

# Obtaining the structure and bond rotational potential of a substituted ethane by NMR spectroscopy of solutions in nematic liquid-crystalline solvents

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(Received 3 August 2005; accepted 21 September 2005; published online 16 November 2005)

Partially averaged dipolar couplings (also referred to as residual dipolar couplings)  $D_{ij}$  can be obtained from the analysis of the NMR spectra of molecules dissolved in liquid-crystalline solvents. Their values for a nonrigid molecule depend upon the bond lengths and angles, the rotational potentials, and the orientational order of the molecules. The molecule studied, 1-chloro-2-bromoethane, is one of the simplest example of a substituted alkane in which the rotational potential has three minimum-energy positions, *trans* and *gauche*± conformations, and the present investigation explores the problems inherent in deriving the form of the potential and the molecular geometry from the set of partially averaged couplings between the protons, and between protons and <sup>13</sup>C nuclei. The geometrical parameters and the rotational potential obtained are compared with the results from a density-functional theory method. © 2005 American Institute of Physics. [DOI: 10.1063/1.2121628]

## I. INTRODUCTION

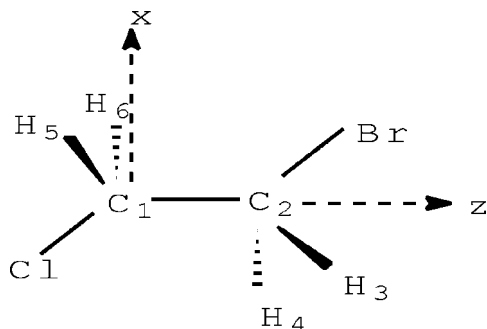
The NMR spectra of liquid-crystalline samples depend upon partially averaged dipolar couplings  $D_{ij}$  between nuclei. The averaging is over the motion of the whole molecule relative to the liquid-crystalline director, involving the polar angles  $\beta$  and  $\gamma$  and also over any internal modes of motion, involving a set of bond rotational angles  $\phi_i$ . Thus, the observed couplings  $D_{ij}(\text{obs})$  are related to the coupling  $D_{ij}(\beta, \gamma, \phi_i)$  when the molecule is in a fixed orientation and conformation by

$$D_{ij}(\text{obs}) = \int D_{ij}(\beta, \gamma, \phi_i) P_{\text{LC}}(\beta, \gamma, \phi_i) \sin \beta d\beta d\gamma d\phi_i, \quad (1)$$

where  $P_{\text{LC}}(\beta, \gamma, \phi_i)$  is the probability that the molecule is in this orientation and conformation. In principle, therefore the set of  $D_{ij}(\text{obs})$  obtained for the interacting nuclei for a molecule can be used to investigate both these kinds of motion and the structure of the molecule for each conformer. The earliest studies of the NMR spectra of molecules in liquid-crystalline phases included examples of flexible molecules,<sup>1</sup>

such as substituted ethanes, but at first it was not appreciated that the averaging of the  $D_{ij}(\beta, \gamma, \phi_i)$  over  $\beta$  and  $\gamma$  is not independent of the averaging over the set  $\phi_i$ . The recognition<sup>2</sup> of the interdependence of whole molecule and internal motion then led to the development of methods of allowing for the more complex nature of the averaging of the dipolar couplings, and of any other physical observables,<sup>3-5</sup> and to their application to both the quite complex structures of mesogenic molecules,<sup>4</sup> and to simpler molecules with just one or two bond rotational motions.<sup>6,7</sup> For molecules with just a single bond rotational motion it should be possible to test models for the bond rotation potential, and a classic case is a molecule such as biphenyl.<sup>8,9</sup> In this case there are a sufficient number of interproton dipolar couplings obtained from an analysis of the proton spectrum of a sample dissolved in a liquid-crystalline solvent to establish the relative positions of the protons within each ring, the separation of the two rings, and test models for the interring rotation potential. There have been a number of such studies on similar molecules to biphenyl, but the same is not the case for simple, substituted ethanes  $X\text{CH}_2\text{CH}_2\text{Y}$ . The reason for this neglect is that now the proton spectrum does not yield a sufficient number of dipolar couplings to establish both the

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FIG. 1. 1-chloro-2-bromoethane in the *trans* conformation.

structures of the rigid molecular fragments  $\text{CH}_2\text{X}$  and  $\text{CH}_2\text{Y}$ , and to test models for the C–C bond rotation potential. Thus, the proton spectrum of a sample of 1-chloro-2-bromoethane,  $\text{ClCH}_2\text{CH}_2\text{Br}$  dissolved in a liquid-crystalline solvent, the representative molecule chosen for the present study, whose structure and atomic labeling is shown in Fig. 1, yields only four  $^1\text{H}$ – $^1\text{H}$  dipolar couplings, which is insufficient to determine the relative positions of the protons, establish the orientational order, and investigate the nature of the conformational distribution  $P_{\text{LC}}(\phi)$ , where

$$P_{\text{LC}}(\phi) = \int P_{\text{LC}}(\beta, \gamma, \phi) \sin \beta d\beta d\gamma. \quad (2)$$

The data set can be increased by recording and analyzing the two  $^{13}\text{C}$  proton satellite spectra. This yields a total of eight dipolar couplings, which is now sufficient to investigate in some detail, albeit not complete, the structure, the form of  $P_{\text{LC}}(\phi)$ , and the orientational order. Two problems remain. First, to obtain a precise structure of a molecule using partially averaged dipolar couplings it is necessary to correct for the averaging over small-amplitude vibrational motion. Thus, the dipolar couplings  $D_{ij}(\text{obs})$  obtained from the spectrum analyses are related to  $D_{ij}(\text{equil})$ , the coupling for the molecule in a fixed, equilibrium structure, and  $D_{ij}(\text{vib})$ , a correction for small-amplitude vibrational motion:

$$D_{ij}(\text{obs}) = D_{ij}(\text{equil}) + D_{ij}(\text{vib}). \quad (3)$$

To calculate the values of  $D_{ij}(\text{vib})$  it is necessary to know the force field which determines the frequencies and amplitudes of vibrational motion. The force field may be derived in principle from experimental data, if the molecule is “rigid,” that is in the absence of bond rotational motion. When bond rotation is present the experimental approach in determining a force field is not usually a viable option, and an alternative is to calculate the vibrational frequencies and amplitudes by an *ab initio* molecular orbital, or a density-functional method. The theoretical approach to vibrational averaging of dipolar couplings has been applied recently to small molecules with single bond rotations such as styrene<sup>10</sup> and acrolein,<sup>11</sup> with very encouraging results, and at the very least gives a good estimate of the effects of vibrational averaging on the derived structural parameters and on the form obtained for  $P_{\text{LC}}(\phi)$ .

