5, it is evident, as expected, that the minimum of magnitude of the S_{zz} order parameter falls at $(T_{\text{red}})_{\text{min}} = 0.82$, the temperature where the interproton dipolar couplings are simultaneously the smallest ones in magnitude and the proton LXNMR spectra are, of course, the narrowest ones (see Figure 2). At this point, we tried to evaluate quantitatively the different contributions playing a role in the remaining ^{13}C –H coupling D_{12}^{obs} . From eq 5, we can write

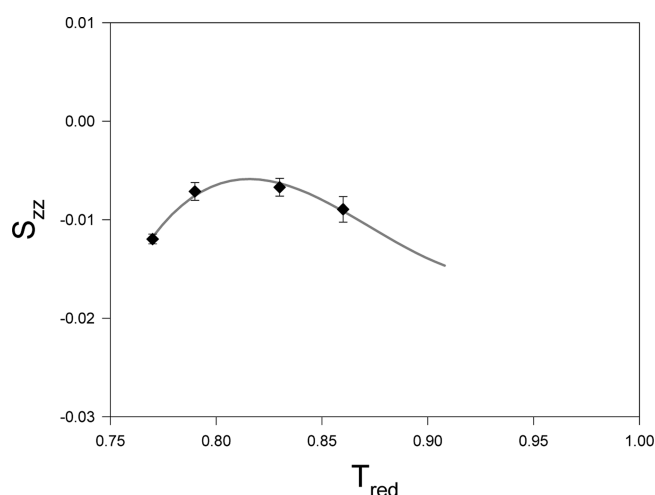
$$\Delta_{12} \equiv (D_{12}^{\text{obs}} - D_{12}^{\text{eq}}) \approx (D_{12}^{\text{a}} + D_{12}^{\text{h}} + D_{12}^{\text{nonrigid}}) \quad (9)$$

where the D_{12}^{eq} are calculated by using the S_{zz} values of Table 2. In Table 3, the so obtained D_{12}^{eq} and Δ_{12} are reported.

Table 2. Values of the S_{zz} Order Parameter of TMA Dissolved in I52 at Different Temperatures^a

T/K (T_{red})	283 (0.77)	290 (0.79)	305 (0.83)	315 (0.86)
$D_{23}(\text{calcd})$	14.29	8.52	8.01	10.68
$D_{25}(\text{calcd})$	−15.42	−9.20	−8.65	−11.53
rms	0.55	1.13	1.08	1.52
S_{zz}	$−0.0119 \pm 0.0005$	$−0.007 \pm 0.0009$	$−0.007 \pm 0.0009$	$−0.009 \pm 0.0013$

^a Obtained from the interproton dipolar couplings D_{23} and D_{25} (see text for more explanations). Moreover, the root mean square (rms) between observed and calculated dipolar couplings is also reported (the relative errors affecting the obtained S_{zz} values have been estimated to be proportional, on average, to the ratio between the rms and the calculated D_{ij} at the different temperatures).

**Figure 5.** Behavior of the S_{zz} order parameter vs T_{red} . The cubic fitting of the curve is also shown in gray.**Table 3.** Values of D_{12}^{eq} and Δ_{12} ^a

T/K (T_{red})	290 (0.79)	305 (0.83)	315 (0.86)
D_{12}^{eq}	6.36 ± 0.25	5.98 ± 0.48	7.97 ± 1.11
Δ_{12}	3.56 ± 0.35	$−1.16 \pm 0.68$	$−5.05 \pm 1.58$

^a See eq 9. Obtained by using the S_{zz} values of Table 2. The errors affecting the D_{12}^{eq} values have been estimated, by error propagation, from the corresponding errors on the order parameter (see Table 2).

By following eq 6, the sum of the harmonic and anharmonic contributions can be collected as

