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The structure of 2,2'-difluorobiphenyl in solid crystalline and liquid crystalline phases

by B. ALDRIDGE, G. DE LUCA, M. EDGAR, S. J. EDGAR, J. W. EMSLEY*,
M. I. C. FURBY and M. WEBSTER

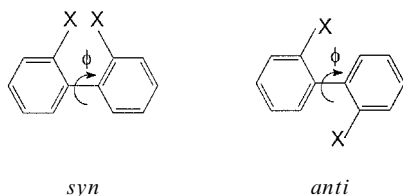
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(Received 21 August 1997; accepted 17 October 1997)

The structure of 2,2'-difluorobiphenyl in the solid, crystalline phase has been determined by X-ray diffraction. In this phase the molecules are all in a single conformation having the two fluorine nuclei in a *syn*-arrangement, with the two ring normals at 58° to one another. The structure of the same molecule, but dissolved in a liquid crystalline solvent has been investigated by NMR spectroscopy. In the liquid crystalline phase there is rotation about the inter-ring bond through an angle ϕ , with a probability distribution $P(\phi)$ which has an absolute maximum at the *syn*-form with ϕ about 51° . There is also a second maximum in $P(\phi)$ at about 130° , corresponding to the *anti*-form. The *syn*- and *anti*-forms are present in the approximate ratio 0.58:0.42.

1. Introduction

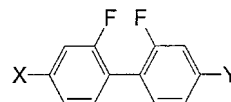
The barrier to rotation about the inter-ring bond in biphenyl is unusual in having a strong dependence on sample phase. In the crystalline solid the molecule is planar and rigid (neglecting small amplitude vibrational motion), whilst in the gas phase there is rotation about the inter-ring bond, with a minimum in the rotational potential at $\phi_{\min} = 45^\circ$, and the potential is symmetric about $\phi = 90^\circ$. The bond rotational motion is still present when biphenyl is dissolved in liquid crystalline solvents [1], but ϕ_{\min} changes to between 34 and 38° . Introducing substituents at the 2- and 2'-positions will in principle destroy the symmetry of the bond rotational potential about 90° , and there may be more than one minimum in the interval $0^\circ < \phi < 180^\circ$, with the twisted *syn*- and *anti*-minima being of different energy.



An X-ray study of 2,2'-dichlorobiphenyl as a crystalline solid showed that the molecules are all in a single conformation with $\phi = 66.8^\circ$ (defined as the angle between the ring normals) [2]. This molecule was also studied as a gaseous sample by electron diffraction, and the data could be interpreted by assuming only the *syn*-form is

present, and ϕ has increased to about 70° [2]. The other 2,2'-dihalogeno derivatives have also been studied as gaseous samples by electron diffraction, and in each case the data were interpreted with the *syn*-form as the only conformer.

The interest in the effect of 2,2'-substitution has been enhanced by the synthesis of compounds of general structure



which have liquid crystalline phases. The molecule 2,2'-difluorobiphenyl (DFBP) has also been the subject of a quantum mechanical study which predicted the bond rotational potential [3]. This concluded that the bond rotational potential has minima at $\phi = 57^\circ$ and 129° , with *syn* being 0.8 kJ mol^{-1} lower in energy. This has prompted us to investigate the structure of DFBP as a crystalline solid by X-ray diffraction, and as a solute in a liquid crystalline solvent by NMR spectroscopy; the results of these investigations are reported here.

2. X-ray investigation of the crystalline solid

2.1. Experimental

Crystals of 2,2'-difluorobiphenyl (Fluorochem Ltd) were obtained from ethanol by slow evaporation and a fragment suitable for X-ray examination obtained by cleavage. Data were collected at 150 K using a Rigaku AFC7S diffractometer equipped with Mo radiation and graphite monochromator. Cell dimensions were obtained from 25 reflections ($35.3^\circ < 2\theta < 43.6^\circ$); no

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decay was observed in the check reflections and the structure was solved by direct methods [4]. Hydrogen atoms were located in the electron density maps and introduced into the model with their positions refined and using a common isotropic thermal parameter. An extinction parameter was also refined, and full-matrix least-squares refinement [5] on F^2 using neutral atom complex scattering factors converged to $R = 0.031$ [492

observed reflections, $I > 2\sigma(I)$]. Crystallographic details are presented in table 1, and tables 2 and 3 give the final atomic coordinates and bond lengths/angles, respectively.

2.2. Discussion of the crystal structure

The structure consists of the expected discrete molecules (figure 1 and table 3). The asymmetric unit consists of a half molecule with the two phenyl residues related by

Table 1. Crystallographic data for 2,2'-difluorobiphenyl.

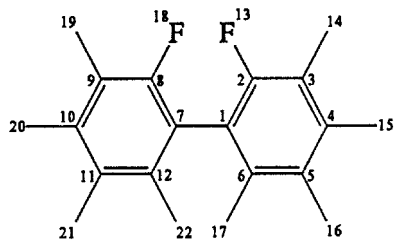
Empirical formula	$C_{12}H_8F_2$
Formula weight	190.18
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	$Fdd2$ (no. 43)
Unit cell dimensions/Å	$a = 12.898(4)$, $b = 23.395(5)$, $c = 5.789(4)$
Volume	$1746.9(13) \text{Å}^3$
Z	8
Density (calculated (150 K))	1.446 Mg m^{-3}
Absorption coefficient (μ)	0.113 mm^{-1}
$F(0\ 0\ 0)$	784
Crystal size	$0.90 \times 0.35 \times 0.20 \text{ mm}$
Theta range for data collection	3.48 to 27.47 degrees
Index ranges ($h\ k\ l$)	0–15, 0–28, 0–7
Reflections collected	541
Independent reflections	541
Refinement method	Full-matrix least-squares on F^2
Type of data collection	$\omega/2\theta$
Abs correction	ψ -scan (3 reflections)
Weighting scheme (w^{-1})	$\sigma^2(F_0^2) + (AP)^2 + BP$; $A = 0.054$, $B = 1.42$ and $P = [\text{Max}(F_0^2, 0) + 2F_c^2]/3$
Data/restraints/parameters	541/1/78
Max shift/error	0.002
Goodness-of-fit on F^2	1.056
R indices [$I > 2\sigma(I)$] ^a	$R1 = 0.031$, $wR2 = 0.082$ (492 refs)
R indices (all data)	$R1 = 0.037$, $wR2 = 0.087$ (541 refs)
Extinction coefficient	0.004(1)
Largest diffraction peak and hole	0.215 and $-0.168 \text{ e \AA}^{-3}$

$$^a R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; wR2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^4]^{1/2}$$

Table 2. Atomic coordinates and isotropic temperature factors ($\times 10^3$).

Atom	x/a	y/b	z/c	$U/\text{Å}^2$
F(13)	0.0015(1)	0.06063(5)	0.4376(2)	29.3(7) ^a
C(1)	$-0.0476(1)$	0.01787(8)	0.7904(3)	20.1(10) ^a
C(2)	$-0.0686(1)$	0.05571(8)	0.6115(3)	22.8(10) ^a
C(3)	$-0.1556(2)$	0.09037(9)	0.6061(4)	27.1(10) ^a
C(4)	$-0.2255(2)$	0.08679(9)	0.7870(4)	27.8(11) ^a
C(5)	$-0.2079(2)$	0.04968(9)	0.9694(4)	27.0(10) ^a
C(6)	$-0.1191(2)$	0.01540(8)	0.9715(4)	23.6(10) ^a
H(14)	$-0.1635(19)$	0.1147(12)	0.4798(68)	35(4)
H(15)	$-0.2851(21)$	0.1100(11)	0.7833(55)	35(4)
H(16)	$-0.2530(23)$	0.0474(12)	1.0815(61)	35(4)
H(17)	$-0.1033(20)$	$-0.0100(11)$	1.1039(71)	35(4)

^aEquivalent isotropic temperature factor from anisotropic atom.