The second general problem is how to optimize the form of  $P_{\text{LC}}(\phi)$ ? This has usually been attempted by expressing  $P_{\text{LC}}(\beta, \gamma, \phi)$  in terms of  $U_{\text{LC}}(\beta, \gamma, \phi)$ , a mean potential:<sup>7</sup>

$$P_{\text{LC}}(\beta, \gamma, \phi) = Q_{\text{LC}}^{-1} \exp[-U_{\text{LC}}(\beta, \gamma, \phi)/k_B T], \quad (4)$$

where

$$Q_{\text{LC}} = \int \exp[-U_{\text{LC}}(\beta, \gamma, \phi)/k_B T] \sin \beta d\beta d\gamma d\phi. \quad (5)$$

The total mean potential is then divided into  $U_{\text{ext}}(\beta, \gamma, \phi)$ , a completely anisotropic mean potential (a “potential of mean torque”), and  $U_{\text{iso}}(\phi)$ , an isotropic part as

$$U_{\text{LC}}(\beta, \gamma, \phi) = U_{\text{ext}}(\beta, \gamma, \phi) + U_{\text{iso}}(\phi).$$

One advantage of this division is that  $U_{\text{iso}}(\phi)$  can be identified with a bond rotation potential  $V(\phi)$ , which serves to define a conformational distribution  $P_{\text{iso}}(\phi)$ :

$$P_{\text{iso}}(\phi) = Q_{\text{iso}}^{-1} \exp[-V(\phi)/k_B T], \quad (6)$$

with

$$Q_{\text{iso}} = \int \exp[-V(\phi)/k_B T] d\phi. \quad (7)$$

Note that in general  $P_{\text{iso}}(\phi) \neq P_{\text{LC}}(\phi)$ .<sup>3</sup>

It is also usual for each bond rotation to expand  $V(\phi)$  as a Fourier series which is truncated at the minimum number of terms which gives the correct periodicity of the potential. For rotation about the C–C bond in an achiral ethane the simplest form is

$$V(\phi) = V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi. \quad (8)$$

The coefficients  $V_n$  can be estimated by calculating the potential energy as a function of  $\phi$  by quantum chemistry methods, and this will be illustrated here by using a density-functional method. Calculating dipolar couplings  $D_{ij}(\text{equil})$  using a rotational potential of this form, comparing with vibrationally corrected couplings  $D_{ij}(\text{corr}) = D_{ij}(\text{obs}) - D_{ij}(\text{vib})$ , and then varying the values of  $V_n$  so as to minimize an error function

$$R = \sum_{i < j} [D_{ij}(\text{corr}) - D_{ij}(\text{calc})]^2 / N \quad (9)$$

is not, however, a viable procedure, because the positions and energies of the three local minima of  $V(\phi)$  are not related to the  $V_n$  in a simple way. To overcome this problem an alternative method for determining  $P_{\text{LC}}(\phi)$  and  $P_{\text{iso}}(\phi)$  has been introduced<sup>12</sup> which expands the probability as a sum of Gaussian functions of amplitude  $A_n$ , position  $m_n$ , and width  $h_n$ . For a 1,2-substituted ethane the specific form is then

$$P_{\text{iso}}(\phi) = \frac{A}{(2\pi h_t^2)^{1/2}} \exp\left[-\frac{(\phi - 180^\circ)^2}{2h_t^2}\right] + \frac{(1/2)(1-A)}{(2\pi h_g^2)^{1/2}} \left\{ \exp\left[-\frac{(\phi - 180^\circ + m_g)^2}{2h_g^2}\right] + \exp\left[-\frac{(\phi - 180^\circ - m_g)^2}{2h_g^2}\right] \right\}, \quad (10)$$

which corresponds to three Gaussian functions centered on  $180^\circ$  and  $180^\circ \pm m_g$ , with widths at half maximum height  $h_t$  and  $h_g$ , with  $A$  being the area under the Gaussian centered at  $180^\circ$ : the *trans* position. The advantage of using Gaussian

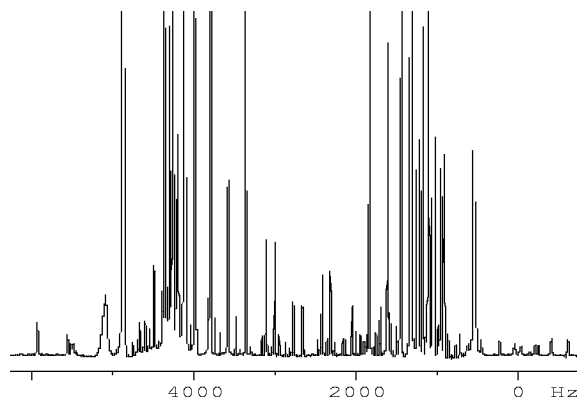


FIG. 2. 600 MHz  $^1\text{H}$  spectrum of 1-chloro-2-bromoethane dissolved in the nematic solvent ZLI 1132 at 300 K. The spectrum has been expanded vertically, which truncates the intensities of the strong lines from the all- $^{12}\text{C}$  isotopomer, but reveals the weak lines from the two singly labelled  $^{13}\text{C}$  isotopomers.

functions is that the relative amounts of *trans* and *gauche* forms can be varied independently of either the positions  $m_i$  of the conformers or the widths  $h_i$  of the Gaussian functions.

The compound chosen for study here has just a single bond rotation, and the potential can be represented by a continuous function,  $V(\phi)$  [or equivalently  $P_{\text{iso}}(\phi)$ ], which can be sampled at small increments  $\Delta\phi$ . The molecule is also small enough that density-functional theory (DFT) calculations can be performed, with full geometry optimization at each interval in  $\phi$ , with modest computing power. The calculations are necessary in order to obtain vibrational force fields at each of the three minimum-energy positions with which to perform vibrational corrections to the observed dipolar couplings. The DFT method B3LYP is known to produce good theoretical estimates of force fields.<sup>13</sup> For longer chain alkane derivatives, such a detailed treatment becomes impracticable with present day computational power, so that vibrational averaging has to be neglected. Moreover, sampling multiple bond rotations at small angular intervals become impractical and more simplified models for  $P_{\text{iso}}(\phi_i)$  have to be used, such as the rotational isomeric state (RIS) in which  $P_{\text{iso}}(\phi_i)$  is sampled for each bond rotation at just the three minima, that is at  $\phi_{\text{trans}}$  and  $\phi_{\text{gauche}\pm}$ . It is of interest therefore to apply this simplified model to the data for 1-chloro-2-bromoethane so as to assess the effects of making these approximations.

