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An investigation of the structure and bond rotational potential of some fluorinated ethanes by NMR spectroscopy of solutions in nematic liquid crystalline solvents

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Abstract

NMR spectra of 1,2-dibromo-1,1-difluoroethane and 1-bromo-2-iodo-tetrafluoroethane dissolved in nematic liquid crystalline solvents have been analysed to yield the magnitudes and signs of the scalar couplings, J_{ij}, and total anisotropic couplings, T_{ij}, between all the ^1H, ^{19}F, and ^{13}C nuclei, except for those between two ^{13}C nuclei. The values obtained for T_{ij} in principle contain a contribution from J_{ij}^{aniso}, the component along the static applied magnetic field of the anisotropic part of the electron-mediated spin–spin coupling. Neglecting this contribution allows partially averaged dipolar couplings, D_{ij}, to be extracted from the T_{ij}, and these were used to determine the structure, orientational order, and the conformational distribution generated by rotation about the C–C bond. The values obtained are compared with the results of calculations by ab initio and density functional methods. The differences found are no greater than those obtained for similar compounds which do not contain fluorine, so that there is no definitive evidence for significant contributions from J_{CF}^{aniso} or J_{FF}^{aniso} in the two compounds studied.
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Keywords: Liquid crystalline; Conformation; Alkanes; Anisotropic spin–spin coupling

1. Introduction

The NMR spectra of molecules dissolved in liquid crystalline solvents depend upon partially averaged dipolar couplings, D_{ij}, between nuclei, and for a rigid molecule these may be used to investigate bond lengths and angles, and orientational order [1]. The correspondence between the bond lengths and angles obtained by this LXNMR method and other structural methods is usually good, provided that a large data set is available and corrections for vibrational averaging are included. For some small molecules it has been found that a vibration–orientation coupling may also be important [2]. For molecules in which

there is rotational motion about bonds, through angles ϕ_i, with $i = 1$ to N_{rot}, where N_{rot} is the number of bond rotations, it is also possible to investigate the nature of the conformer distribution, $P_{LC}(\phi_i)$ [3], but now this is expected to be influenced by the liquid crystalline solvent. Thus, the anisotropic, solute–solvent intermolecular potential, which is responsible for the orientational order of the dissolved molecule, will in principle affect the conformer distribution. It is necessary to distinguish between $P_{LC}(\phi_i)$, the conformer distribution determined directly from $D_{ij}(obs)$, the observed, partially averaged, dipolar couplings, and $P_{iso}(\phi_i)$, the distribution appropriate for the same temperature but without any orientational order. There will also be a possible contribution to $P_{iso}(\phi_i)$ from the chemical nature of the solvent molecules [4], so that this distribution may depend on the solvent, and may also be

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different from that for an isolated molecule, as would be calculated by a quantum mechanical method or determined experimentally by microwave spectroscopy. These interesting phenomena can be investigated only if a method is developed for relating sets of observed dipolar couplings to the bond lengths, bond angles, the orientational order, and the conformer distributions. Such a method should be able to calculate the vibrational corrections to the couplings, and contain a theoretical model for how the orientational order varies with conformation. A procedure to do this has been developed and has been applied to a number of simple, flexible molecules chosen so as to test the various assumptions inherent to the method [5–10]. The test molecules contained only ^1H and ^{13}C as the magnetically active nuclei, and in this work attention is turned to flexible molecules which also contain ^{19}F nuclei, which introduces an extra complication. Thus, in general, the spectrum of a molecule in an ordered phase depends on the values of scalar couplings, J_{ij}, and T_{ij}, the partially averaged component in the direction of the applied magnetic field of the total, anisotropic coupling tensor. There is a contribution to T_{ij} from D_{ij}, the partially averaged dipolar coupling, and also from J_{ij}^{aniso}, which is the partially averaged anisotropic part of the electron-mediated coupling tensor $\mathbf{J}$ [11]. Both experiment and theory suggest that J_{ij}^{aniso} is negligibly small when ^1H is one of the coupled nuclei, but that it may be appreciable in magnitude for coupling between ^{19}F and either ^{19}F or ^{13}C. Attempts have been made to determine the magnitude of J_{CF}^{aniso} in 1,4-difluorobenzene [12], CH_3F, and CF_3H, and J_{FF}^{aniso} in the latter molecule, by both LXNMR and quantum chemical calculations [13]. The conclusion reached is that in these molecules the anisotropies are <1.7% of the corresponding dipolar coupling, but it is not known in general whether neglecting this term will lead to appreciable errors when using dipolar couplings involving ^{19}F to determine structure in other molecules, and in particular in investigating their conformational equilibrium. We investigate here two substituted fluorinated ethanes, whose structures are given in Fig. 1, and which have rotational motion about only one bond.

The structure and conformational distribution will be determined by the same approach used for 1-chloro-2-bromoethane [10]. This involves analysing the spectra given by the isotopomers containing ^{13}C at natural abundance to yield values of T_{ij}, which are assumed to be uncontaminated by J_{ij}^{aniso}, and so are equated to being the experimental, partially averaged dipolar couplings D_{ij}(obs). These are then corrected for the effects of harmonic, vibrational motion, and compared with values calculated using the Additive Potential (AP) method for averaging over the bond rotational motion [14]. The aim is to see if this procedure leads to a reasonable structure and conformational distribution when the anisotropies in spin–spin couplings are neglected. The definition of reasonable here is imprecise since there are no other methods for obtaining the structure and conformation of these molecules in solution which do not suffer from uncertainties. We will compare our structures with the results of quantum chemical calculations. The bond rotational potential, and hence the conformational distribution, will be calculated by the MP2 ab initio, and the DFT method with the B3LYP functional. These give results appropriate for an isolated molecule, whereas the LXNMR method refers to the molecules in a liquid phase, and, whereas differences in the conformational distributions obtained by the two methods are possible, the molecular geometries are less likely to be dependent on the phase.

2. Experimental

The substituted ethanes were purchased from Aldrich. Samples of each were prepared as approximately 10% solutions by weight in the individual nematic liquid crystalline solvents ZLI 1132 and ZLI 1167, which were obtained from Merck Ltd. The samples were contained in normal, 5 mm o.d. sample tubes, and their spectra recorded at 300 K. Samples were also prepared in a mixture of ZLI 1132 ($\Delta\chi$, the anisotropy in the magnetic susceptibility, positive) and ZLI 1167 ($\Delta\chi$ negative). The relative amounts of the two solvents was initially 1:1 by weight. The spectra of solutes dissolved in this mixed solvent were then recorded at 301 K, and the concentration ratio of the mixed solvent changed by small amounts until coexisting spectra were obtained corresponding to the director being both parallel and perpendicular to $\mathbf{B}_0$. The temperature was then adjusted in steps of 0.1 °C until the best resolution for both spectra was obtained.
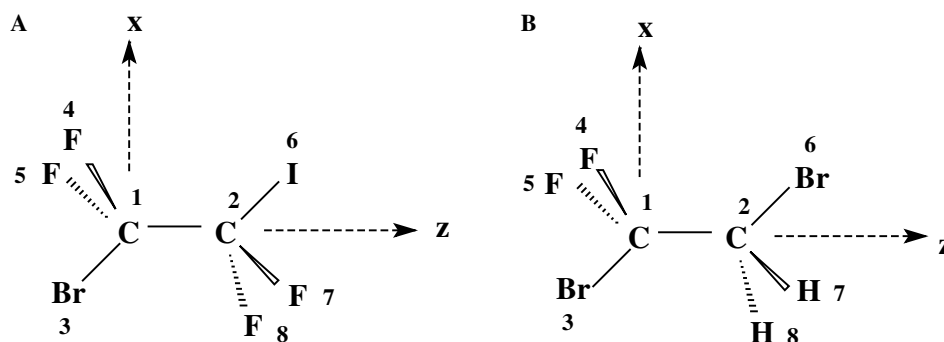

Fig. 1. Structure and atomic labelling of 1-bromo-2-iodo-tetrafluoroethane (A) and 1,2-dibromo-1,1-difluoroethane (B).