Table 3. Bond lengths, r_{ij} , and angles, θ_{ijk} , for 2,2'-difluorobiphenyl in the crystalline solid.

Bond length		Bond angle			
i, j	$r_{ij}/\text{\AA}$	i, j, k	$\theta_{ijk}/^\circ$	i, j, k	$\theta_{ijk}/^\circ$
2,13	1.358(2)	2,1,6	117.2(2)	4,5,6	120.0(2)
1,2	1.389(3)	2,1,7	121.4(2)	4,5,16	120(2)
1,6	1.398(3)	6,1,7	121.5(2)	6,5,16	120(2)
1,7	1.485(4)	13,2,3	118.2(2)	5,6,1	120.7(2)
2,3	1.385(3)	13,2,1	118.5(2)	5,6,17	121(2)
3,4	1.385(3)	3,2,1	123.3(2)	1,6,17	118(2)
4,5	1.386(4)	2,3,4	118.4(2)		
5,6	1.398(3)	2,3,14	118(2)		
3,14	0.93(4)	4,3,14	124(2)		
4,15	0.94(3)	3,4,5	120.5(2)		
5,16	0.87(3)	3,4,15	119(2)		
6,17	0.99(4)	5,4,15	121(2)		

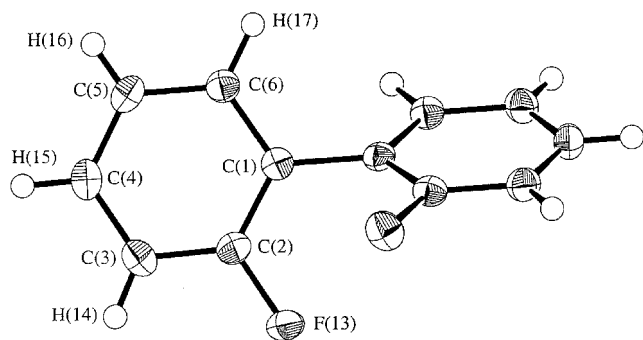


Figure 1. Discrete molecule of 2,2'-difluorobiphenyl in the crystal structure showing the thermal ellipsoids at the 50% probability level.

a two-fold axis and the two planar phenyl groups [maximum deviation 0.003(1) Å] are inclined to each other with a dihedral angle of 58°. The F substituent lies out of the phenyl plane by 0.047(3) Å and the two fluorine atoms of the molecule are in the *syn*- rather than *anti*-positions. There is no evidence for disorder in the structure and it was not possible to establish the absolute configuration of the selected crystal. The structure is isomorphous with the disordered 2-fluorobiphenyl [6].

3. NMR investigation of a sample dissolved in a nematic liquid crystalline solvent

3.1. NMR experiments

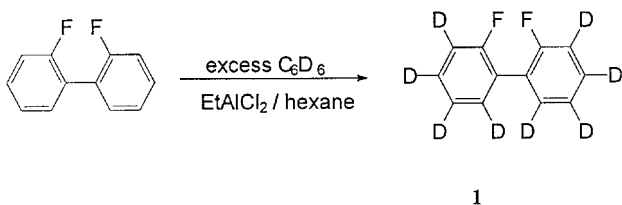
The spectra were recorded on approximately 5 wt % solutions in the liquid crystalline solvents with a Bruker MSL 200 spectrometer. Two liquid crystalline solvents were used, both being mixtures which have a nematic phase at temperatures conveniently close to room temperature, and both available from Merck Ltd. One solvent, ZLI 1167, was chosen because it does not contain aromatic groups, which enabled $^{13}\text{C}\{-^1\text{H}\}$ spectra of DFBP to be obtained. These spectra proved to have interesting general features, and their analysis is discussed elsewhere [7]. Dipolar couplings, D_{ij}^{CF} , were obtained and are given in table 4. The $^1\text{H}\{-^2\text{H}\}$, and ^2H spectra of the ZLI 1167 sample were also recorded and their analysis to yield D_{ij}^{HH} and D_{ij}^{HF} is discussed here. The other solvent used was ZLI 1132, which does contain aromatic groups and so is not useful for ^{13}C NMR of the solute, but it does give well-resolved proton spectra.

3.2. Synthesis of deuteriated samples

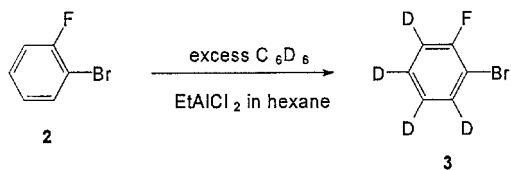
The proton and fluorine spectra of DFBP in liquid crystalline solvents are very complex, and have so far defied analysis. The spectra may be simplified by using partially deuteriated samples, followed by deuterium decoupling.

Table 4. D_{ij}^{CF} and D^{FF} obtained from the $^{13}\text{C}\{-^1\text{H}\}$ spectra of a sample of 2,2'-difluorobiphenyl dissolved in ZLI 1167 [7].

i, j	$D_{ij}^{\text{CF}}/\text{Hz}$	i, j	D^{FF}/Hz
1,13	-166.2 ± 0.1	13,18	27.5 ± 0.5
1,18	18.8 ± 0.1		
2,13	-275.7 ± 0.1		
2,18	63.7 ± 0.1		
3,13	306.9 ± 0.1		
3,18	46.9 ± 0.1		
4,13	47.5 ± 0.1		
4,18	37.6 ± 0.1		
5,13	-7.5 ± 0.1		
5,18	41.1 ± 0.1		
6,13	-48.6 ± 0.1		
6,18	52.2 ± 0.1		

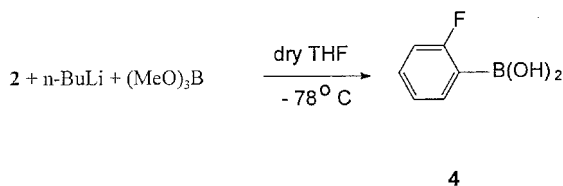
3.2.1. Preparation of 2,2'-difluorobiphenyl-*d*₈

Ethyl aluminium dichloride catalyst (3 ml of a 50% solution in hexane, Aldrich Chemical Co. Ltd) was added by syringe under nitrogen to a stirred solution of DFBP (3 g) dissolved in C₆D₆ (30 ml). The solution was stirred at room temperature for 48 h, and then the excess of catalyst was removed by adding D₂O (2 ml). The mixture was shaken with ether (2 × 50 ml), and the combined organic extracts were dried overnight with MgSO₄. The MgSO₄ was removed by filtration and washed with ether; the solvent was subsequently removed under vacuum to give a yellow product **1** (2.55 g). The ¹H spectrum of **1** showed a deuterium content of approximately 90%.