The bond lengths, bond angles, and  $V(\phi)$  for 1-chloro-2-bromoethane have not been obtained previously by any other measurement technique, which makes it difficult to judge the precision of the results that we report here for the molecule in a particular liquid-crystalline solution. The best that can be done is to compare with the results of the density-functional calculation, bearing in mind that this refers to an isolated molecule.

## II. EXPERIMENT

The sample of 1-chloro-2-bromoethane was purchased from Sigma-Aldrich. A solution approximately 10% by weight was prepared in the nematic liquid-crystalline solvent ZLI 1132, which was obtained from Merck Ltd. The sample

TABLE I. Dipolar couplings  $D_{ij}$  in Hertz and chemical shifts  $\delta_{ij} = \delta_i - \delta_j$  in ppm, obtained for a sample of 1-chloro-2-bromoethane dissolved in the nematic solvent ZLI 1132. The chemical shifts and scalar couplings,  $J_{ij}$  in Hertz, obtained from samples dissolved in chloroform are also given.

	No $^{13}\text{C}$	$^{13}\text{C}$ on $\text{C}_1$	$^{13}\text{C}$ on $\text{C}_2$
$D_{13}=D_{14}$		82.0±1.3	
$D_{15}=D_{16}$		1118.1±0.3	
$D_{23}=D_{24}$			1179.6±0.8
$D_{25}=D_{26}$			75.0±1.1
$D_{34}$	1064.3±1.1	1063.5±0.7	1064.6±0.8
$D_{35}=D_{46}$	211.3±0.6	208.6±0.8	210.0±0.5
$D_{36}=D_{45}$	183.1±0.7	182.2±0.9	182.4±0.4
$D_{56}$	1032.2±1.0	1032.5±1.1	1032.2±0.2
$\delta_{35}$	-0.186±0.002	-0.183±0.003	-0.187±0.002
$\delta_{12}$		11.58±0.01	
Chloroform solution			
$J_{15}$	153.8±0.1		
$J_{13}$	-3.1±0.1		
$J_{23}$	155.1±0.1		
$J_{25}$	-3.7±0.1		
$J_{34}$	-8.5±0.1		
$J_{35}$	5.9±0.1		
$J_{36}$	9.7±0.1		
$J_{56}$	-9.5±0.1		

was contained in a normal, 5-mm-o.d. sample tube, and the proton spectrum shown in Fig. 2 recorded at 600 MHz at 300 K. The spectra in Fig. 2 were analyzed to obtain a full set of dipolar couplings between the interacting nuclei for the two isotopomers containing a single  $^{13}\text{C}$  nucleus. To do this it is necessary, in general, to determine also the scalar couplings since these affect the line positions in the spectra from the liquid-crystalline solutions. In favorable cases the  $J_{ij}$  and  $D_{ij}$  are both obtained as independent parameters by analyzing the oriented molecule spectrum, but this is not true, in particular, for the couplings involving  $^{13}\text{C}$  nuclei. The magnitudes of the  $^nJ_{\text{CH}}$  were obtained from the spectrum of a sample dissolved in  $\text{CDCl}_3$ , and their signs from theoretical predictions, combined with a comparison with previous experimental investigations. These were used as fixed parameters in the analysis of the 600 MHz proton spectrum.

The four protons form an AA'BB' spin system, with sufficient lines resolved to determine all the interproton dipolar couplings. Analysis of the spectra from the single  $^{13}\text{C}$  isotopomers requires the identification of the weak lines from the 1% of  $^{13}\text{C}$ -containing molecules, and this was facilitated by separating these from the lines from the all- $^{12}\text{C}$  isotopomer by a two-dimensional (2D) heteronuclear single quantum correlation (HSQC) experiment, as described in detail previously.<sup>14</sup>

The satellite spectra were analyzed with the aid of the iterative computer program ARCANA which has the capability of displaying the calculated spectra from the three iso-

protons with the correct relative intensities: one from the four protons in the all- $^{12}\text{C}$  isotopomer, and one each from the  $^{13}\text{C}_1$  and  $^{13}\text{C}_2$  isotopomers.<sup>15</sup> Each of the three spectra was analyzed separately. The results are given in Table I.

The HSQC spectrum correlates the  $^1\text{H}$  to the  $^{13}\text{C}$  resonances, and to assign the chemical shifts to particular nuclei it is sufficient to make an assumption about the chemical shift difference of either the protons or the carbons, but not of both. Thus, assigning the high-field  $^1\text{H}$  resonances to the  $\text{CH}_2\text{Br}$  protons, simultaneously assigns the  $^{13}\text{C}$  resonance in this group to be also at higher field. This assignment agrees with the predicted substituent effects of Cl and Br atoms on the chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in similar compounds in isotropic solvents.<sup>16</sup> In the liquid-crystalline samples there is a contribution to shielding from the anisotropies in the shielding constants, and so the chemical shift differences will not be identical to those in isotropic solvents. We have assumed that this effect does not change the sign of the chemical shift differences of either the protons or the  $^{13}\text{C}$  nuclei in 1-chloro-2-bromoethane dissolved in the nematic solvent ZLI 1132. Note that this assignment of the chemical shifts differs from that given in Ref. 14. Changing the chemical shift assignments is equivalent to interchanging Cl and Br in the structure in Fig. 1. The present assignment is also in agreement with the magnitudes of the two  $^2J_{\text{HH}}$  couplings.<sup>16</sup>

### III. CONFORMATIONAL ANALYSIS

#### A. General considerations

The aim is to determine the information content of the set of dipolar couplings, that is, how much experimental information can be obtained from the dipolar couplings on the structure of the molecule, the form of  $V(\phi)$ , the potential for

rotation about the C–C bond, and the orientational order in the liquid-crystalline solvent. The values of  $D_{ij}(\text{equil})$  are averages over rotation about the C–C bond, and also over motion of the molecule as a whole relative to the director of the liquid-crystalline phase, thus

$$D_{ij}(\text{equil}) = Q_{\text{LC}}^{-1} \int D_{ij}^{\text{equil}}(\beta, \gamma, \phi) \times \exp[-(U_{\text{ext}}(\beta, \gamma, \phi) + V(\phi))/k_B T] \times \sin \beta d\beta d\gamma d\phi. \quad (11)$$