3. NMR analyses

The primary aim of the spectral analyses was to obtain a full set of dipolar couplings between the interacting nuclei in each sample for the two isotopomers containing a single ^{13}C nucleus. To do this it is necessary, in general, to also determine the scalar couplings since these affect the line positions in the spectra from the liquid crystalline solutions. In favourable cases, the J_{ij} and D_{ij} are both obtained as independent parameters by analysing the spectrum of an oriented molecule, but this is not true in the ethanes studied here for the couplings involving ^{13}C nuclei. The magnitudes of the $^nJ_{CX}$ were obtained from the spectra of samples dissolved in $CDCl_3$, and their signs from theoretical predictions, or by comparison with previous experimental investigations. The relative signs of the $^nJ_{CX}$ and $^nD_{CX}$ were obtained for 1,2-dibromo-1,1-difluoroethane and 1-bromo-2-iodo-tetrafluoroethane by recording spectra in the mixed ZLI 1132/ZLI 1167 solvent.

3.1. Spectra of 1,2-dibromo-1,1-difluoroethane

Proton and carbon spectra of a sample dissolved in $CDCl_3$ were recorded on a Bruker DPX 400 spectrometer. The proton spectrum is the A part of an $AA'XX'$ spin system, and as such is expected to show a maximum of 10 lines. In practice, only 4 lines are observed, and neither $^2J_{HH}$ nor $^2J_{FF}$ affect the spectrum, and it was possible to obtain only the magnitude of both $^3J_{HF}$ couplings. The signs of the $^3J_{HF}$ couplings are assumed to be positive, on the basis of the signs determined for these couplings in similar compounds [15]. The fluorine spectrum on this sample was recorded on a Bruker AM 360 spectrometer, and also shows only 4 lines, and does not yield a value for $^2J_{FF}$.

The $^{13}C-\{^1H\}$ spectrum is comprised of two triplets, from which the magnitudes of $^1J_{CF}$ and $^2J_{CF}$ were measured to give the values in Table 1. The sign of $^1J_{CF}$ was assigned to be negative, based on both theoretical predictions and experimental determinations, albeit in a rather small range of compounds [16]. The sign of $^2J_{CF}$ in $CFCl_2CFCl_2$ has been determined to be of opposite sign to $^1J_{CF}$ [16], and the same relative signs were obtained for these couplings in trifluoroacetic acid [17]. On this basis $^2J_{CF}$ is given a positive sign. The fully coupled ^{13}C spectrum was then used to obtain the magnitudes of $^1J_{CH}$ and $^2J_{CH}$. The sign of $^1J_{CH}$ can be confidently assigned to be positive, whilst the much smaller $^2J_{CH}$ is probably negative, based on results for other compounds [18]. Carbons were straightforwardly assigned on the basis of the relative deshielding effect of F on C1 and on the relative J_{CF} values.

To determine the relative signs of the $^nJ_{CK}$ and $^nD_{CK}$, (where K is either ^1H or ^{19}F and n is 1 or 2) a sample of 1,2-dibromo-1,1-difluoroethane dissolved in the mixed ZLI 1132/ZLI 1167 solvent was prepared which by careful

Table 1
Dipolar, D_{ij}, and scalar, J_{ij}, couplings, in Hertz obtained from the analysis of the 360 MHz ^1H and the 338 MHz ^{19}F spectra of a sample of 1,2-dibromo-1,1-difluoroethane dissolved in $CDCl_3$ and the liquid crystalline solvent ZLI 1132 at 300 K
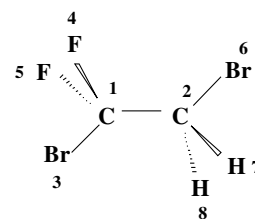
i,j	D_{ij}	J_{ij}
1,4	898.0 ± 0.2	-304.5 ± 0.1
1,7	121.5 ± 0.1	-3.6 ± 0.1
2,4	89.3 ± 0.2	27.3 ± 0.1
2,7	1743.5 ± 0.2	156.4 ± 0.1
4,5	866.6 ± 0.2	—*
4,7**	286.2 ± 2.5	13.3 ± 0.1
4,8**	188.4 ± 2.5	12.7 ± 0.1
7,8	1695.1 ± 0.3	—*

* Does not affect the spectra.
** Assignment can be inter-changed without changing the spectrum.

adjustment of the temperature produced spectra corresponding both to the director being parallel or perpendicular to B_0 [19]. The ^{13}C spectrum of this sample consisted of a triplet of triplets for each singly ^{13}C-labelled isotopomer for the case of the director aligned parallel to B_0, and a similar set of nine lines for the case of perpendicular alignment. For each carbon, from the line positions it is possible to measure:

$$(^nJ_{CK} + 2^nD_{CK})_{parallel} = |a|, \qquad (1)$$

$$(^nJ_{CK} - ^nD_{CK})_{perpendicular} = |b|. \qquad (2)$$

These two equations give:

$$3^nJ_{CK} = \pm a + 2(\pm b), \qquad (3)$$

$$3^nD_{CK} = \pm a - (\pm b). \qquad (4)$$

The magnitude of $^nJ_{CK}$ could change from the isotropic to the liquid crystalline phase, but this is expected to be a small effect, so that the value measured from the spectrum in $CDCl_3$ can be used to determine the relative signs of a and b, and the magnitude and sign relative to $^nJ_{CK}$ of $^nD_{CK}$. If the absolute sign of $^nJ_{CK}$ is known then so too is that of $^nD_{CK}$. Once the relative signs of a and b have been derived it is possible to use Eq. (3) to obtain a value for $^nJ_{CK}$ for the liquid crystalline sample.

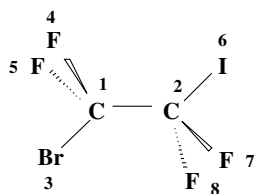Having established the magnitudes and signs of the couplings to ^{13}C it remained to obtain a complete set of dipolar couplings from the proton and fluorine spectra of the single ^{13}C isotopomers (recorded on a Bruker AM 360 spectrometer) on a single sample at the same temperature (nominally 300 K). The data obtained are given in Table 1. Note that: (i) the geminal couplings J_{45} and J_{78} do not affect the spectra, and (ii) interchanging D_{47} and D_{48} does not change the calculated spectrum.