3.2.2. Synthesis of 2,2'-difluoro-3,4,5,6-tetradeuterio-biphenyl (**5**)

The preparation of compound **3** from starting material **2** followed the same recipe as for **1**, and gave 2.88 g of product. The level of deuteriation however was too low, and it was increased by adding 25 ml of C₆D₆ and 2.5 ml of catalyst to the crude product and repeating the procedure. The final level of deuteriation was approximately 95%.

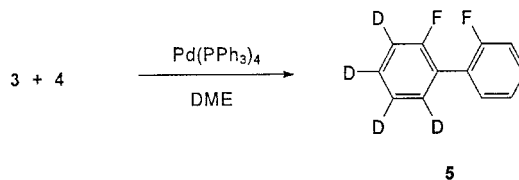
The boronic acid derivative **4** was then prepared from **2**:



n-Butyl lithium (30 ml, 1.6 M in hexane) was added dropwise to a stirred, cooled (−78°C) solution of **2** (4.10 g) in dry THF (42 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 3 h, and then a pre-cooled solution of trimethyl borate (5.15 g) in dry THF was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature overnight and HCl added (10%,

32 ml); the mixture was stirred for 1 h, shaken with ether (2 × 50 ml) and the combined ether extracts were washed with water and dried (MgSO₄). After filtration the solvent was removed under vacuum to yield colourless crystals of **4** (3.2 g).

The final step was the reaction of **3** with **4**:



A solution containing **4** (0.727 g), **3** (0.700 g), Pd(PPh₃)₄ (0.153 g), DME (10 ml), ethanol (3 ml) and Na₂CO₃ (2M, 7.8 ml) was stirred at room temperature overnight. The completion of the reaction was checked by TLC. The product, **5**, was extracted into ether (2 × 50 ml), and the extract washed with brine and dried (MgSO₄). After filtration, the solvent was removed under vacuum, and the brown product was purified using a silica separating column (silica in petrol/DCM solvent).

3.3. Analysis of the NMR spectra

Figure 2 shows the ¹H-²H spectrum of DFBP-*d*₈ dissolved in ZLI 1132. The spectrum originates from the 10% of molecules containing protons, and at this level of deuteriation the most abundant isotopomers contain one proton per molecule. Thus, there are four ABX spin systems (*X* ≡ H), each of which gives four lines of measurable intensity, whose separations yield $|(J_{AX} + 2D_{AX})|$ and $|(J_{BX} + 2D_{BX})|$. The values of *J*_{AX} and *J*_{BX} have been obtained for a solution of DFBP in CDCl₃, and these were used here to obtain the dipolar couplings.

In order to assign the lines in figure 2 it was necessary to consider the deuterium spectrum from the same

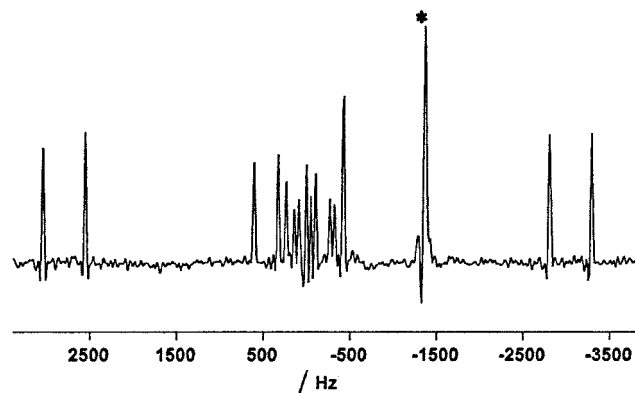
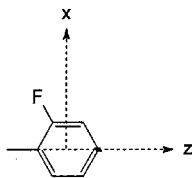


Figure 2. 200 MHz ¹H-²H spectrum of a sample of 2,2'-difluorobiphenyl randomly deuteriated to 90% overall ²H content and dissolved in the nematic liquid crystalline solvent ZLI 1132. The peak * is from an impurity.

sample (figure 3). The quadrupolar splittings, $\Delta\nu_i$, for a deuterium at the i th site in the rigid fragment are related to local order parameters, $S_{\alpha\beta}^R$, and $l_{xai}^2 = \cos^2 \theta_{xai}$, where θ_{xai} is the angle between axis a and x at the i th site, by

$$\begin{aligned} \Delta\nu_i = & 3/4q_{CDi}\{S_{zz}^R(3l_{zai}^2 - 1) + \eta_i l_{zbi}^2\} \\ & + 1/3(S_{xx}^R - S_{yy}^R)(l_{xai}^2 + \eta_i(l_{xbi}^2 + 1)) \\ & + 2S_{xz}^R(l_{zai}^2 l_{xai}^2 - 1/2l_{xbi}^2 l_{zbi}^2 + \eta_i l_{zbi}^2 l_{xbi}^2) \end{aligned} \quad (1)$$

where q_{CDi} is the component of the quadrupolar tensor along the C–D bond (the a axis), and the asymmetry parameter $\eta_i = (q_{bb} - q_{cc})/q_{CDi}$. The xyz axes are with y parallel to the normal to the ring plane.



The abc axes are principal axes for the quadrupolar tensor. At this stage in the analysis, the ring can be assumed to have a regular hexagon structure, q_{CDi} can be set equal to 182 kHz and η_i to zero for each site. This simplifies equation (1) to

$$\begin{aligned} \Delta\nu_{14} = \Delta\nu_{17} = & -34.125S_{zz}^R + 34.125(S_{xx}^R - S_{yy}^R) \\ & + 177.314S_{xz}^R \\ \Delta\nu_{16} = & -34.125S_{zz}^R + 34.125(S_{xx}^R - S_{yy}^R) \\ & - 177.314S_{xz}^R \\ \Delta\nu_{15} = & 273.00S_{zz}^R. \end{aligned} \quad (2)$$

The pair of lines with the maximum quadrupolar splittings arises from the deuterons at position 15, since it can be confidently predicted that the molecule will align so as to give S_{zz}^R large and positive. This enables S_{zz}^R to be estimated. The lines from position 14 have a large dipolar splitting from the interaction with the adjacent fluorine, and a smaller splitting from the coupling to the fluorine at 18. This can be seen in the deuterium spectrum, and enables $\Delta\nu_{14}$ to be assigned. The quadrupolar splitting closest in magnitude is then assigned to $\Delta\nu_{17}$. The remaining lines are then assigned to $\Delta\nu_{16}$. Choosing the signs of the quadrupolar splittings (table 5) then enables a set of order parameters to be obtained. These can be used to calculate the dipolar couplings between the nuclei in the rigid fragment from

$$\begin{aligned} D_{ij} = & -(\mu_0/4\pi)\gamma_i\gamma_j h[S_{zz}^R(3l_{zij}^2 - 1) \\ & + (S_{xx}^R - S_{yy}^R)l_{xij}^2 + 4S_{xz}^R l_{xij}^2 l_{zij}^2]/8\pi^2 r_{ij}^3 \end{aligned} \quad (3)$$

where r_{ij} is the magnitude of the distance between i and j . It then proved possible to choose a set of signs for the quadrupolar splittings which yield a set of dipolar

couplings which predict a proton spectrum close to that in figure 2, allowing the peaks to be assigned, and giving the dipolar couplings in table 6.