To evaluate the average it is necessary to adopt models for both  $U_{\text{ext}}(\beta, \gamma, \phi_i)$  and  $V(\phi)$ . The former will be approximated by the additive potential (AP) model,<sup>4</sup> whose starting assumption is to write  $U_{\text{ext}}(\beta, \gamma, \phi)$  as

$$U_{\text{ext}}(\beta, \gamma, \phi) = -\varepsilon_{2,0}(\phi)C_{2,0}(\beta) - 2 \text{Re} \varepsilon_{2,2}(\phi)C_{2,2}(\beta, \gamma), \quad (12)$$

where the  $C_{2,n}(\beta, \gamma)$  are modified spherical harmonics, and the  $\varepsilon_{2,m}(\phi)$  are conformationally dependent interaction parameters. The method is named from the assumption that the  $\varepsilon_{2,m}(\phi)$  can be expressed as sums of contributions,  $\varepsilon_{2,p}(j)$  from rigid fragments of the molecule, thus

$$\varepsilon_{2,m}(\phi) = \sum_j \sum_p \varepsilon_{2,p}(j) D_{p,m}^2(\Omega_j), \quad (13)$$

and  $D_{p,m}^2(\Omega_j)$  is the Wigner matrix describing the orientation of fragment  $j$  relative to a molecular reference frame.

Equation (11) can be expressed as

$$D_{ij}(\text{equil}) = \int D_{ij}^{\text{equil}}(\phi) P_{\text{LC}}(\phi) d\phi, \quad (14)$$

where

$$D_{ij}^{\text{equil}}(\phi) = - (K_{ij}/r_{ij}^3) \left[ \begin{array}{l} S_{zz}^\phi (3 \cos^2 \theta_{ijz}^\phi - 1) + (S_{xx}^\phi - S_{yy}^\phi) (\cos^2 \theta_{ijx}^\phi - \cos^2 \theta_{ijy}^\phi) \\ + 4S_{xy}^\phi \cos \theta_{ijx}^\phi \cos \theta_{ijy}^\phi + 4S_{xz}^\phi \cos \theta_{ijx}^\phi \cos \theta_{ijz}^\phi + 4S_{yz}^\phi \cos \theta_{ijy}^\phi \cos \theta_{ijz}^\phi \end{array} \right] \quad (15)$$

with

$$K_{ij} = \frac{\mu_0 \hbar \gamma_i \gamma_j}{16\pi^2}. \quad (16)$$

The constants  $\mu_0$ , and  $\gamma_i$  and  $\gamma_j$  are the magnetic constant and magnetogyric ratios, respectively, and  $K_{ij}$  is independent of the conformation. The geometrical parameters  $r_{ij\phi}$  and  $\theta_{ijx}^\phi$ , etc., which are angles between  $r_{ij\phi}$  and molecular axis  $x$ , refer to the molecule being in the conformation defined by  $\phi$ .

The conformationally dependent order parameters,  $S_{xy}^\phi$ , etc., are defined with respect to reference axes  $xyz$  fixed in a rigid subunit of the molecule. They are obtained from the conformationally dependent potential of mean torque,  $U_{\text{ext}}(\beta, \gamma, \phi)$ , for example,

$$S_{xx}^\phi = Z^{-1}(\phi) \frac{1}{2} \int (3 \cos^2 \theta_x - 1) \times \exp[-U_{\text{ext}}(\beta, \gamma, \phi)/k_B T] \sin \beta d\beta d\gamma, \quad (17)$$

with

$$Z(\phi) = \int \exp[-[U_{\text{ext}}(\beta, \gamma, \phi)/k_B T] \sin \beta d\beta d\gamma. \quad (18)$$

The angle  $\theta_x$  is that between  $x$  axis and the liquid-crystal director.

#### B. Calculation of the vibrational corrections $D_{ij}(\text{vib})$

It is straightforward to calculate the effect that small-amplitude vibrations have on the dipolar couplings when there are no large-amplitude motions, such as bond rotation.



This is referred to as the rigid molecule case. Both harmonic and anharmonic terms can contribute to  $D_{ij}(\text{vib})$ , but only the former, larger term will be considered here, and in this case, for a rigid molecule:<sup>17</sup>

$$D_{ij}(\text{vib}) = -K_{ij} \sum_{\alpha\beta} S_{\alpha\beta} \Phi_{\alpha\beta,ij}^h \quad (19)$$

with

$$\Phi_{\alpha\beta,ij}^h = \left[ C_{\alpha\beta}^{ij} - 5 \sum_{\gamma} \cos \theta_{\gamma} (C_{\alpha\gamma}^{ij} \cos \theta_{\beta} + C_{\beta\gamma}^{ij} \cos \theta_{\alpha}) + \frac{5}{2} \cos \theta_{\alpha} \cos \theta_{\beta} \sum_{\gamma\delta} C_{\gamma\delta}^{ij} (7 \cos \theta_{\gamma} \cos \theta_{\delta} - \delta_{\gamma\delta}) \right] \cdot r_{ij}^{-5} \quad (20)$$

$\theta_{\alpha}$  is the angle between the  $i, j$  direction and the molecule fixed Cartesian system  $\alpha$  axis, and

$$C_{\alpha\beta}^{ij} = \sum_{\nu=1}^{3N} (u_{i\alpha}^{(\nu)} - u_{j\alpha}^{(\nu)})(u_{i\beta}^{(\nu)} - u_{j\beta}^{(\nu)}) \frac{A}{\omega_{\nu}} \coth\left(\frac{B\omega_{\nu}}{T}\right) \quad (21)$$

with

$$A = \frac{h}{8\pi^2 c} \quad (22)$$

and

$$B = \frac{ch}{2k_B}. \quad (23)$$

$u_{i\alpha}^{(\nu)}$  is the Cartesian displacement relative to the  $\nu$ th normal mode of vibrational frequency  $\omega_{\nu}$  of the  $i$ th nucleus along the  $\alpha$  axis,  $T$  is the temperature,  $c$  is the velocity of light, and  $k_B$  is the Boltzmann constant.