$$(D_{12}^a + D_{12}^h) = -S_{zz}\Gamma_{12} \quad (10)$$

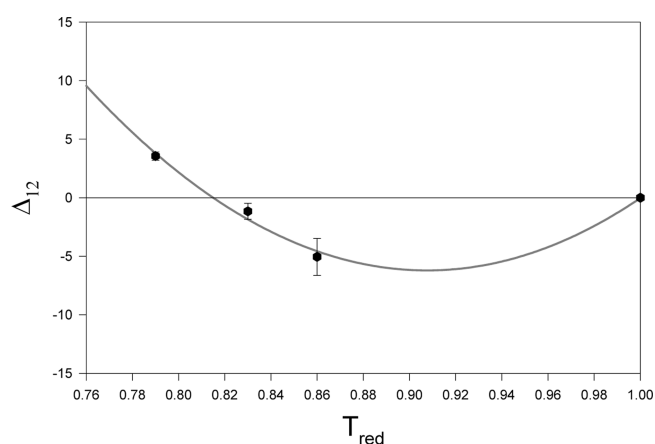
where

$$\Gamma_{12} = [K_{12}(^a\Phi_{12}^{zz} + ^h\Phi_{12}^{zz})] \quad (11)$$

so that eq 9 becomes

$$\Delta_{12} \approx -S_{zz}\Gamma_{12} + D_{12}^{\text{nonrigid}} \quad (12)$$

Because S_{zz} vs T_{red} is known from the interproton dipolar couplings (its behavior has been extrapolated to the whole range of T_{red} by a cubic fitting, as shown in Figure 5), if we are able to determine the Γ_{12} term of eq 11, we have all the ingredients to quantitatively assess (of course within the approximations used in the derivation) the D_{12}^{nonrigid} contribution from eq 12. To evaluate Γ_{12} without force fields and theoretical calculations about harmonic and anharmonic vibrational corrections affecting

**Figure 6.** Behavior of the Δ_{12} values of Table 3 vs T_{red} . The quadratic fitting of the curve is also shown in gray (the value $\Delta_{12} = 0$ at $T_{red} = 1$ has been added as a boundary condition).

D_{12} , it can be useful to plot the different Δ_{12} (Table 3) as a function of T_{red} (Figure 6).

We observe that Δ_{12} crosses through 0, changing its sign, exactly at $T_{red} = 0.82$, which, as we already said, is the $(T_{red})_{min}$ of the three interproton dipolar couplings (see Figure 4). We do not know if this is a coincidence or not (this is an interesting point, deserving additional investigations, but it is, at the moment, out of the scope of the work; further studies are planned to shed more light on this observation); however, we can exploit this fact to proceed with our derivation. Because when $\Delta_{12} = 0$ then $D_{12}^{\text{obs}} = D_{12}^{\text{eq}}$, this result seems to suggest, intriguingly, that at least at $T_{red} = 0.82$, only the equilibrium contributions survive for all the dipolar couplings, including D_{12} . Of course, this can occur when the single D_{12}^a , D_{12}^h , and D_{12}^{nonrigid} are negligibly small (as it is, according to our crude assumptions, for interproton couplings in the whole temperature range), or as we suspect, it is the case for the $^{13}\text{C}-\text{H}$ coupling D_{12} , when there is a particular temperature (in this case, exactly $T_{red} = 0.82$), where (possibly by chance) a perfect balance of the effects exists, such that from eq 12

$$(D_{12}^{\text{nonrigid}})_{T_{red}=0.82} = \Gamma_{12}(S_{zz})_{T_{red}=0.82} \quad (13)$$

Coming back to our first aim of determining Γ_{12} in order to calculate D_{12}^{nonrigid} , we cannot directly exploit eq 13 for this purpose, because the nonrigid contribution itself is involved. On the other hand, if we consider Γ_{12} to be independent of T_{red} (which is a reasonable approximation), we can exploit the fact that the function $\Delta_{12}(T_{red})$ reaches its minimum at $T_{red} = 0.91$ (see Figure 6); so, its derivative calculated there has to vanish. In light of

what was said above, from eq 12, the following relation holds:

$$\left(\frac{\partial \Delta_{12}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} = -\Gamma_{12} \left(\frac{\partial S_{zz}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} + \left(\frac{\partial D_{12}^{\text{nonrigid}}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} = 0 \quad (14)$$

so that Γ_{12} is given by

$$\Gamma_{12} = \left(\frac{\partial D_{12}^{\text{nonrigid}}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} / \left(\frac{\partial S_{zz}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} \quad (15)$$

By introducing eq 15 in eq 12 we obtain the following explicit general equation giving the D_{12}^{nonrigid} contribution as a function of T_{red} (in other words, the magnitude of the vibrational–reorientational correlation at a chosen T_{red}):

$$D_{12}^{\text{nonrigid}}(T_{\text{red}}) \approx \Delta_{12}(T_{\text{red}}) + S_{zz}(T_{\text{red}})\Gamma_{12} \\ = \Delta_{12}(T_{\text{red}}) + S_{zz}(T_{\text{red}})\left(\frac{B}{A}\right) \quad (16)$$

where $A = \partial S_{zz}/(\partial T_{\text{red}})_{T_{\text{red}}=0.91}$ and $B = \partial D_{12}^{\text{nonrigid}}/(\partial T_{\text{red}})_{T_{\text{red}}=0.91}$. Of course, in order to use eq 16, we should be able to evaluate the terms A and B . The term A can be easily calculated by the cubic fitting

$$S_{zz}(T_{\text{red}}) = -8.5765 \\ + 29.702T_{\text{red}} - 34.1819(T_{\text{red}})^2 \\ + 13.0565(T_{\text{red}})^3 \quad (17)$$

shown in gray in Figure 5. As a consequence, we have

$$A = \left(\frac{\partial S_{zz}}{\partial T_{\text{red}}}\right)_{T_{\text{red}}=0.91} \\ = 29.7020 - 68.3638(0.91) + 39.1695(0.91)^2 \\ = -0.0728 \quad (18)$$