3.2. Spectra of 1-bromo-2-iodo-tetrafluoroethane

A first ^{13}C spectrum recorded on a sample dissolved in $CDCl_3$ at 100 MHz showed only one chemically shifted multiplet (a triplet of triplets) of the two expected. The missing multiplet was detected by using a sample with an increased concentration, and with a long (10 s) delay between pulses, which shows that the ^{13}C resonating at the higher field has a much longer spin–lattice relaxation time, T_1. The large difference in the relaxation times can be attributed to the importance for C_1 of scalar relaxation of the second kind involving the Br nucleus [20]. This relaxation mechanism can be important when the two scalar coupled nuclei have similar resonance frequencies, as do ^{13}C (100.577 MHz) and ^{79}Br (100.214 MHz). The faster relaxing ^{13}C is therefore that attached to bromine, and the initially missing multiplet is that for C_2, which is attached to iodine. This assigns the chemical shift of C_2 to being 22.436 ppm to high field of C_1. The values of the coupling constants measured from the ^{13}C spectrum are given in Table 2.

The fluorine spectrum at 338 MHz of a sample 1-bromo-2-iodo-tetrafluoroethane dissolved in $CDCl_3$ shows only 6 lines rather than the 20 expected for a fully resolved $AA'XX'$ spin system. The only information obtained from such a deceptively simple spectrum is $\frac{1}{2}|J_{AX} + J_{AX'}|$ = 9.4 Hz, and the chemical shift difference of 3.017 ppm. The spectra from the two single ^{13}C isotopomers were detected and yielded the magnitudes of $^1J_{CF}$ and $^2J_{CF}$, and these enabled the chemical shifts to be assigned

such that the ^{19}F in the CF_2Br group are at the higher field. Both the ^{19}F resonances show an isotope shift, $^1\Delta\delta_F(^{13/12}C)$[21] produced by being attached to ^{13}C, which are -0.137 ppm for those attached to C_2, and -0.134 for those on C_1. The negative sign signifies a shift to high field.

A 338 MHz ^{19}F spectrum of a sample of 1-bromo-2-iodo-tetrafluoroethane dissolved in ZLI 1132 is shown in Fig. 2.

The strong lines are those from an $AA'BB'$ spin system formed by the four fluorine nuclei in the all-^{12}C isotopomer, and yields all the scalar and dipolar couplings, as given in Table 2. This highlights one advantage of recording spectra in a liquid crystalline rather than an isotropic solvent, in that it may allow the scalar couplings to be obtained when these could not be measured from the spectrum of the isotropic sample. The weak lines in Fig. 2 from the two single ^{13}C isotopomers were also detected and analysed to give the magnitudes of the D_{ij}, J_{ij} and chemical shifts shown in Table 2. In these analyses the $^nJ_{CF}$ were fixed at the values obtained from the spectra of a solution in $CDCl_3$. It was also found that allowing the values of J_{34} and J_{56} to be varied when analysing the ^{13}C satellite spectra led to very imprecise magnitudes being obtained, with errors of about ± 8 Hz. These large errors probably arise because some key lines in the satellite spectra are obscured by the strong lines from the all-^{12}C molecules. The values of these two $^2J_{FF}$ couplings were therefore kept fixed at the values determined from analysis of the strong lines.

The values of the J_{ij} and D_{ij} obtained for the three isotopomers are essentially identical. The invariance of the J_{ij} to replacement of ^{12}C by ^{13}C shows that the isotope replacement has a negligible effect on the structure and conformation of the molecule. The similar invariance of the D_{ij} reinforces this conclusion, and also shows that the isotope replacement has a negligible effect on orientational ordering.

Table 2

Dipolar, D_{ij}, and scalar, J_{ij}, couplings, in Hertz, and the chemical shifts, in Hertz, obtained from the analysis of the 338 MHz ^{19}F spectra of a sample of 1-bromo-2-iodo-tetrafluoroethane dissolved in the liquid crystalline solvent ZLI 1132 at 300 K

i,j	D_{ij}	J_{ij}
1,4	1370.9 ± 0.1	-311.2 ± 0.2*
1,7	245.3 ± 0.1	36.6 ± 0.2*
2,4	200.6 ± 0.1	41.5 ± 0.2*
2,7	1545.3 ± 0.1	-318.3 ± 0.2*
4,5	1436.9 ± 0.1	178.3 ± 0.1
4,7	561.0 ± 0.1	-8.4 ± 0.1
4,8	331.1 ± 0.1	-10.1 ± 0.1
7,8	1694.8 ± 0.1	209.5 ± 0.1

Chemical shifts (arbitrary reference)/Hz

Isotopomer	All-^{12}C	$^{13}C_1$	$^{13}C_2$
v_4	-422.7 ± 0.1	-427.8 ± 0.1	-473.1 ± 0.1
v_7	197.9 ± 0.1	146.6 ± 0.1	191.8 ± 0.1

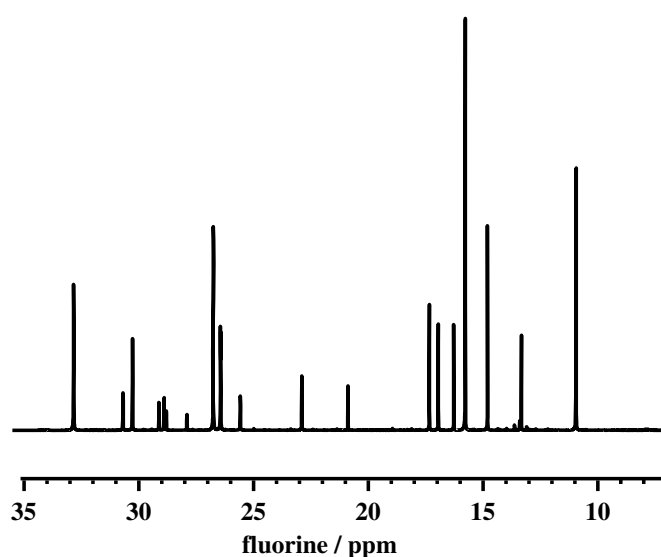* Kept fixed at the value obtained for the sample dissolved in $CDCl_3$.

Fig. 2. 338 MHz ^{19}F spectrum of 1-bromo-2-iodo-tetrafluoroethane dissolved in the nematic solvent ZLI 1132.

The chemical shifts do, however, change on isotope replacement, as found already for the isotropic sample, such that $^1\Delta\delta_F(^{13/12}C_1) = -0.149 \pm 0.001$ ppm, $^1\Delta\delta_F(^{13/12}C_2) = -0.151 \pm 0.001$ ppm, $^2\Delta\delta_F(^{13/12}C_1) = -0.018 \pm 0.001$ ppm, and $^2\Delta\delta_F(^{13/12}C_2) = -0.015 \pm 0.001$ ppm.

Fig. 3 shows ^{19}F spectra of a sample of 1-bromo-2-iodo-tetrafluoroethane dissolved in the mixture of ZLI 1132/ZLI 1167.