The calculation of  $D_{ij}(\text{vib})$  requires a knowledge of  $u_{i\alpha}^{(\nu)}$  and  $\omega_{\nu}$ , and for a rigid molecule the frequencies and displacement coordinates could be obtained in principle, from an analysis of the vibrational spectrum to yield an experimental force field. Such analyses are sometimes possible, and of course desirable in providing a fundamental understanding of the origins of the vibrational spectrum, but for the more restricted objective of calculating corrections to dipolar couplings it is simpler, and of sufficient precision, to calculate the force field by quantum-mechanical methods. Such an approach also has the considerable advantage of being applicable to molecules, such as substituted ethanes, in which there is bond rotational motion, and now the vibration correction  $D_{ij}^{\text{vib}}(\phi)$  is conformationally dependent. The observed dipolar couplings are the average,

$$D_{ij}(\text{obs}) = \int [D_{ij}^{\text{equil}}(\phi) + D_{ij}^{\text{vib}}(\phi)] P_{\text{LC}}(\phi) d\phi. \quad (24)$$

It should be noted that vibrational wave functions and energies can be calculated only for minimum-energy structures on the path of a bond rotation. This theoretical method of obtaining  $D_{ij}(\text{vib})$  has been applied previously to the case of styrene,<sup>10</sup> which has a single set of minimum-energy structures generated by bond rotation, acrolein, which has two minimum-energy forms,<sup>11</sup> and now to the present molecule,

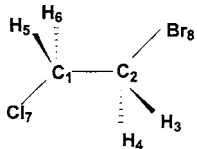
which has three minima in the bond rotation potential. Thus, the frequencies and coordinate displacements were calculated for 1-chloro-2-bromoethane for the *trans* ( $\phi=180^\circ$ ) and *gauche* ( $\phi=70^\circ$  and  $290^\circ$ , as found by calculation with full geometrical optimization) forms. The calculation was by the density-functional method B3LYP/6-311+G\*, which has been shown to give good results for vibrational force fields. Note that it is necessary when calculating  $D_{ij}(\text{vib})$  to exclude the vibrational mode which corresponds to a torsional oscillation about the C–C bond, since the effect of this motion is included in the averaging over  $\phi$  by Eq. (24). The remaining modes for the *trans* form,  $u_{i\alpha}^{(\nu)}(180)$  and  $\omega_{\nu}(180)$ , are then used when  $\phi$  is in the range of  $120^\circ$ – $240^\circ$ ,  $u_{i\alpha}^{(\nu)}(70)$  and  $\omega_{\nu}(70)$  when  $\phi$  is between  $0^\circ$  and  $120^\circ$ , and  $u_{i\alpha}^{(\nu)}(290)$  and  $\omega_{\nu}(290)$  when  $\phi$  is in the range of  $240^\circ$ – $360^\circ$ .

### C. The structure and conformation of 1-chloro-2-bromoethane

Three dipolar couplings are obtained between the protons and  $^{13}\text{C}$  nuclei within each of the two rigid subunits  $\text{CH}_2\text{X}$  of the molecule, which are not sufficient to determine the relative positions of the three nuclei and the three local order parameters required for calculation of  $D_{ij}(\text{equil})$ . This means that the relative positions of the interacting nuclei cannot be determined separately from the form of  $P_{\text{LC}}(\phi)$ . All eight measured couplings must therefore be used to test various models for both structure and conformation.

A second general problem is how to represent the potential of mean torque  $U_{\text{ext}}(\beta, \gamma, \phi)$ , that is, the choice of fragment interaction parameters  $\varepsilon_{2,p}(j)$  to be used in Eq. (13). There is no unique choice, but in most molecules choosing which fragments to use is not a difficult, or indeed crucial decision, because different choices give the same result. For example, in the present molecule in the *trans* form, as represented in Fig. 1,  $xz$  is a mirror plane, and this means that  $y$  is a principal axis for both the tensors  $\varepsilon(\text{trans})$  and  $S^{\text{trans}}$ , and any three independent fragment tensor components,  $\varepsilon_{2,0}(j)$ , will combine to give the correct total tensor  $\varepsilon(\text{trans})$ . A natural choice for many molecules is to use an axially symmetric tensor directed along each of the bonds, since this often, but not always, produces the correct symmetry. In the present case this would mean choosing  $\varepsilon_{\text{CC}}$ ,  $\varepsilon_{\text{CBr}}$ ,  $\varepsilon_{\text{CCl}}$ , and  $\varepsilon_{\text{CH}}$ , the latter being identical for all four CH bonds. Clearly this is too many for just the *trans* form, but for this structure the C–Br and C–Cl bonds are almost parallel, so that  $\varepsilon_{\text{CBr}}$  and  $\varepsilon_{\text{CCl}}$  are not independent. Attempts to calculate  $D_{ij}^{\text{equil}}(\phi)$  using this choice for the interaction tensors did not lead to either stable or sensible results. This is because of the near tetrahedral structure of the two C– $\text{CH}_2\text{X}$  groups. Stable and, as will be shown, sensible results were obtained by choosing  $\varepsilon_{zz}$ ,  $\varepsilon_{xx} - \varepsilon_{yy}$ , and  $\varepsilon_{\text{Cl-Br}}$  which is along the Cl–Br direction. The magnitude of  $\varepsilon_{\text{Cl-Br}}$  is taken to be independent of the bond rotation angle, but it varies in direction as  $\phi$  changes.

TABLE II. The energies  $E$  in  $\text{kJ mol}^{-1}$ , bond lengths  $r_{ij}$  in  $\text{\AA}$ , and angles  $\theta_{ijk}$  and  $\tau_{ijkl}$  in degrees, calculated for 1-chloro-2-bromoethane in the *trans* and *gauche* forms by MP2/6-311G and B3LYP/6-311+G\*. The *gauche* minima are at  $180^\circ \pm \phi_{gauche}$ .



	MP2/6-311G		B3LYP/6-311+G*	
	<i>trans</i>	<i>gauche</i>	<i>trans</i>	<i>gauche</i>
$\phi_{gauche}$		108.7		110.0
$E$		11.9		8.9
$r_{12}$	1.512	1.515	1.511	1.511
$r_{15}$	1.087	1.089	1.087	1.091
$r_{23}$	1.087	1.089	1.087	1.090
$r_{17}$	1.899	1.888	1.820	1.809
$r_{28}$	2.004	1.995	1.980	1.972
$\theta_{123}$	112.5	111.5	112.3	112.1
$\theta_{215}$	112.0	110.7	112.1	112.0
$\theta_{128}$	108.6	112.4	109.3	113.5
$\theta_{217}$	108.7	111.7	109.1	113.2
$\tau_{3128}$	116.7	117.7	117.7	120.4
$\tau_{5217}$	117.2	118.1	118.1	118.0

#### IV. TESTING MODELS FOR THE STRUCTURE AND CONFORMATION

##### A. Are the structure and rotation potential calculated by the density functional consistent with the observed dipolar couplings?