The calculation of the term B is a little bit more complicated. Assuming B is constant within a very narrow range of T_{red} in the proximity of the minimum of Δ_{12} ($T_{\text{red}} = 0.91$), we will consider the following limit expressions:

$$D_{12}^{\text{nonrigid}}(T_{\text{red}} = 0.91) \approx \Delta_{12}(0.91) + S_{zz}(0.91)\left(\frac{B}{A}\right) \quad (19a)$$

$$\lim_{T_{\text{red}} \rightarrow 0.91^+} D_{12}^{\text{nonrigid}}(T_{\text{red}}) \equiv D_{12}^{\text{nonrigid}}(0.91) \quad (19b)$$

$$\lim_{T_{\text{red}} \rightarrow 0.91^-} D_{12}^{\text{nonrigid}}(T_{\text{red}}) \equiv D_{12}^{\text{nonrigid}}(0.91) \quad (19c)$$

The limits reported above for eqs 19b and 19c (approaching 0.91 from the left and right but, of course, never reaching exactly 0.91) have been calculated numerically from eq 16, by exploiting eq 17 for the evaluation of the function $S_{zz}(T_{\text{red}})$ and the following quadratic (eq 20):

$$\Delta_{12}(T_{\text{red}}) = 590.0644 - 1313.9702T_{\text{red}} \\ + 723.8776(T_{\text{red}})^2 \quad (20)$$

Table 4. Values of the D_{12}^{nonrigid} Contributions Referred to the Temperatures Where Observed Data D_{12}^{obs} are Available^a

T/K (T_{red})	290 (0.79)	305 (0.83)	315 (0.86)
D_{12}^{nonrigid}	3.44 ± 0.39	-2.15 ± 0.72	-5.00 ± 1.64

^a The errors affecting the values have been estimated by error propagation, starting from those affecting the Δ_{12} and the order parameters (of course, the errors, even though quite large, cannot quantify the degree of approximation used in the derivation).

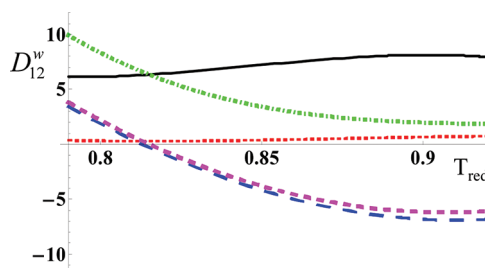


Figure 7. Different D_{12} contributions as a function of T_{red} : D_{12}^{nonrigid} (blue large-dashed line); $D_{12}^a + D_{12}^h$ (red dotted line); and D_{12}^{eq} (black solid line). For comparison, $D_{12}^{\text{obs}} = D_{12}^{\text{eq}} + D_{12}^a + D_{12}^h + D_{12}^{\text{nonrigid}}$ (green dotted-dashed line) and $\Delta_{12} \equiv D_{12}^{\text{obs}} - D_{12}^{\text{eq}} = D_{12}^a + D_{12}^h + D_{12}^{\text{nonrigid}}$ (pink small-dashed line) have been plotted. It is worthwhile to remember that the large errors affecting the curves are not shown in the figure.

(shown in gray in Figure 6) for the evaluation of the function $\Delta_{12}(T_{\text{red}})$. By using the A value of eq 18, we verified that eqs 19b and 19c converge to eq 19a for $B = \partial D_{12}^{\text{nonrigid}}/(\partial T_{\text{red}})_{T_{\text{red}}=0.91} = -3.487$. Finally, by introducing the A and B values in eq 16 we obtain

$$D_{12}^{\text{nonrigid}}(T_{\text{red}}) \approx \Delta_{12}(T_{\text{red}}) + 47.9S_{zz}(T_{\text{red}}) \quad (21)$$

By calculating the nonrigid contributions for D_{12}^{obs} at the three experimental temperatures, we obtained the following results (reported in Table 4). Of course, knowing D_{12}^{nonrigid} , D_{12}^{eq} , and D_{12}^{obs} as functions of T_{red} , we can also obtain, by difference, the contribution $(D_{12}^a + D_{12}^h)$ vs T_{red} . It is interesting to observe the behavior of the different contributions plotted in Figure 7, even though it is worthwhile to emphasize that the information emerging from the figure should be considered just at a semiquantitative level (as a matter of fact, the figure could be rather deceptive because the large errors affecting the curves are not explicitly shown).