It was possible to identify the strong lines from the all-^{12}C molecules for the cases of the director parallel and perpendicular to $\mathbf{B}_0$. The two spectra differ because $(D_{ij})_{\text{perpendicular}} = -1/2(D_{ij})_{\text{parallel}}$, and similarly there is a change in δ^{aniso}, the anisotropic part of the chemical shift: $(\delta^{\text{aniso}})_{\text{perpendicular}} = -1/2(\delta^{\text{aniso}})_{\text{parallel}}$. The data from these analyses gave the relative signs of all the FF scalar and dipolar couplings. Table 2 gives the absolute signs of these couplings which were derived by assuming $^1J_{CF}$ to be negative and $^2J_{FF}$ to be positive [13].

It was possible to identify the lines from the separate single ^{13}C isotopomers in the ZLI 1132/ZLI 1167 mixture corresponding to the director being parallel to $\mathbf{B}_0$, but not when it was perpendicular. The following procedure was therefore followed in order to determine the signs of the couplings between ^{13}C and ^{19}F. A sample of 1-bromo-2-iodo-tetrafluoroethane was dissolved in ZLI 1167 at a similar concentration to that in ZLI 1132. Comparing the ^{13}C spectra from these two samples, and assuming that the orientational order of the molecules relative to the director in each sample is very similar, so that Eqs. (1)–(4) are assumed to hold, gave the values of $^1D_{CF}$ to be positive, knowing the $^1J_{CF}$ to be negative. A check on the validity of this approach is to derive values for $^1J_{CF}$ and $^1D_{CF}$ from Eqs. (3) and (4), and these are indeed within 7% of the values measured for the sample in ZLI 1132.

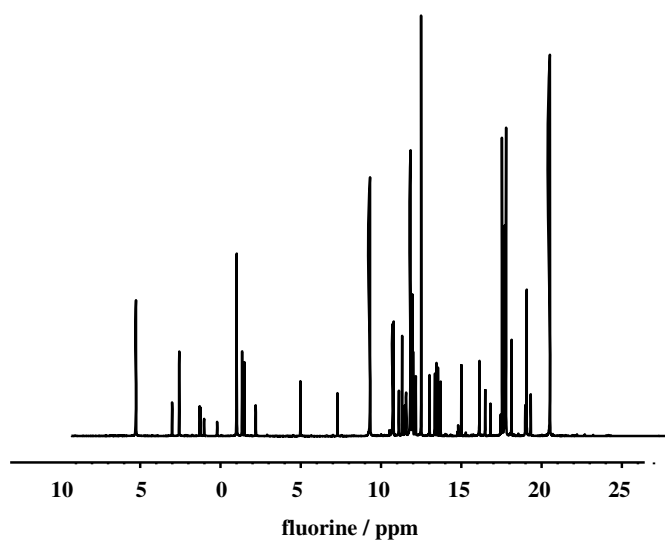The same procedure gave the $^2D_{CF}$ and $^2J_{CF}$ couplings to have the same sign, and so both couplings are positive.

Fig. 3. 338 MHz ^{19}F spectrum of a sample of 1-bromo-2-iodo-tetrafluoroethane dissolved in the mixed nematic solvent ZLI 1132/ZLI 1167.

The values of the dipolar and scalar couplings are given in Table 2.

4. Conformational analysis

4.1. General considerations

The aim is to use the observed dipolar couplings, $D_{ij}(\text{obs})$, obtained by assuming that all the values of J_{ij}^{aniso} are negligible in magnitude, to determine the form of $V(\phi)$, the potential for rotation about the C–C bond, and some, but not all the bond lengths and angles. The values of $D_{ij}(\text{obs})$ are averages over rotation through the angle ϕ 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

$$D_{ij}(\text{obs}) = \int D_{ij}(\beta,\gamma,\phi) P_{LC}(\beta,\gamma,\phi) \sin\beta\, d\beta\, d\gamma\, d\phi, \quad (5)$$

where $P_{LC}(\beta,\gamma,\phi)$ is the probability that the bond rotation angle is between ϕ and $\phi + d\phi$ when the director lies in the intervals β and $\beta + d\beta$ and γ and $\gamma + d\gamma$ relative to a reference frame fixed in the molecule. To carry out the averaging in Eq. (5) it is necessary to adopt a model for $P_{LC}(\beta,\gamma,\phi)$, and to do this it is convenient to define a mean potential, $U_{LC}(\beta,\gamma,\phi)$, as

$$U_{LC}(\beta,\gamma,\phi) = U_{\text{ext}}(\beta,\gamma,\phi) + U_{\text{iso}}(\phi), \quad (6)$$

such that

$$P_{LC}(\beta,\gamma,\phi) = Z^{-1}\exp[-U_{LC}(\beta,\gamma,\phi)/k_B T], \quad (7)$$

where $U_{\text{iso}}(\phi)$ is the mean energy which depends on the conformation but not on the orientation of the molecule in the liquid crystalline phase. It refers to the liquid crystalline phase, but it is expected to be virtually identical to $V(\phi)$, which for rotation about one bond is usually represented as a truncated Fourier series

$$V(\phi) = \sum_n V_n \cos n\phi. \quad (8)$$

The term $U_{\text{ext}}(\beta,\gamma,\phi)$ in Eq. (6) is a totally anisotropic contribution to the mean potential, and so it vanishes in the isotropic phase, and Z is the normalisation factor,

$$Z = \int \exp[-U_{LC}(\beta,\gamma,\phi)/k_B T] \sin\beta\, d\beta\, d\gamma\, d\phi. \quad (9)$$

Note that there are two, distinct conformational probabilities, $P_{\text{iso}}(\phi)$, which refers to the molecule in the liquid crystalline solvent, but in an isotropic environment, and $P_{LC}(\phi)$ which is for the liquid crystalline phase. They are given by

$$P_{\text{iso}}(\phi) = Q_{\text{iso}}^{-1}\exp[-V(\phi)/k_B T], \quad (10)$$

with

$$Q_{\text{iso}} = \int \exp[-V(\phi)/k_B T]\, d\phi, \quad (11)$$

and

$$P_{LC}(\phi) = Q_{LC}^{-1} \int \exp[-U_{LC}(\beta,\gamma,\phi)/k_BT] \sin\beta \, d\beta \, d\gamma \quad (12)$$

with

$$Q_{LC} = \int \exp[-U_{LC}(\beta,\gamma,\phi)/k_BT] \sin\beta \, d\beta \, d\gamma \, d\phi. \quad (13)$$

In general, $P_{iso}(\phi)$ and $P_{LC}(\phi)$ are not equal.

In the additive potential (AP) method [14], $U_{ext}(\beta,\gamma,\phi)$ is written as

$$U_{ext}(\beta,\gamma,\phi) = -\varepsilon_{2,0}(\phi)C_{2,0}(\beta) - 2\mathrm{Re}\varepsilon_{2,2}(\phi)C_{2,2}(\beta,\gamma), \quad (14)$$

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

$$\varepsilon_{2,m}(\phi) = \sum_q \sum_p \varepsilon_{2,p}(q) D^2_{p,m}(\Omega_{q\phi}), \quad (15)$$

and $D^2_{p,m}(\Omega_{q\phi})$ is the Wigner matrix describing the orientation of fragment q, in the conformation defined by ϕ, relative to a molecular reference frame.