Calculations were carried out using the density-functional method B3LYP/6-311+G\*, and also, for comparison, by the *ab initio* method, MP2/6-311G, in each case with full geometry optimization at fixed  $10^\circ$  intervals in  $\phi$  in order to determine the variation of the energy with the bond rotation angle. Calculations were then done to locate the value of  $\phi$  at the *gauche* local minima. The results are shown in Table II.

The calculations of the geometry suggest that the parameters which affect the relative positions of the carbon and hydrogen nuclei are not strongly dependent on  $\phi$  when the molecule is in the positions of minimum energy, and that it is a reasonable approximation to assume that the geometry of the *trans* form is maintained over the bond rotation.

##### B. Are the geometry and rotational potential calculated by the DFT method consistent with the dipolar couplings?

The geometry calculated by the density-functional method was used in the calculation of the dipolar couplings since this method was also used to compute the vibrational frequencies and coordinate displacements.

The truncated Fourier expansion given in Eq. (8) was used to describe the bond rotational potential, with coefficients obtained by fitting the curve calculated by the density-functional method. These are  $V_0=16.55$ ,  $V_1=9.96$ ,  $V_2=3.26$ , and  $V_3=9.89$ , in each case in  $\text{kJ mol}^{-1}$ .

Fitting the  $D_{ij}(\text{obs})$  to the values of  $D_{ij}^{\text{equil}}(\phi) + D_{ij}^{\text{vib}}(\phi)$  calculated with the geometry and  $V(\phi)$  fixed at that obtained by the density-functional method, and evaluating the averages over  $\phi$  (using steps of  $1^\circ$ ) by the AP method gives an unacceptable rms error of 26 Hz. The variable parameters in this fitting process were the three interaction parameters  $\varepsilon_{zz}$ ,  $\varepsilon_{zz} - \varepsilon_{yy}$ , and  $\varepsilon_{\text{CIBr}}$ . Adding an interaction parameter  $\varepsilon_{\text{CH}}$  for each of the four C–H bonds leads to a reduction in the rms error, but not to an acceptable fit to the data set. It can be concluded that the combination of the DFT geometry and potential curve is not consistent with the NMR data.

#### V. CHANGING THE GEOMETRY AND THE ROTATIONAL POTENTIAL TO FIT THE DIPOLAR COUPLINGS

The relative positions of the protons and carbons are described by seven coordinates, but one bond distance must be fixed, which reduces to six the number of geometrical unknown parameters. At least three interaction parameters are required, and so there are nine unknown parameters compared with eight dipolar couplings. It is necessary, therefore, to fix some of the geometrical parameters, and it was decided to keep all the C–H bond lengths equal in length, which reduces the number of unknown parameters to eight, and with the DFT form for  $V(\phi)$ , the observed and calculated dipolar couplings can be brought into perfect agreement. However, the geometrical parameters obtained  $r_{\text{CH}}=1.13 \text{ \AA}$ ,  $\theta_{123}=104.8^\circ$ ,  $\theta_{217}=106.2^\circ$ ,  $\tau_{4213}=113.9^\circ$ , and  $\tau_{7126}=114.4^\circ$  are considerably different from the DFT geometry suggesting that either the geometry or the form of the rotational potential obtained by the DFT calculation is not appropriate for this molecule in the fluid, condensed phase.

Keeping the geometry fixed at that calculated by the DFT method, and varying the Fourier coefficients does not lead to acceptable results, because the two factors which most strongly influence the averaging of the dipolar couplings, the position  $m_g$  and relative energy  $\Delta E_{rg}$  of *gauche* and *trans* conformers, are not simply related to the values of the  $V_n$ . To circumvent this problem the probability  $P_{\text{LC}}(\phi)$  is expressed as the sum of three Gaussian functions, as in Eq. (10), and with the DFT geometry fixed the observed couplings were matched to those observed, including vibrational corrections, by varying  $m_g$ ,  $A$ , and  $h_t=h_g$ . The latter equality is based on the linewidths predicted by the DFT calculation, which obtained near equality and a value of  $\sim 10$  Hz. However, these three potential parameters for this molecule are strongly correlated. Varying  $A$  and  $m_g$  with  $h_t=h_g$  fixed at 5, 10, 15, and 20 Hz, gave rms values in the range of 5–7 Hz,  $A=0.74\text{--}0.78$ , and  $m_g=100^\circ\text{--}97^\circ$ , showing that with the Gaussian probability function and the DFT geometry it is not possible to obtain an acceptable solution.

Fixing  $h_t=h_g$ , and  $m_g$ , and with  $r_{\text{CH}}$  having the DFT value of  $1.087 \text{ \AA}$ , the variable parameters are  $A$ , the four angles defining the positions of the four protons, and the three interaction coefficients. Thus there are a total of eight variables, compared with eight dipolar couplings, and so an exact agreement between observed and calculated dipolar couplings is obtained. When  $m_g$  is fixed at the DFT value of  $110^\circ$ , and  $h_t=h_g$  is given a value of 10 Hz, which is close to

TABLE III. The angles  $\theta_{ijk}(\circ)$  and  $\tau_{ijk}(\circ)$ , and the interaction parameters  $\varepsilon_{zz}$ ,  $\varepsilon_{xx}-\varepsilon_{yy}$  and  $\varepsilon_{\text{ClBr}}$  in  $\text{kJ mol}^{-1}$ , obtained by bringing the observed  $D_{ij}(\text{obs})$  and calculated values of  $D_{ij}(\text{equil})+D_{ij}(\text{vib})$  into best least-squares agreement. Averaging over the bond rotation was done with steps of  $1^\circ$  using the Gaussian probability distribution and optimizing the amplitude  $A$  of the Gaussian centered on  $\phi=180^\circ$ , and with the two *gauche* functions at  $70^\circ$  and  $290^\circ$ . The widths of the Gaussian functions were fixed at  $h_t=h_g=10$  Hz. The parameters obtained without applying vibrational corrections are also given.