At a first glance, it is manifest that, in our just described scenario β , the nonrigid contribution (blue large-dashed line) basically represents the whole Δ_{12} (pink small-dashed line). In other words, the difference between “observed” and “equilibrium” dipolar coupling terms seems to be essentially due to the reorientational–vibration correlation, whereas, on the contrary, the sum of the harmonic and anharmonic contributions (red dotted line) plays a very minor role. This predominance is reasonably due to the fact that our solute is a very symmetric and quasi-spherical molecule, so that a very low orientational ordering (linearly affecting D_{12}^a and D_{12}^h) has to be expected. It is interesting at this point to emphasize that, from both our α and β descriptions, a kind of “methane-like” behavior can probably be invoked for our solute. In other words, we could be in the presence of a phenomenon similar to that observed for methane^{9a–e,3b,d,e,g,k} and other very symmetric (about spherical)

molecules^{9c,f-i} dissolved in uniaxial orienting mesophases, where the dipolar couplings should vanish because of the high molecular symmetry. On the contrary, non-null (even though very small) dipolar couplings are observed. The origin of the phenomenon cannot lie on the orientational order parameters that, as said above, are predicted to be null as a result of the structural symmetry of the undistorted molecule. On the other hand, structural deformations of the solute exerted by the liquid crystal medium, representing the first “historical” explanations of the phenomenon,^{9f-h,2} have been subsequently discarded and finally basically rejected (even though this hypothesis has been aired again¹⁰). At present, the more reliable explanation for the existence of dipolar couplings seems to consist in the correlation between molecular vibrations and overall reorientational rotations (the so-called “tumbling”) of the solute.^{3mj} As said above, we suspect we are in a similar situation (as a matter of fact, the D_{12}^{obs} value is very low, much smaller than the J_{12} indirect coupling), so that the behavior of TMA in IS2 can be probably associated with that of methane and similar molecules in nematic solutions. Of course, we cannot exclude that our results and conclusions are biased by the imperfect reliability of our observed dipolar couplings and/or by the adopted assumptions and approximations. In particular, the β explanation describes a situation where the order parameter would have a minimum of magnitude at $(T_{\text{red}})_{\text{min}} = 0.82$, and no intuitive reasons why this would occur are immediately available (possible suggestions include competition between opposite ordering/disordering mechanisms and collective phase order effects due to the TMA doping). At the same time, we are quite convinced that the significant values of D_{12}^{nonrigid} , predicted by both α and β scenarios, are physically sensible, thus representing a very important contribution to the experimental D_{12}^{obs} .

4. CONCLUSIONS

The intriguing behavior of the very weak orientational ordering of TMA in IS2, studied by LXNMR spectroscopy at different T_{red} values, allowed for a quantitative assessment, within a certain number of approximations, of the nonrigid contribution (as a result of the reorientational–vibrational correlation) affecting the observed direct $^1\text{D}_{13\text{C-H}}$ dipolar coupling. Two possible scenarios (α and β) for the interpretation of the observations have been presented and discussed with their pros and cons. In any case, the obtained issue is that the reorientational–vibrational interaction represents a fundamental contribution to the value of the observed experimental dipolar coupling. This result recalls the importance of the nonrigid contributions shown in the past for perfectly symmetric molecules (such as methane and analogues) dissolved in liquid crystalline phases. Obviously, this result lends itself to a series of considerations about the reliability of the derivation and, of course, of the consequent outcome. Anyway, apart from the more or less important consequences of the approximations (discussed at length in the Results and Discussion section), we think that our final results are to be considered quite plausible in indicating the magnitude of the D_{12}^{nonrigid} term. Important points remain to be explained about both α and β , namely, the reasons and the mechanisms of the unexpected and intriguing behavior of the whole spectral width vs T , clearly shown in Figure 2 and, as a consequence, the possibility to decide unambiguously between α and β (or other possible solutions we were unable to see). Anyway, this is another story; the mentioned problems will be addressed in our future works in addition to trying to obtain more reliable dipolar couplings from a more careful spectral analysis (which probably

needs to be performed by fitting to the overall line shape and not only to peak frequencies).

AUTHOR INFORMATION

Corresponding Author

*E-mail: giorgio.celebre@unical.it. Phone: +39-0984493321. Fax: +39-0984493301.

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