The values of $D_{ij}(obs)$ must be corrected for the averaging effects of small amplitude vibrational motion to give $D_{ij}(equil)$

$$D_{ij}(obs) = D_{ij}(equil) + D_{ij}(vib), \quad (16)$$

which refer to the molecule in the equilibrium geometry, and which can be calculated by adopting a geometry for the molecule, and values for the $\varepsilon_{2,p}(q)$, and V_n. The calculated $D_{ij}(equil)$ are then brought into best agreement with $D_{ij}(obs) - D_{ij}(vib)$ by varying some, or all of these factors. The ideal case for application of the AP method is when it is reasonable to assume that the geometry is independent of ϕ, and there are sufficient dipolar couplings between nuclei within each of the q rigid sub-units so that the relative positions of the interacting nuclei i and j within a rigid sub-unit can be determined from

$$\begin{aligned} D_{ij}(equil) = & -\left(K_{ij}/r_{ij}^3\right)[S_{aa}(q)(3\cos^2\theta_{ija}-1) \\ & + (S_{bb}(q) - S_{cc}(q))(\cos^2\theta_{ijb} - \cos^2\theta_{ijc}) \\ & + 4S_{ab}(q)\cos\theta_{ija}\cos\theta_{ijb} + 4S_{ac}(q) \\ & \times \cos\theta_{ija}\cos\theta_{ijc} + 4S_{bc}(q)\cos\theta_{ijb}\cos\theta_{ijc}] \end{aligned} \quad (17)$$

with

$$K_{ij} = (\mu_0/4\pi)h\gamma_i\gamma_j/8\pi^2. \quad (18)$$

The $S_{\alpha\beta}(q)$ are local order parameters for the qth sub-unit, $\mathbf{r}_{ij}$ is the vector connecting nuclei i and j whose orientation relative to reference axes (abc) fixed in q is defined by the angles θ_{ija}, etc. This situation does not apply to the ethanes studied here, nor to ethane-like fragments in more complicated aliphatic chains. It is necessary, therefore, to use the whole of the set of $D_{ij}(obs)$ to test models for the geometry,

the form of the potential, and the method for constructing the potential of mean torque.

5. Structure and conformation of 1,2-dibromo-1,1-difluoroethane

5.1. Are the dipolar couplings obtained for 1,2-dibromo-1,1-difluoroethane consistent with the geometry and bond-rotation potential calculated by the DFT method?

The geometry of 1,2-dibromo-1,1-difluoroethane was calculated by the DFT method B3LYP/6-311+G*, as implemented in the Gaussian program suite [22], with full geometry optimization at 10° steps in ϕ between 0° and 180°. The energies obtained were used to obtain $V(\phi)$ as a 4-term Fourier series

$$V(\phi) = V_0 + V_1\cos\phi + V_2\cos 2\phi + V_3\cos 3\phi, \quad (19)$$

with the coefficients V_n given in Table 3. The bond lengths and angles for the optimized structure at the lowest energy, *trans* ($\phi = 180°$) are also given in Table 3. Calculations were also done with the MP2/6-311+G* method, and the results obtained are given in Table 3. The differences between the geometries and the rotation potential obtained

Table 3
Bond lengths and angles obtained for 1,2-dibromo,1,1-difluoroethane in the *trans* conformation by MP2/6-311+G* and B3LYP/6-311+G* calculations. The Fourier components V_n for rotation about the C–C bond are also given
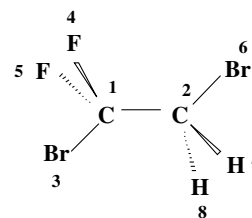
	MP2/6-311+G*	B3LYP/6-311+G*
Bond lengths (Å)		
r_{CC}	1.503	1.514
r_{CF}	1.415	1.345
r_{CH}	1.087	1.086
r_{C1Br}	1.985	1.985
r_{C2Br}	1.982	1.966
Bond angles (°)		
θ_{412}	111.6	112.3
τ_{4123}	120.3	119.2
θ_{721}	109.4	109.8
τ_{7126}	118.7	119.2
θ_{312}	112.1	108.4
θ_{621}	110.9	112.2
Potential coefficients (kJ mol^{-1})		
V_0	15.19	15.15
V_1	2.35	4.66
V_2	−0.35	0.67
V_3	12.12	10.65
ϕ_g	61°	63°
$P_{trans}/\%$	74	84

give an indication of the reliability of these calculations. The only major difference is in the values of the C–F bond length.

It is essential when using the AP method to decide on which fragment interaction parameters, $\varepsilon_{2,p}(q)$ to use to construct the conformationally dependent potential of mean torque. This choice is not unique, and to obtain a set which can be optimized in the procedure of fitting calculated to observed couplings is not obvious for substituted alkanes. For the molecule 1-chloro-2-bromo-ethane
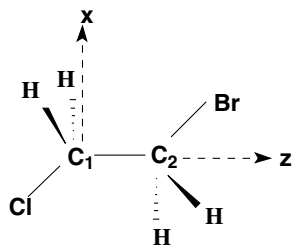
stable iterations were possible with ε_{zz} and $\varepsilon_{xx} - \varepsilon_{yy}$ for the fragment containing the reference xyz frame, plus $\varepsilon_{\text{Cl–Br}}$ directed along the Cl–Br direction [10]. A similar choice was tried for 1,2-dibromo-1,1-difluoroethane, that is ε_{zz} and $\varepsilon_{xx} - \varepsilon_{yy}$ plus $\varepsilon_{\text{Br–Br}}$ but without success: the rms error

$$R = \sum_{i<j} [D_{ij}(obs) - D_{ij}(calc)]^2 / N, \tag{20}$$

where $D_{ij}(calc)$ is the value of $[D_{ij}(equil) + D_{ij}(vib)]$ calculated for a trial geometry, could not be reduced to zero even when the number of observed couplings, N, was equal to the number of variable parameters. The probable reason for this difference is that the conformational dependence of the orientational order of 1-chloro-2-bromo-ethane is determined almost entirely by the orientation of the Cl–Br direction, but for 1,2-dibromo-1,1-difluoroethane the situation is more complex. However, adding an interaction parameter $\varepsilon_{47} = \varepsilon_{58}$, and reducing the other variables by one, does give a set which produces stable, convergent iterations in the fitting procedure.

The values of $D_{ij}(vib)$ were obtained by assuming that only small-amplitude, harmonic vibrations contribute to the vibrational force field, and the latter, together with the vibrational frequencies, was calculated by the DFT method with the B3LYP/6-311+G* functional, as described in detail for 1-chloro-2-bromo-ethane [10].

The analysis of the spectra showed that the couplings $D_{47} = D_{58}$ cannot be distinguished from $D_{48} = D_{57}$. It is expected that the calculated geometry and rotation potential are close to the correct values, and so may be used to calculate dipolar couplings which should be close to those observed. The couplings in doubt were omitted from the data set, and calculated couplings were brought into best agreement with those observed by iterating on the four interaction parameters to give the results shown in Table 4, which shows that the most probable assignment is with $D_{47} > D_{48}$, and this will be used in all calculations.