Figure 4 shows the $^1\text{H}\{-^2\text{H}\}$ spectrum from a sample of DFBP- d_4 (compound 5) dissolved in ZLI 1132. The dipolar couplings between all the nuclei within the rigid fragment are predicted from equation (3) with the order parameters obtained from the deuterium spectrum. These were used as starting parameters in an iterative analysis of the observed spectrum. The $^1\text{H}\{-^2\text{H}\}$ spectrum, however, also depends on D^{FF} , whose value could not be predicted in this way since it depends on the averaging by rotation about the inter-ring bond. To overcome this problem, a value of D^{FF} was estimated by scaling the value of 27.5 Hz obtained from the ^{13}C spectrum of the sample dissolved in ZLI 1167 by the ratio of the order parameters S_{zz} . The order parameter for the ZLI 1132 solution was at first taken to be -2 times that obtained for the sample dissolved in ZLI 1167. This is a good approximation, but it is not exact. An iterative analysis of the $^1\text{H}\{-^2\text{H}\}$ spectrum then gave values for all the intra-ring couplings, which could be used to obtain a better estimate for S_{zz} by the procedure discussed in more detail later, and hence to a new estimate for D^{FF} . Re-analysing the proton spectrum of the ZLI 1132 spectrum gave a new set of intra-ring couplings (shown in table 7) which in fact are very close to those obtained with the original estimate of D^{FF} . The procedure used to estimate D^{FF} is reasonable, since the molecular order parameters for the two samples are very similar, but they will not be identical. The low sensitivity of the intra-ring couplings to small changes in D^{FF} , however, ensure that the data in table 7 are reliable. The same procedure was followed to analyse the spectra given by the sample dissolved in ZLI 1167; the parameters are given in table 7.

3.4. Derivation of the structure and bond rotational potential

The three sets of dipolar couplings, comprising the single set obtained from the carbon spectra for a sample dissolved in ZLI 1167 and those extracted from analysing the d_4 isotopomer in both solvents, will be used separately to determine the structure and bond rotational potential. The procedure used, however, is identical in each case. First, the couplings between nuclei in the rigid fragment are used together with equation (3) to obtain a geometry for this fragment, and a set of local order parameters. This geometry is then kept fixed, and the full set of couplings used to characterize the bond rotational potential. To do this it is necessary to consider how the dipolar couplings are averaged by the combination of the motion of the whole molecule relative to the liquid crystal director, with the bond rotational

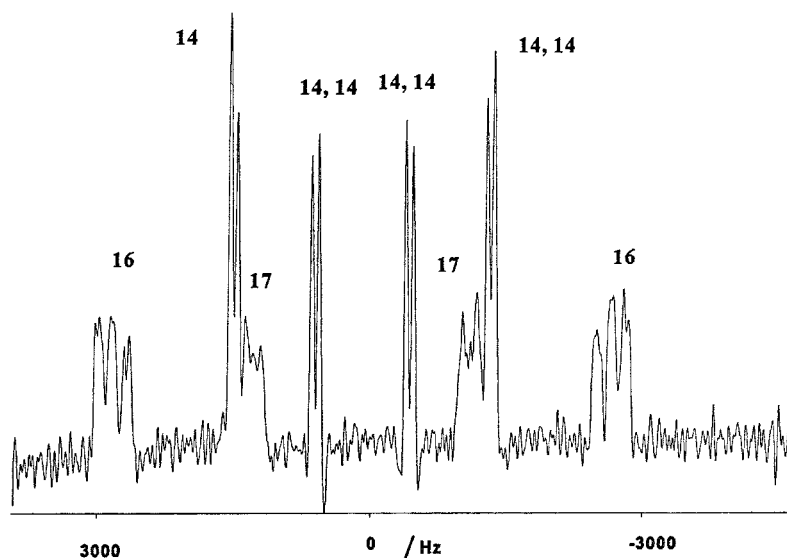
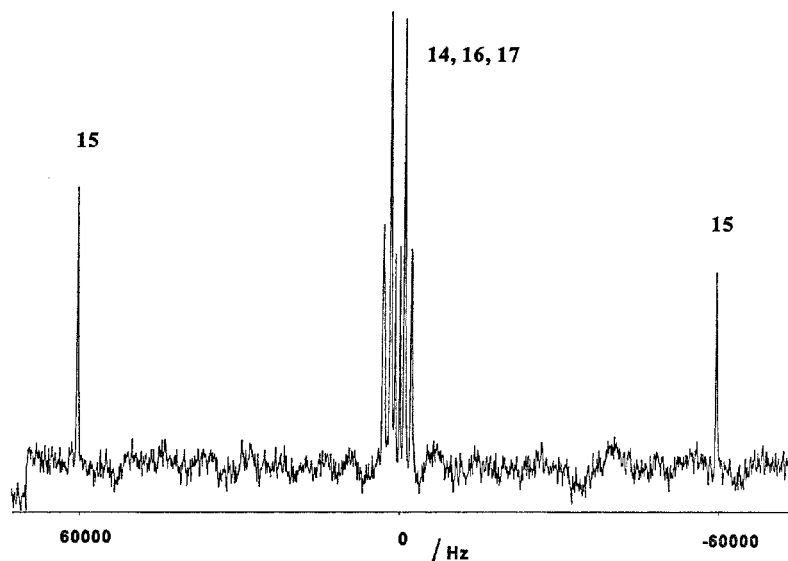


Figure 3. 30.7 MHz ^2H spectra of a sample of 2,2'-difluorobiphenyl randomly deuteriated to 90% overall ^2H content and dissolved in the nematic liquid crystalline solvent ZLI 1132.

motion. Thus:

$$D_{ij} = \int D_{ij}(\beta, \gamma, \phi) P_{\text{LC}}(\beta, \gamma, \phi) \sin \beta d\beta d\gamma d\phi \quad (4)$$

where $D_{ij}(\beta, \gamma, \phi)$ is the value of the dipolar coupling for the molecule in a fixed conformation, specified by ϕ , and with the director having polar angles β and γ in a molecular reference frame. $P_{\text{LC}}(\beta, \gamma, \phi)$ is the probability density for the molecule in this conformation and orientation. In order to calculate averaged couplings from equation (4) it is necessary to adopt a model for $P_{\text{LC}}(\beta, \gamma, \phi)$, and here the Additive Potential (AP) model has been used [9]. In this model a mean potential, $U_{\text{LC}}(\beta, \gamma, \phi)$, is defined by

$$P_{\text{LC}}(\beta, \gamma, \phi) = Z^{-1} \exp\{-U_{\text{LC}}(\beta, \gamma, \phi)/RT\} \quad (5)$$

with

$$Z = \int \exp[-U_{\text{LC}}(\beta, \gamma, \phi)/RT] \sin \beta d\beta d\gamma d\phi. \quad (6)$$

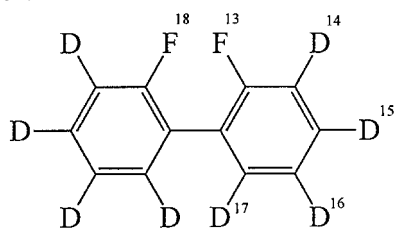
The mean potential is then divided into a potential of mean torque, $U_{\text{ext}}(\beta, \gamma, \phi)$, which vanishes in the isotropic phase, and an internal potential, $U_{\text{int}}(\phi)$, which does not.

$$U_{\text{LC}}(\beta, \gamma, \phi) = U_{\text{ext}}(\beta, \gamma, \phi) + U_{\text{int}}(\phi). \quad (7)$$

In the AP model $U_{\text{ext}}(\beta, \gamma, \phi)$ is written as

$$U_{\text{ext}}(\beta, \gamma, \phi) = -\varepsilon_{2,0}(\phi) C_{2,0}(\beta, \gamma) - 2\varepsilon_{2,2}(\phi) C_{2,2}(\beta, \gamma) \quad (8)$$

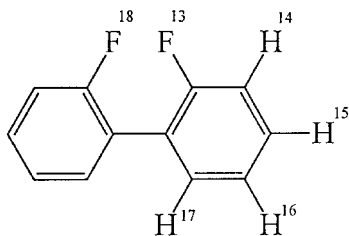
Table 5. The magnitude of the quadrupolar splittings, $|\Delta\nu_i|$, and the total spin–spin coupling constants $|T_{ij}|$ for the deuterons in 2,2'-difluorobiphenyl- d_8 dissolved in ZLI 1132.