Calculated dipolar couplings

$i, j$	$D_{ij}(\text{equil})$ (Hz)	$D_{ij}(\text{vib})$ (Hz)	$100 \times D_{ij}(\text{vib})/D_{ij}(\text{equil})$
1,3	81.6	0.4	0.5
1,5	1168.1	-50.0	-4.3
2,3	1238.6	-59.0	-4.8
2,5	74.6	0.4	0.5
3,4	1093.2	-28.9	-2.6
3,5	208.3	3.0	1.4
3,6	186.8	-3.7	-2.0
5,6	1055.1	-22.9	-2.2

Fitting parameters		
Vibrational averaging		
	with	without
$\varepsilon_{zz}$	-0.0128	-0.0173
$\varepsilon_{xx}-\varepsilon_{yy}$	0.111	0.108
$\varepsilon_{\text{ClBr}}$	1.514	1.443
$A_t$	0.69	0.70

Geometrical parameters			
NMR			DFT
	with vibrational averaging	without vibrational averaging	
$\theta_{123}$	107.2	107.3	112.3
$\theta_{215}$	108.4	108.6	112.1
$\tau_{4218}$	118.5	119.0	117.7
$\tau_{5127}$	119.8	120.1	118.1

the widths calculated by DFT, then the results shown in Table III are obtained for the angles defining the positions of the four protons, and for  $A$ , the amplitude of the Gaussian centered on the *trans* position. The calculations were done both with and without vibrational corrections to the dipolar couplings.

Figure 3 shows the Gaussian distribution obtained together with  $P(\phi)$  calculated by the DFT method. Note that  $P_{\text{LC}}(\phi)$  is essentially identical with  $P_{\text{iso}}(\phi)$ , which is to be expected for a molecule with a low degree of orientational order.

The Gaussian function for the *trans* form corresponds to

a total probability of 0.69 in the range of  $\phi=180^\circ \pm 50^\circ$ , whilst in the same range the DFT probability integrates to 0.95.

Vibrational averaging has a significant effect on the dipolar couplings, with the ratio  $D_{ij}(\text{vib})/D_{ij}(\text{equil})$  being largest for the one-bond C-H couplings at  $\sim -4\%$ , which is similar in sign and magnitude to values found for  $^1D_{\text{CH}}$  couplings in other compounds.<sup>10,11,17,18</sup> Note that although this ratio has a similar magnitude for the two  $^3D_{\text{HH}}$  couplings the values are of opposite sign. The effect on the derived geometry of including vibrational averaging is to reduce the two torsional angles by about  $0.4^\circ$ , but the reduction in the CCH bond angles is only  $0.1^\circ$ . The values determined for the bond angles of  $\theta_{123}=107.2^\circ$  and  $\theta_{215}=108.4^\circ$  are both significantly smaller than the average of the values calculated by the two quantum-chemical methods ( $112.2^\circ$  and  $111.7^\circ$ , respectively), whilst the torsion angles  $\tau_{4218}=118.5^\circ$ , and  $\tau_{5127}=119.8^\circ$  are much closer to the calculated average values ( $117.1^\circ$  and  $117.6^\circ$ , respectively).

Calculations were also performed to establish the dependence of the derived angles and the relative proportions of *gauche* and *trans* forms on the assumed values of  $m_g$  and  $h_t=h_g$ . Thus calculations were performed with  $m_g$  fixed at  $110^\circ$  and  $h_t=h_g$  in the range of 5–20 Hz. These showed that acceptable solutions are obtained, provided that  $h_t=h_g < 17$  Hz and that in the range  $h_t=h_g=5-16$  Hz, with  $m_g=110^\circ$ , the proportion found for the *trans* conformer is constant at 69%, whilst the two CCH bond angles decrease from  $108.1^\circ$  to  $105.2^\circ$  for  $\text{C}_1\text{C}_2\text{H}_4$ , and  $109.4^\circ$  to  $106.2^\circ$  for  $\text{C}_2\text{C}_1\text{H}_7$ . The two torsion angles change by less than  $0.5^\circ$  over the same range. Fixing  $h_t=h_g=10$  Hz and changing  $m_g$  over the range of  $110^\circ \pm 6^\circ$ ,  $\text{C}_1\text{C}_2\text{H}_4$  changes from  $109.4^\circ$  for  $m_g=104^\circ$  to  $102.6^\circ$  for  $m_g=116^\circ$ , whilst for the same range  $\text{C}_2\text{C}_1\text{H}_7$  changes from  $110.9^\circ$  to  $103.1^\circ$ . The torsion angles again are much less sensitive to change, both changing by  $+2^\circ$  over the range of  $m_g$  values. The proportion predicted for the *trans* conformer for these calculations varies over the range of 64% (for  $m_g=116^\circ$ )–73% for  $m_g=104^\circ$ . If it is assumed that the CCH bond angles should be close to the tetrahedral value, then it is concluded that the value of  $m_g=110^\circ$  predicted by the DFT method for an isolated molecule is too large by perhaps as much as  $6^\circ$  for the molecule in the liquid-crystalline phase.

It is not possible to decide which of the two geometries, that determined from the NMR data and given in Table III or that calculated by the DFT method, are closer to the correct structure for the molecule in the condensed phase, since both the treatment of the experimental data and the calculation methods are subject to systematic errors. It is also possible that both methods are giving precise geometries, and that the difference between the structures is real and is because the NMR data are for the molecule in a particular condensed, fluid phase, whilst the calculated structures are for a single, isolated molecule. This difference in environment may also be the reason why the NMR data predict the *trans* form to be 69% abundant, whilst the DFT calculation finds 95%.

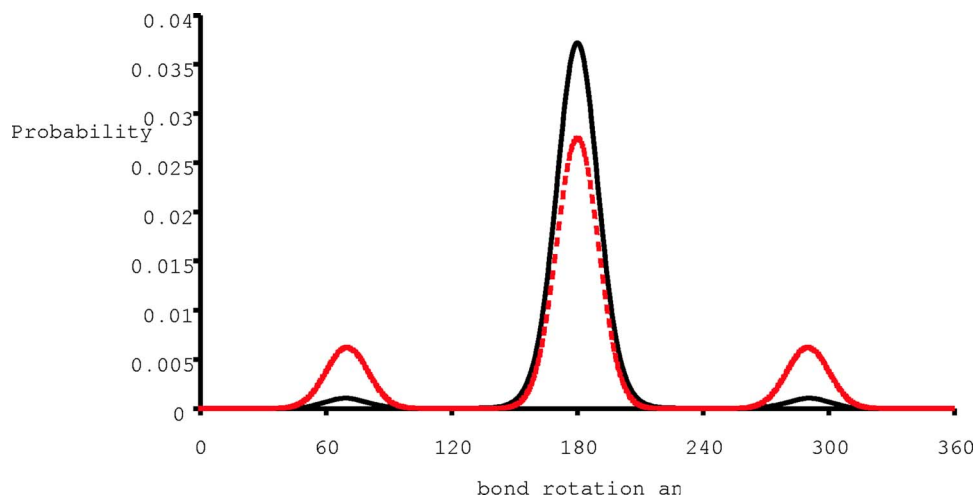


FIG. 3. The probability distribution  $P(\phi)$  obtained from the DFT calculations (continuous, black line) compared with  $P_{LC}(\phi)=P_{iso}(\phi)$  obtained by fitting the dipolar couplings with a sum of Gaussian functions (dashed, red line).