Table 4
Values of $D_{ij}(equil)$ and $D_{ij}(vib)$ (in Hz) calculated for 1,2-dibromo-1,1-difluoroethane with the geometry and bond rotational potential obtained by the B3LYP/6-311+G* method, and brought into best agreement with those observed by varying the four interaction parameters ε_{zz}, $\varepsilon_{xx} - \varepsilon_{yy}$, $\varepsilon_{47} = \varepsilon_{58}$, and $\varepsilon_{\text{Br–Br}}$
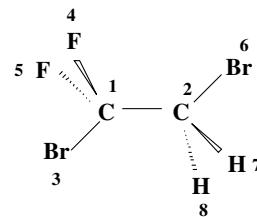
i,j	$D_{ij}(equil)$	$D_{ij}(vib)$	$D_{ij}(equil) + D_{ij}(vib)$	$D_{ij}(vib)/D_{ij}(equil)/\%$
1,4	924.8	−8.1	916.7	−0.9
1,7	113.6	0.6	114.2	0.5
2,4	94.8	0.0	94.8	0.0
2,7	1827.5	−94.4	1733.1	−5.2
4,5	850.0	−3.8	846.2	−0.4
4,7*	317.0	1.5	318.5	0.5
4,8*	197.9	−1.2	196.7	−0.6
7,8	1760.4	−53.7	1706.7	−3.1

The couplings D_{47}, D_{48}, D_{57}, and D_{58} were excluded from the fitting process.
* Excluded from the data set.

The vibrational corrections to couplings involving the ^{19}F nucleus are considerably smaller than those involving ^{1}H, thus $^1D_{\text{CF}}(vib)/^1D_{\text{CF}}(equil) = -0.9\%$, whilst $^1D_{\text{CH}}(vib)/^1D_{\text{CH}}(equil) = -5.2\%$, similarly $^2D_{\text{FF}}(vib)/^2D_{\text{FF}}(equil) = -0.5\%$, and $^2D_{\text{HH}}(vib)/^2D_{\text{HH}}(equil) = -3.0\%$. This reflects the dependence of the vibrational amplitudes on $m^{-\frac{1}{2}}$, where m is the atomic mass.

The results in Table 4 show that the observed dipolar couplings are not consistent with the combination of the geometry and bond rotational potential obtained by the DFT calculation, and the same is true when the MP2/6-311+G* results are used.

5.2. Optimising the geometry of 1,2-dibromo-1,1-difluoroethane with the bond rotational potential fixed at that calculated by the DFT method

When the rotational potential is fixed it is possible to bring observed and calculated dipolar couplings into exact agreement by varying the four interaction coefficients ε_{zz}, $\varepsilon_{xx} - \varepsilon_{yy}$, $\varepsilon_{47} = \varepsilon_{58}$, and $\varepsilon_{\text{Br–Br}}$, and the angles $\theta_{412} = \theta_{512}$, $\tau_{4123} = -\tau_{5123}$, $\theta_{721} = \theta_{821}$, $\tau_{7216} = -\tau_{8216}$, with all the bond lengths fixed at the values obtained by the DFT calculation for the *trans* conformer. The results are shown in Table 5, where the values obtained for the angles are compared with those calculated by the DFT method.

It can be concluded therefore that neglecting any contributions to the total anisotropic couplings T_{FF} and T_{CF} from $J_{\text{FF}}^{\text{aniso}}$ and $J_{\text{CF}}^{\text{aniso}}$, and fixing the bond rotational potential at the form calculated by the DFT method does give a

Table 5
The angles defining the positions of the ^1H and ^{19}F nuclei in 1,2-dibromo-1,1-difluoroethane determined by bringing observed and calculated dipolar couplings into agreement using the AP method and fixing the C–H and C–F bond lengths and the rotation potential at values calculated by the B3LYP/6-311+G* method
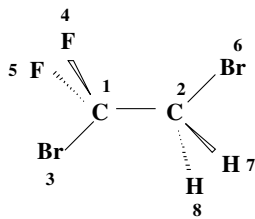
	NMR	DFT
Angles (°)		
θ_{412}	114.8	112.3
τ_{4123}	117.4	119.2
θ_{721}	110.1	109.8
τ_{7126}	117.9	119.2
Interaction parameters (kJ mol^{-1})		
ε_{zz}	3.02	
$\varepsilon_{xx} - \varepsilon_{yy}$	−0.27	
$\varepsilon_{Br–Br}$	2.07	
$\varepsilon_{47} = \varepsilon_{58}$	−1.22	

reasonable, but not necessarily correct, structure for the molecule.

5.3. The effect of changing the conformational distribution in 1,2-dibromo-1,1-difluoroethane

Is it possible to fit the dipolar couplings by fixing the geometry at that calculated by the DFT method and changing the rotational potential, $V(\phi)$? It is well established that rotational potentials can be affected by the nature of the phase (solid, liquid, and gas), or by the solvent for a dissolved molecule [4]. It is not easy to explore this question by allowing the Fourier coefficients to vary since each of the main features of $V(\phi)$ depend in a complex way on all the values of V_n. An alternative approach, proposed originally by Celebre et al. [23], is to use a model for the probability, $P_{iso}(\phi)$, which for a substituted ethane is a sum of three gaussian functions centered at $\phi = 180°$, and $180° \pm m_g°$

$$P_{iso}(\phi) = \frac{A}{\left(2\pi h_t^2\right)^{\frac{1}{2}}} \exp\left[-\frac{(\phi - 180)^2}{2h_t^2}\right] + \frac{\frac{1}{2}(1-A)}{\left(2\pi h_g^2\right)^{\frac{1}{2}}}$$
$$\times \left\{ \exp\left[-\frac{(\phi - 180 + m_g)^2}{2h_g^2}\right] \right.$$
$$\left. + \exp\left[-\frac{(\phi - 180 - m_g)^2}{2h_g^2}\right] \right\}, \quad (21)$$

where ϕ is the (3126) dihedral angle.

The parameter A defines the relative intensities of the _trans_ and _gauche_ forms and h_t and h_g are the half-width at half height of the gaussian functions. The DFT

Table 6
The percentage of the _trans_ conformer, A, and the angles defining the positions of the ^{19}F nuclei, and r_{CF}, the C–F bond length in 1,2-dibromo-1,1-difluoroethane determined by bringing observed and calculated dipolar couplings into agreement using the AP method and fixing $h_t \cong h_g = 11$ Hz, and $m_g = 63°$, and the geometry of the fragment C–CH$_2$Br at that calculated by the B3LYP/6-311+G* method
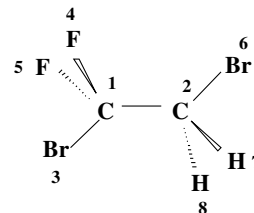
	NMR	DFT
Angles (°)		
θ_{412}	115.5	112.3
τ_{4123}	119.3	119.2
Bond length (Å)		
r_{CF}	1.373	1.345
trans conformer (%)	73	84
Interaction parameters (kJ mol^{-1})		
ε_{zz}	3.59	
$\varepsilon_{xx} - \varepsilon_{yy}$	−0.37	
$\varepsilon_{Br–Br}$	2.39	
$\varepsilon_{47} = \varepsilon_{58}$	−1.47	

calculation of $V(\phi)$ predicts that $h_t \cong h_g = 11$ Hz, and $m_g = 63°$. The ratio of _trans_ to _gauche_ forms is predicted to be 0.84 by B3LYP and 0.74 by MP2. It is not possible to get an acceptable fit to the data by fixing the geometry at the DFT structure and varying A, $h_t = h_g$, and m_g.