Quadrupolar splittings		Spin–spin coupling constants		
i	$ \Delta\nu_i /\text{Hz}$	i, j	$ T_{ij} (\text{HF})$	J_{ij}/Hz^a
14	1925 ± 20	13,14	896.5 ± 0.5	1.5
15	120055 ± 20	14,18	76.0 ± 0.5	0.0
16	5478 ± 20			
17	2547 ± 20			

^aScaled by 0.1535 ($=\gamma_D/\gamma_H$) from the values of J_{HF} .

Table 6. Magnitude, $|T_{ij}|$, of the total spin–spin coupling constants obtained from the $^1\text{H}\{-^2\text{H}\}$ NMR spectrum of the sample of 2,2'-difluorobiphenyl- d_8 dissolved in ZLI 1132.



i, j	$ T_{ij} /\text{Hz}$	J_{ij}/Hz^a
13,14	3847 ± 5	10.0
14,18	488 ± 5	0.0
13,15	654 ± 3	4.96
15,18	367 ± 3	0.0
13,16	54 ± 1	-0.16
16,18	405 ± 1	0.0
13,17	423 ± 2	8.34
17,18	318 ± 2	0.0

^aFrom reference [8].

and the conformationally dependent interaction parameters, $\varepsilon_{2,m}(\phi)$, are constructed as a sum of contributions, $\varepsilon_{2,p}(j)$, from each of the j rigid fragments in the molecule:

$$\varepsilon_{2,m}(\phi) = \sum_I \sum_P \varepsilon_{2,p}(j) D_{p,m}^2(\Omega_j) \quad (9)$$

where $D_{p,m}^2(\Omega_j)$ is the Wigner matrix describing the orientation of the j th fragment in the molecular reference frame.

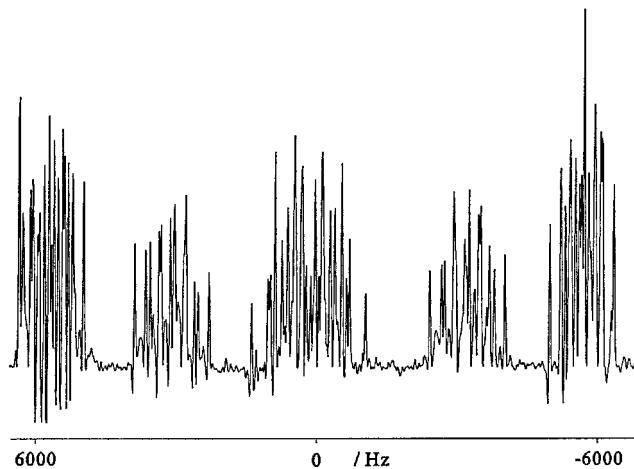


Figure 4. 200 MHz $^1\text{H}\{-^2\text{H}\}$ spectrum of a sample of 2,2'-difluorobiphenyl- d_4 (compound 5) dissolved in the nematic liquid crystalline solvent ZLI 1132.

Knowing $P_{LC}(\beta, \gamma, \phi)$ allows the orientational order parameters and their conformational dependence to be calculated, and of particular relevance here, it is also possible to obtain $P_{LC}(\phi)$, the probability density for bond rotation, as

$$P_{LC}(\{\phi\}) = Z^{-1} \int \exp[-U_{LC}(\beta, \gamma, \phi)/RT] \sin \beta d\beta d\gamma. \quad (10)$$

The probability distribution refers to the molecule in the liquid crystalline phase, and it is also possible to obtain $P_{iso}(\phi)$, the probability for an isotropic sample at the same temperature:

$$P_{iso}(\phi) = Q^{-1} \exp[-U_{int}(\phi)/RT] \quad (11)$$

with

$$Q = \int \exp[-U_{int}(\phi)/kT] d\phi. \quad (12)$$

For DFBP there are two identical rigid sub-units to be considered when constructing $U_{ext}(\beta, \gamma, \phi)$ from equations (8) and (9), and symmetry dictates that there must be three non-zero values of $\phi_{2,p}(j)$. It is convenient in fact to consider the fragment to be composed of two parts: the aromatic ring which requires $\varepsilon_{2,0}^R$ and $\varepsilon_{2,2}^R$, and the C–F bond, which requires just $\varepsilon_{2,0}^{CF}$. It is also more convenient for the calculations to use Cartesian tensors, thus:

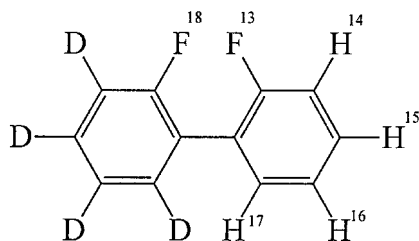
$$\varepsilon_{2,0}^R = (3/2)^{1/2} \varepsilon_{zz}^R \quad (13)$$

$$\varepsilon_{2,2}^R = 1/2(\varepsilon_{xx}^R - \varepsilon_{yy}^R) \quad (14)$$

$$\varepsilon_{2,0}^{CF} = (3/2)^{1/2} \varepsilon_{aa}^{CF} \quad (15)$$

where a is directed along the C–F bond.

Table 7. Chemical shifts, δ_i , dipolar couplings, D_{ij}^{HH} and D_{ij}^{HF} , obtained from the analysis of the $^1\text{H}\{-^2\text{H}\}$ spectrum of samples of 2,2'-difluorobiphenyl- d_4 (compound 5) dissolved in the nematic solvents ZLI 1167 and ZLI 1132.



<i>i</i>	δ_i/Hz	
	ZLI 1132	ZLI 1167
17	69.5 ± 3.5	38.2 ± 2.6
16	19.1 ± 4.0	-12.1 ± 2.6
15	215.9 ± 0.8	-42.5 ± 0.8
14	0.0 ± 0.7	0.0 ± 0.6

<i>i, j</i>	J_{ij}/Hz^a	D_{ij}/Hz	
		ZLI 1132	ZLI 1167
16,17	8.0	-3758.0 ± 0.8	1636.9 ± 0.5
15,17	2.0	-485.9 ± 0.4	212.3 ± 0.5
15,16	8.0	24.6 ± 0.4	-12.7 ± 0.5
14,17	0.0	5.8 ± 0.4	-2.9 ± 0.3
14,16	2.0	279.3 ± 0.4	-114.9 ± 0.3
13,17	8.34	222.3 ± 0.7	-97.6 ± 0.7
13,16	-0.16	38.8 ± 0.7	-12.6 ± 0.7
17,18	0.0	-180.1 ± 0.6	80.9 ± 2.5
16,18	0.0	-212.1 ± 0.6	96.5 ± 2.5
14,15	8.0	252.5 ± 0.4	-95.9 ± 0.4
13,15	4.96	-342.8 ± 0.6	153.3 ± 0.8
15,18	0.0	-201.7 ± 0.6	89.0 ± 0.8
13,14	10.0	-3155.2 ± 0.7	1377.9 ± 0.7
14,18	0.0	-269.6 ± 0.6	117.2 ± 0.6
13,18	16.6	-63.3 ± 1.2	27.5 ± 0.5

^aFrom reference [9] and kept fixed in the analysis.