## VI. ANALYSIS OF THE NMR DATA USING THE RIS APPROXIMATION FOR THE CONFORMATIONAL DISTRIBUTION

The RIS approach is to assume that only the minimum-energy structures are populated on a bond rotation pathway. For ethanes this corresponds to the two *gauche* and the single *trans* forms. The relative probabilities of the *trans* and *gauche* forms depend on the energy difference between them,  $E_{ig}$ . The calculation of  $D_{ij}(\text{equil})$  is done by the same method as before, but with the integral in Eq. (24) replaced by a sum over the three minimum-energy states. The *gauche* forms are assumed to be at  $\phi=70^\circ$  and  $290^\circ$ , as predicted by the DFT calculations.

It is also possible to calculate  $D_{ij}^{\text{vib}}(n)$ , but now all the normal modes are included, since the torsional mode is no longer taken into account by the separate averaging over the whole of the bond rotation pathway. The results of the RIS calculations are shown in Table IV.

The magnitudes of  $D_{ij}(\text{vib})$  calculated in the RIS model differ from those obtained with Gaussian potential, as expected, but the geometrical parameters and the amount of the *trans* isomer obtained by the two methods of describing the conformational distribution differ by less than 1%.

## VII. CONCLUSIONS

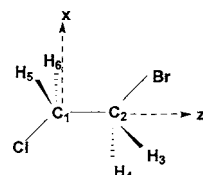
The structure and the bond rotational probability distribution  $P_{iso}(\phi)$  are not consistent with the values calculated by the molecular orbital or density-functional methods. The reasons for this discrepancy could have two principal sources. The first is that the quantum-chemical calculations refer to an isolated molecule, whereas the NMR structure is for the molecule in a particular liquid solvent. Note that there is an effect on the probability distribution which is from the anisotropic part of the intermolecular forces, but for a weakly ordered solute, as is the case here, this effect is small, that is,  $P_{LC}(\phi)=P_{iso}(\phi)$ . The discrepancy in the values of  $P_{iso}(\phi)$  could certainly arise because of the effect of the solvent molecules since these effects have been shown to be large for similar molecules dissolved in isotropic solvents.<sup>19</sup> The discrepancies in the geometry are unlikely to be a solvent effect, and this leads to the second reason for the differences between the NMR and calculated structures, which is that ei-

TABLE IV. The angles  $\theta_{ijk}(\circ)$  and  $\tau_{ijkl}(\circ)$ , and the interaction parameters  $\epsilon_{zz}$ ,  $\epsilon_{xx}-\epsilon_{yy}$  and  $\epsilon_{ClBr}$  in  $\text{kJ mol}^{-1}$ , obtained by bringing the observed  $D_{ij}(\text{obs})$  and calculated values of  $D_{ij}(\text{equil})+D_{ij}(\text{vib})$  into best least-squares agreement. Averaging over the bond rotation was approximated by the RIS method. The parameters obtained without applying vibrational corrections are also given.

$i, j$	$D_{ij}(\text{equil})$ (Hz)	$D_{ij}(\text{vib})$ (Hz)	$100 \times D_{ij}(\text{vib})/D_{ij}(\text{equil})$
1,3	81.8	0.2	0.2
1,5	1194.8	-76.7	-6.4
2,3	1251.8	-72.2	-5.8
2,5	74.9	0.1	0.1
3,4	1107.1	-42.8	-3.9
3,5	211.1	0.2	0.1
3,6	188.9	-5.8	-3.1
5,6	1084.4	-52.2	-4.8

Fitting parameters			
Vibrational averaging			
	with	without	
$\epsilon_{zz}$	-0.017	-0.032	
$\epsilon_{xx}-\epsilon_{yy}$	0.078	0.121	
$\epsilon_{ClBr}$	1.529	1.427	
$P_{iso}(\text{trans})$	0.70	0.71	
Geometrical parameters			
NMR vibrational averaging			
	with	without	DFT
$\theta_{123}$	108.2	108.3	112.3
$\theta_{215}$	109.6	109.5	112.1
$\tau_{4218}$	118.7	118.7	117.7
$\tau_{5127}$	119.9	119.7	118.1



Calculated dipolar couplings



ther one or both of these methods of obtaining the structure are in error. Comparisons of these two methods, and also with structures obtained from rotational spectroscopy, are usually within much closer agreement.<sup>20</sup> There are cases, however, involving small molecules, such as methyl fluoride<sup>21</sup> and methyl iodide,<sup>22</sup> when very large, and temperature- and solvent-dependent discrepancies are observed. These cases are most probably because of multiple site-specific interactions between the solute and solvent molecules. For rigid molecules this phenomenon is easily identified because of violations of geometrical consistency, but this test is not applicable in the present case. The bond angles derived here from the NMR data are reasonable, being closer to tetrahedral geometry for the two carbon atoms than predicted by the quantum-chemical calculations. However, it will be interesting to use the methodology developed here to investigate whether the derived geometry and the conformational distribution are dependent on the liquid-crystalline solvent used, and such studies are in progress.

The geometrical and conformational parameters derived by the NMR method for 1-chloro-2-bromoethane are not changed appreciably either by neglecting the effect of vibrational averaging or by assuming the simple RIS model for  $P_{\text{iso}}(\phi)$ . This suggests that extensions of this NMR method to larger molecules, with more bonds about which rotation occurs, and when vibrational averaging and sampling of the whole of the possible conformational space are not feasible, will be possible.

## ACKNOWLEDGMENT

This work has been supported by MIUR PRIN "Cristalli Liquidi e Macromolecole per Strutture Nanorganizzate."

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