It is possible to fit the data by fixing $h_t \cong h_g = 11$ Hz, and $m_g = 63°$, and the structure of the C–CH$_2$Br group at that calculated by the DFT method and varying the two angles, the C–F bond length and the proportion of the _trans_ conformer, with results shown in Table 6.

The bond length obtained of 1.373 Å is between those calculated by the DFT and MP2 methods, and is within the range of values obtained for other fluorinated alkanes [24], and the percentage found for the _trans_ conformer of 73% is very close to that calculated of 74% by the MP2 method. The value obtained for θ_{412} from the NMR data of 115.5° is significantly larger than the value of 112.3° calculated by the DFT method, which may be a genuine difference between these two methods of obtaining the structure, or it may originate from a contribution of J_{FF}^{aniso} and J_{CF}^{aniso} to the observed values of T_{FF} and T_{CF}.

5.4. Possible contributions of J_{FF}^{aniso} and J_{CF}^{aniso} to the anisotropic couplings in 1,2-dibromo-2,2-difluoroethane

If it is assumed that the DFT geometry is correct, but the rotational potential is changed by dissolving the molecule in the liquid crystalline solvent, then differences between observed and calculated dipolar couplings reveal contributions of the anisotropies in spin–spin coupling.

A calculation was made with the DFT geometry, fixing $h_t \cong h_g = 11$ Hz, and $m_g = 63°$, and varying ε_{zz}, $\varepsilon_{xx} - \varepsilon_{yy}$, $\varepsilon_{47} = \varepsilon_{58}$, ε_{Br-Br} and the fraction of the *trans* form to bring the five dipolar couplings D_{17}, D_{27}, D_{47}, D_{48}, and D_{78} into best agreement. This did not produce exact agreement, as might be expected when there are 5 variables to fit to 5 dipolar couplings, which shows that the variables are not truly independent. The values of $\Delta_{ij}^{aniso} = \{D_{ij}(\text{obs}) - [D_{ij}(\text{equil}) + D_{ij}(\text{vib})]\}/D_{ij}(\text{obs})$ obtained are: $\Delta_{14}^{aniso} = -18\%$, $\Delta_{24}^{aniso} = -19\%$ and $\Delta_{45}^{aniso} = -22\%$. These values are reduced to -9%, -17%, and -10% if the C–F bond length is increased to 1.373 Å, but are still an order of magnitude larger than the fractional anisotropies in fluoromethanes [12]. This suggests that a part, at least, of $D_{XF}(\text{obs}) - [D_{XF}(\text{equil}) + D_{XF}(\text{vib})]$, where $X = C$ or F, arises from a difference between the geometry calculated for the isolated molecule and that appropriate for the condensed phase.

It is interesting to explore the effect on the parameters obtained by the procedure which gives the results in Table 6, but allowing a contribution of J_{FF}^{aniso} and J_{CF}^{aniso} to the values of T_{FF} and T_{CF} of $\pm 1\%$, as suggested by the study of the fluorinated methanes [12]. Doing so produces values of r_{CF}, θ_{412} and τ_{4123} in the ranges $r_{CF} = 1.371–1.410$ Å, $\theta_{412} = 115.1–115.9°$, and $\tau_{4123} = 118.8–119.8°$, whilst the amount of the *trans* form varies from 71 to 76%. Clearly it is possible that neglecting the contributions of the anisotropies in spin–spin coupling does have a significant effect on the derived structural parameters, but note that the large discrepancy between the NMR and DFT values for θ_{412} persists when this approximate allowance is made for contributions of the anisotropies in the spin–spin couplings.

The only firm conclusion that can be reached for 1,2-dibromo-1,1-difluoroethane is that the magnitudes of the contributions to the total anisotropic couplings T_{FF} and T_{CF} from J_{FF}^{aniso} and J_{CF}^{aniso} cannot be detected unless both the geometry and rotational potential are known from another source.
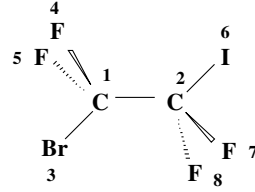
6. 1-Bromo-2-iodo-tetrafluoroethane

6.1. Fitting the dipolar couplings of 1-bromo-2-iodo-tetrafluoroethane to the geometry and rotational potential calculated by quantum chemical methods

The structure and bond rotational potential of the tetra-fluorinated ethane were calculated by both MP2 and B3LYP methods. In the case of B3LYP the 6-311+G* basis set was used for all the atoms except for the iodine. For the latter, the best available basis set in the Gaussian on-line data base was the 6-311G [22]. For the MP2 calculations the basis set used was 6-21G for all the atoms.

The geometries of the *trans* form calculated by these methods are shown in Table 7, together with the calculated Fourier coefficients, V_n, of the rotational potential. The vibrational force field was calculated by the B3LYP method and so the geometry and rotational potential

Table 7
Bond lengths, angles and the Fourier coefficients, V_n, obtained for 1-dibromo-2-iodo-tetrafluoroethane in the *trans* conformation by MP2/6-21G and B3LYP/6-311+G* calculations

	MP2/6-21G	B3LYP/6-311+G*
Bond lengths (Å)		
r_{CC}	1.530	1.558
r_{CF14}	1.384	1.341
r_{CF27}	1.379	1.343
r_{CBr}	1.985	1.960
r_{CI}	2.205	2.198
Bond angles (°)		
θ_{412}	108.4	109.5
τ_{4123}	120.9	120.5
θ_{721}	109.0	109.3
τ_{7216}	120.4	120.7
θ_{312}	110.8	111.2
θ_{621}	111.8	111.8
Fourier coefficients (kJ mol^{-1})		
V_0	23.6 ± 0.2	16.8 ± 0.1
V_1	14.1 ± 0.3	6.4 ± 0.1
V_2	2.6 ± 0.3	1.9 ± 0.1
V_3	11.6 ± 0.3	12.4 ± 0.1
ϕ_g	$70°$	$65°$

obtained by this method will be used in the attempts to fit the dipolar couplings. Note that as with 1,2-dibromo-1,1-difluoroethane, the DFT method predicts a considerably shorter C–F bond length than the MP2 calculations.

As with the difluoro compound, it was found that a similar set of four interaction parameters, ε_{zz}, $\varepsilon_{xx} - \varepsilon_{yy}$, ε_{Br-I}, and $\varepsilon_{47} = \varepsilon_{58}$ were necessary for stable iterations. With the geometry and the bond rotation potential fixed at the values calculated by the DFT method, it was not possible to bring calculated dipolar couplings into agreement with those observed. Note, that as with 1,2-dibromo-1,1-difluoroethane, the vibrational corrections are small (vide infra), and do not alter this conclusion.

It was also not possible to bring observed and calculated couplings into good agreement by keeping the bond rotational potential fixed and varying the geometry. However, using the gaussian potential approach (Eq. (21)), and allowing the proportion in the *trans* form to vary, with $h_t = h_g = 10$ Hz, the value which matches the linewidth of the conformer probability distribution calculated by the DFT method, and varying the angles $\theta_{721} = \theta_{821}$, $\tau_{7216} = \tau_{8216}$ and the bond distance $r_{14} = r_{15} = r_{27} = r_{28}$ brings observed and calculated couplings into exact agreement, with the fitting parameters given in Table 8.