The internal potential, $U_{\text{int}}(\phi)$, is expressed as:

$$U_{\text{int}}(\phi) = V_0 + V_1 \cos \phi + V_2 \cos 2\phi + V_4 \cos 4\phi + U_{\text{steric}}. \quad (16)$$

The $\cos n\phi$ terms are the minimum number which give a potential with the correct rotational symmetry. The term U_{steric} is included to allow for the contributions of short range repulsion and attractive forces, and is approximated as

$$U_{\text{steric}} = \sum_{ij} E_{ij} [(A_{ij}/r_{ij})^{12} - (A_{ij}/r_{ij})^6]. \quad (17)$$

The summation is over only those pairs of atoms whose distances depend on ϕ . The A_{ij} and E_{ij} terms are

constructed from values A_i and E_i [10, 11]

$$E_{ij} = E_i + E_j \quad (18)$$

$$A_{ij} = (A_i A_j)^{1/2}. \quad (19)$$

A_i and E_i depend only on the type of atom, and they were fixed at the values given in table 8.

The general procedure is to vary ϵ_{zz}^R , $(\epsilon_{xx}^R - \epsilon_{yy}^R)$, $\epsilon_{aa}^{\text{CF}}$, V_1 , V_2 and V_4 in order to bring calculated values of D_{ij} into agreement with those observed. Note that V_0 simply adjusts the minimum value of the potential to zero, and its value does not affect the orientational probability distributions.

4. Characterization of the structure and bond rotational potential from the D_{ij}^{CF} and D_{ij}^{FF}

4.1. Structure of the rigid fragment

There are seven values of D_{ij}^{CF} between the C and F nuclei in the rigid ring fragment, and these depend on 16 coordinates and three order parameters. It is not possible, therefore, to obtain all the carbon and fluorine coordinates from the data, and most of them must be assumed from other evidence. Calculations were done with all the atomic coordinates fixed at the values determined for the crystalline sample, which are shown in table 2. This produced small, but significant deviations, Δ_{ij} , between the observed and calculated values. A similar calculation was done with the geometry obtained by the molecular orbital method (see figure 5), and the Δ_{ij} are similar to those found using the X-ray structure. In both cases the deviations can be appreciably reduced by changing the position of the F atom. To do this the C-F bond was fixed at 1.35 Å and the F atom rotated in the xy plane about C2 as the origin. This gave the results shown in table 9. The refined geometries are shown in figure 5. The displacement of the F atom is small, and so too are the Δ_{ij} , and so further geometrical refinement was not attempted.

4.2. Bond rotational potential

The averages of the D_{ij}^{CF} and D_{ij}^{FF} over the bond rotation were calculated from equation (4) and brought into agreement with those observed by varying ϵ_{zz}^R , $\epsilon_{xx}^R - \epsilon_{yy}^R$, $\epsilon_{aa}^{\text{CF}}$, and the parameters defining the bond rotational potential, $U_{\text{int}}(\phi)$. Calculations were per-

Table 8. Values of the coefficients E_i and A_i used to describe the repulsive term in the bond rotational potential.

<i>i</i>	$A_i/\text{\AA}$	$E_i/\text{kJ mol}^{-1}$	Ref.
H	2.42	0.03	[10]
C	3.55	0.07	[10]
F	2.94	0.06	[11]

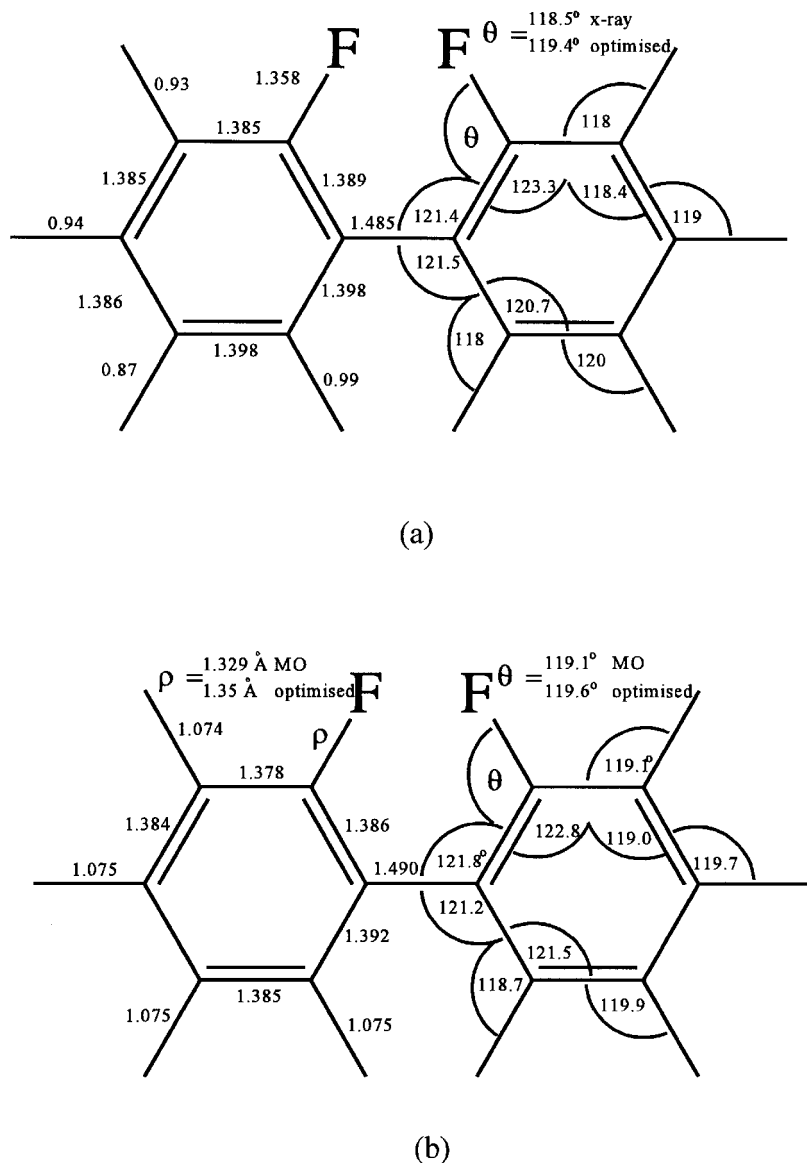


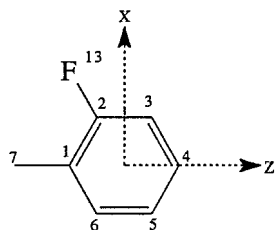
Figure 5. The bond lengths and angles derived from (a) the X-ray diffraction of the solid crystal and (b) the molecular orbital calculations [3].

formed using both the X-ray and MO geometries. These produced almost identical results for $P_{LC}(\phi)$, and so only the calculations with the MO geometry are discussed here. Three methods for obtaining $P_{LC}(\phi)$ were tested. The simplest kept the bond lengths and angles fixed, and the steric term in $U_{int}(\phi)$ was omitted. The second method also used a fixed geometry, but the steric term was included. In reality the geometry will change as ϕ varies in order to allow for steric repulsions. The MO calculations explored this effect by optimizing the geometry at several values of ϕ , and an appreciable change was found, particularly with ϕ close to 0° or 180° . In the third method a simple allowance for this geometrical change was made by expressing the angle $\theta = C_1C_2F$ as

$$\begin{aligned} \theta/\text{deg} = & 120.1 + 0.45 \cos \phi + 1.6 \cos 2\phi \\ & + 0.3 \cos 3\phi + 0.35 \cos 4\phi. \end{aligned} \quad (20)$$

This produces a change which closely matches that calculated. In fact, the probability distributions obtained with inclusion of the steric term in $U_{int}(\phi)$, but with and without the inclusion of angle relaxation, are almost identical. This is because the major changes in the calculated dipolar couplings are only when ϕ is close to 0° or 180° , and these positions have very low probabilities. The results for this third method are not therefore considered any further. The agreement between observed and calculated D_{ij}^{CF} and D^{FF} is equally good for the first two methods, as shown in table 10, which also gives the optimized fitting parameters. The first point to note is that the $P_{LC}(\phi)$ obtained by the two methods are very similar and so only that obtained with the inclusion of the steric term is shown in figure 6. Note too that the difference between $P_{LC}(\phi)$ and $P_{iso}(\phi)$ is negligible, and so only the former is shown.

Table 9. The deviations $\Delta_{ij} = D_{ij}(\text{observed}) - D_{ij}(\text{calculated})$, the order parameters and the coordinates of the carbons and fluorine in the rigid fragment of 2,2'-difluorobiphenyl determined by bringing observed and calculated D_{ij}^{CF} and D_{ij}^{FF} for the solution in ZLI 1167 into best agreement. The positions of the carbons were fixed at either those determined by X-ray or the molecular orbital (MO) calculation [3].



Order parameter	Geometry	
	X-ray	MO
S_{xx}	0.0883 ± 0.0005	0.0876 ± 0.0001
S_{xz}	0.0108 ± 0.0002	0.0086 ± 0.0002
S_{yy}	0.1345 ± 0.0002	0.1335 ± 0.0002
S_{zz}	-0.2228 ± 0.0001	-0.2211 ± 0.0003

i	$x/\text{\AA}$	$z/\text{\AA}$	$x/\text{\AA}$	$z/\text{\AA}$
1	0.0	0.7425	0.0	0.7448
2	-1.1822	1.4698	-1.1777	1.4748
3	-1.2233	2.8542	-1.2014	2.8522
4	-0.0251	3.5488	-0.0020	3.5446
5	1.1733	2.8713	1.1971	2.8504
6	1.1928	1.4735	1.1903	1.4657
7	0.0	-0.7425	0.0	-0.7448
13	-2.3711	-0.8114	-1.3627	0.8281
	± 0.0001	± 0.0010	± 0.0001	± 0.0005

i, j	Δ_{ij}/Hz	D_{ij}/Hz	Δ_{ij}/Hz	D_{ij}/Hz
1,13	0.1	-186.1	0.1	-186.1
2,13	-0.1	-275.7	-0.1	-275.7
3,13	-0.2	306.7	-0.2	306.7
4,13	1.2	48.7	1.1	48.6
5,13	-0.6	-8.1	-0.6	-8.1
6,13	-0.2	-48.8	-0.3	-48.9
7,13	0.1	18.8	0.1	18.8

The data in table 10 reveal that $P_{\text{LC}}(\phi)$ is peaked at two positions corresponding to the *syn*-form, with ϕ as $50\text{--}51^\circ$, being the most probable form ($55\text{--}58\%$); the *anti*-form, with ϕ as $129\text{--}132^\circ$, is also appreciably populated (about $42\text{--}45\%$). These populations are the integrals of $P_{\text{LC}}(\phi)$ between 0° and 90° for *syn*, and 90° and 180° for *anti*.

5. Characterization of the structure and bond rotational potential from the D_{ij}^{HH} and D_i^{HF}

5.1. Structure of the rigid fragment

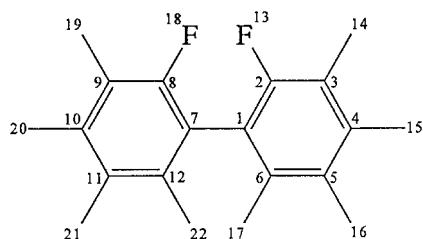
The independent set of couplings obtained from the analysis of the samples dissolved in ZLI 1132 or ZLI 1167 are given in table 7, and it is seen that only four individual intra-ring couplings are well determined. This means that there is insufficient information to determine the relative positions of the protons and the fluorines within the rigid phenyl fragment. The C–H bond lengths determined by the X-ray experiments are very different from those calculated by the molecular orbital method. It has been pointed out that the positions of hydrogen atoms show a systematic difference when determined by X-ray rather than neutron diffraction, the X-ray experiments yielding C–H bond lengths on average 0.096\AA shorter [12, 13]. This is because the scattering centre for X-rays is displaced from the position of the hydrogen nucleus. The systematic error in the position of the protons determined by X-rays is revealed by the NMR data. Thus, fixing the protons at the positions found by X-rays, the F atom at the location which fits the C–F couplings and varying the three order parameters to fit the four well determined D_{ij}^{HF} gave large errors, Δ_{ij}^{HF} , between observed and calculated couplings.

Repeating the calculation, but with the proton positions from the MO calculation, gave much smaller values of Δ_{ij}^{HF} , and these are shown in table 11 for both sets of dipolar couplings. The much better agreement between observed and calculated couplings obtained for the ZLI 1132 as opposed to the ZLI 1167 spectra simply reflects the different degrees to which these spectra are deceptively simple. The positions of the protons determined by the MO calculations were used in all subsequent calculations.