For molecules which are weakly ordered in the liquid crystalline solvent, which is the present case, $P_{LC}(\phi) \approx P_{iso}(\phi)$, and so both distributions are essentially a single Gaussian

Table 8
The bond angles and C–F bond lengths, the fragment interaction parameters, $\varepsilon_{2,m}(q)$, the proportion, P_{trans}, for 1-bromo-2-iodo-tetrafluoroethane dissolved in the nematic solvent ZLI 1132, which bring calculated dipolar couplings into exact agreement with those observed
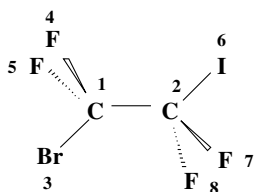
	NMR	DFT
Bond lengths (Å)		
r_{CF14}	1.341 (fixed)	1.341
r_{CF27}	1.379	1.343
Bond angles (°)		
θ_{412}	109.5 (fixed)	109.5
τ_{4123}	120.5 (fixed)	120.5
θ_{721}	105.7	109.3
τ_{7216}	119.2	120.7
Interaction parameters (kJ mol⁻¹)		
ε_{zz}	8.75	
$\varepsilon_{xx} - \varepsilon_{yy}$	−23.29	
ε_{Br-I}	13.84	
$\varepsilon_{47} = \varepsilon_{58}$	1.12	
Potential parameters		
% *trans*	100	84
h, (fixed)/Hz	10	10

with a maximum at the *trans* position. Constraining all the C–F bond lengths to be equal to 1.373 Å, the value found for the difluoro compound, produces only a small degradation in the fit of the calculated to observed dipolar couplings, and to small changes in the geometrical parameters, and the conformer distribution function is still predicted to be centered on the *trans* position.

The value obtained for θ_{721} of 105.7° is significantly different from that of 109.3° calculated by the DFT method, and although this may be revealing a real discrepancy between the two methods of determining the structure, it may also be indicating that J_{FF}^{aniso} and J_{CF}^{aniso} have significant magnitudes.

6.2. Possible contributions of J_{FF}^{aniso} and J_{CF}^{aniso} to the anisotropic couplings in 1-bromo-2-iodo-tetrafluoroethane

Assuming the geometry obtained by the DFT method is correct, except for the C–F bond lengths, allows values of J_{FF}^{aniso} and J_{CF}^{aniso} to be obtained. Fitting the eight observed couplings by fixing the geometry at the DFT values, but with all the C–F bond lengths equal to 1.373 Å, and varying the four interaction parameters and A, the fraction of the *trans* form, gave the values of $\Delta_{ij}^{aniso} = J_{ij}^{aniso}/D_{ij}(\text{obs})$ shown in Table 9.

The large values of Δ_{17}^{aniso} and Δ_{24}^{aniso} for the two-bond compared with the one-bond C–F couplings could simply reflect the relatively small magnitudes of D_{17} and D_{24}. Thus, although both J_{ij}^{aniso} and D_{ij} values depend on the

Table 9
The values of $[\Delta_{ij}^{aniso} = \{D_{ij}(\text{obs}) - [D_{ij}(\text{equil}) + D_{ij}(\text{vib})]\}/D_{ij}(\text{obs})]/\%$ for 1-bromo-2-iodo-tetrafluoroethane dissolved in the nematic solvent ZLI 1132 obtained with the bond angles fixed at those calculated by the DFT method, but with all C–F bond lengths equal to 1.373 Å
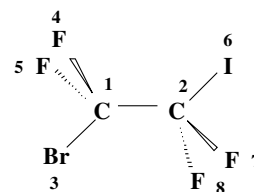
i,j	$[\Delta_{ij}^{aniso} = \{D_{ij}(\text{obs}) - [D_{ij}(\text{equil}) + D_{ij}(\text{vib})]\}/D_{ij}(\text{obs})](\%)$
1,4	−1
1,7	−7
2,4	6
2,7	−1
4,5	−1
4,7	0
4,8	0
7,8	1

The gaussian probability distribution was used with $h_t \cong h_g = 10$ Hz, and $m_g = 65°$. The variables were the interaction coefficients ε_{zz}, $\varepsilon_{xx} - \varepsilon_{yy}$, $\varepsilon_{47} = \varepsilon_{58}$, ε_{Br-I} and A, the fraction of the *trans* form, which was found to be 100%.

molecular ordering, the tensors J_{ij}^{aniso} and D_{ij} do not have the same principal axes, and this means that it is possible for J_{ij}^{aniso} to remain finite when D_{ij} is zero. The ratio Δ_{ij}^{aniso} can therefore depend strongly, and non-linearly, on the absolute value of the dipolar coupling.

7. Conclusions

There is no clear evidence of a significant contribution of the anisotropy in the J couplings in either of the two molecules studied here. There are differences between the geometries determined from the dipolar couplings obtained by assuming all values of J_{ij}^{aniso} to be zero and those calculated by the DFT method, but these are no greater than those obtained for 1-chloro-2-bromoethane, for which anisotropies in the J couplings are not expected to have significant magnitudes. It is perhaps surprising that values of Δ_{FF}^{aniso} and Δ_{CF}^{aniso} are considerably larger for 1,2-dibromo-2,2-difluoroethane than for 1-bromo-2-iodo-tetrafluorethane, and of course this may reflect differences in the ability of the DFT calculations to determine the geometry of the molecules in solution. Another reason for this large difference could be that in both the molecules the values obtained for Δ_{FF}^{aniso} and Δ_{CF}^{aniso} are averages over the rotation about the C–C bond. Both NMR and DFT calculations for the difluoro compound predict a substantial amount of the gauche forms, whereas for the tetra fluoro compound the NMR data are consistent with a distribution centered wholly on the *trans* form. There has yet to be any theoretical predictions for the dependence of J_{ij}^{aniso} on a bond rotational angle.

The methodology described here for obtaining the geometry and conformational distribution of a substituted ethane does involve several important assumptions, as well

as the neglect of contributions of J_{ij}^{aniso}: (i) only harmonic vibrational corrections are significant, and these can be approximated for a non-rigid molecule by the values calculated at the minimum energy positions alone; (ii) solvent–solute interactions may affect the rotational potential, but not the bond lengths and angles, and last but not least, (iii) that the conformational dependence of orientational order is described correctly by the *AP* model.

All these assumptions need to be tested by further studies on simple molecules to see if they lead to geometries and conformational distributions which can be regarded as reasonable.

It should also be noted that for some small, rigid molecules, the geometries derived from partially averaged dipolar couplings obtained from NMR spectra of samples dissolved in a range of liquid crystalline solvents seem to be solvent-dependent [2,25,26]. This probably is not a true variation of structure with solvent, but stems from a correlation between vibrational and molecular reorientational motion [2,27]. The possibility that this phenomenon is important for the two fluorinated ethanes studied here cannot be excluded from data obtained on a single solvent at a single temperature. Again this points to the importance of repeating the analysis described here for simple, flexible molecules in a range of liquid crystalline solvents.

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