5.2. Bond rotational potential

The inter-ring D_{ij}^{FH} couplings plus the four independent intra-ring D_{ij}^{HF} obtained from the spectral analyses of the samples dissolved in the two liquid crystalline solvents were used to explore the shape of the bond rotational potential. As noted earlier, the spectra do not yield a value of D^{FF} directly, and so the analysis of the bond rotational potential was carried out with and without the inclusion of the estimate made for this coupling. The set of calculated D_{ij}^{HH} , D_{ij}^{HF} and D^{FF} were brought into agreement with those observed by varying the same parameters as used with D_{ij}^{CF} and D^{FF} as data. The same three methods of obtaining $P_{\text{LC}}(\phi)$ were explored, that is with and without the steric term in $U_{\text{int}}(\phi)$, and with and without geometry relaxation. The forms of $P_{\text{LC}}(\phi)$ obtained by all these calculations are very similar, and so the only results given are for those

Table 10. Results of bringing observed and calculated D_{ij}^{CF} and D^{FF} obtained for the sample in ZLI 1167 into agreement by varying ε_{zz}^R , $\varepsilon_{xx}^R - \varepsilon_{yy}^R$, ε_{aa}^{CF} , V_1 , V_2 and V_4 . A=no steric term; B=with steric term.



i, j	$D_{ij}(\text{obs})/\text{Hz}$	Δ_{ij}/Hz	
		A	B
1,13	-186.2	0.2	0.2
2,13	-275.7	0.1	-0.1
3,13	306.9	0.1	-0.1
4,13	47.5	1.2	1.2
5,13	-7.5	-0.6	-0.6
6,13	-48.6	-0.2	-0.2
7,13	18.8	0.1	0.1
8,13	63.7	0.1	0.1
9,13	46.9	-0.4	-0.2
10,13	37.6	-0.9	-0.9
11,13	41.1	-0.2	-0.6
12,13	52.2	0.1	0.3
13,18	27.5	-0.1	-0.1
$V_1/\text{kJ mol}^{-1}$		-0.17 ± 0.02	-0.58 ± 0.10
$V_2/\text{kJ mol}^{-1}$		5.3 ± 1.4	-2.8 ± 1.4
$V_4/\text{kJ mol}^{-1}$		6.4 ± 2.0	1.3 ± 1.5
$\varepsilon_{zz}^R/\text{kJ mol}^{-1}$		-0.700 ± 0.002	-0.700 ± 0.002
$\varepsilon_{xx}^R - \varepsilon_{yy}^R/\text{kJ mol}^{-1}$		-0.334 ± 0.009	-0.340 ± 0.012
$\varepsilon_{aa}^{CF}/\text{kJ mol}^{-1}$		0.097 ± 0.003	0.098 ± 0.003
$\phi(\text{syn})/^\circ$		51 ± 1	50 ± 1
%syn		55 ± 1	58 ± 1
$\phi(\text{anti})/^\circ$		129 ± 1	132 ± 1
%anti		45 ± 1	42 ± 1

Figure 6. A comparison of the distribution function $P_{LC}(\phi)$ derived from the molecular orbital calculations [3] (\blacklozenge) with those obtained from the ^{13}C (—) and ^1H data (\times) for the sample of 2,2'-difluorobiphenyl dissolved in the nematic solvent ZLI 1167, and from the ^1H data for a sample dissolved in the nematic solvent ZLI 1132 (—+—). The $P_{LC}(\phi)$ obtained from the NMR data all used the same method; that is, the steric term is included and the geometry was fixed during rotation.

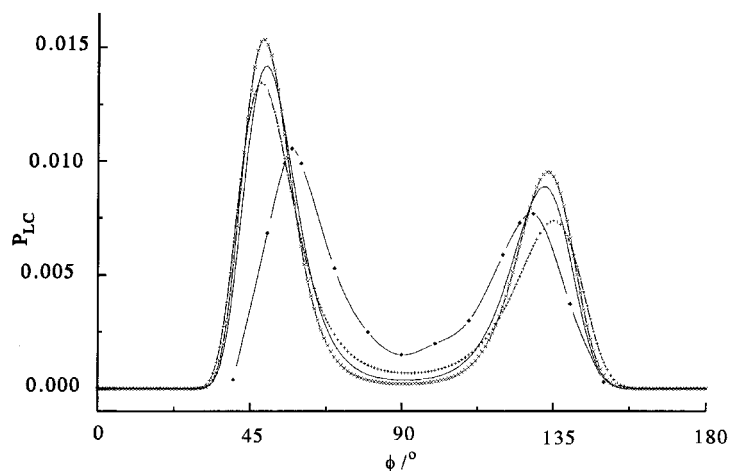
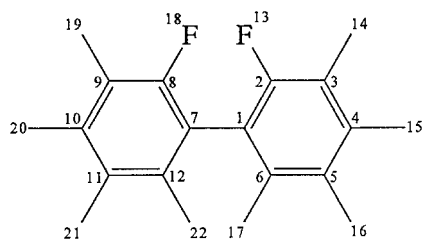


Table 11. Results of bringing observed D_{ij}^{HH} and D^{HF} within one ring into agreement with the experimental D_{ij} for 2,2'-difluorobiphenyl-d₄ in ZLI 1132 and ZLI 1167 using the MO geometry.



Order parameter	Solvent	
	ZLI 1132	ZLI 1167
S_{xx}	-0.1817 ± 0.0001	0.0812 ± 0.0003
S_{xz}	-0.0178 ± 0.0001	0.0039 ± 0.0002
S_{yy}	-0.2842 ± 0.0001	0.1216 ± 0.0003
S_{zz}	0.4659 ± 0.0002	-0.2029 ± 0.0006

i	$x/\text{\AA}$	$z/\text{\AA}$
17	2.1174	0.9224
16	2.1311	3.3819
15	-0.0076	4.6185
14	-2.1535	3.3642
13	-2.3627	0.8281

i, j	Weight ^a	ZLI 1132		ZLI 1167	
		Δ_{ij}/Hz	$D_{ij}(\text{calc})/\text{Hz}$	Δ_{ij}/Hz	$D_{ij}(\text{calc})/\text{Hz}$
16,17	1	0.1	-3757.9	-0.2	1636.7
15,17	0	-10.5	-496.4	2.1	210.2
14,17	0	-1.0	6.8	5.0	-7.9
13,17	0	6.3	228.5	4.3	-101.9
15,16	0	7.2	31.8	40.4	-53.1
14,16	0	1.8	277.5	9.1	-124.0
13,16	0	6.6	32.2	0.0	-12.6
14,15	1	-0.1	252.5	0.1	-95.9
13,15	1	0.2	-342.6	-0.5	152.9
13,14	1	-0.1	-3155.3	0.3	1378.2

^aDipolar couplings are either included (weight = 1) or excluded (weight = 0) in the calculation.

which included an estimated D^{FF} , and the steric term in $U_{\text{int}}(\phi)$, but neglecting geometry relaxation. The differences, Δ_{ij} , between observed and calculated couplings, and the optimized fitting parameters are given in table 12. The rotational probabilities, $P_{\text{LC}}(\phi)$ are shown in figure 6.

The general features of $P_{\text{LC}}(\phi)$ found for the two solvents from the D_{ij}^{HH} , D_{ij}^{HF} and D^{FF} data sets are very similar to those obtained from the ¹³C data.

6. Conclusion

The NMR data clearly support the existence of two maxima in the bond rotational probability distribution of 2,2'-difluorobiphenyl when it is in a liquid phase. The distribution $P_{\text{mol}}(\phi)$ obtained by the molecular orbital calculation is also shown in figure 6, and it is seen that this is in close agreement with the $P_{\text{LC}}(\phi)$ obtained by NMR. An exact agreement between the distributions is not to be expected, even if there is a real dependence of the rotational potential on phase. This is because of the approximations used in both the NMR and molecular orbital methods. The NMR method is dependent on using a particular model for the conformationally dependent potential of mean torque, and does not allow the averaging effects on dipolar couplings of all the vibrational degrees of freedom. The approximations used, however, are not expected to change fundamentally the conclusion that 2,2'-difluorobiphenyl in the liquid phase is mainly in the *syn*-form, but with appreciable amounts of the *anti*. This distribution is essentially the same in the isolated molecule. On crystallization, the lowest energy form, the *syn*, is selected. The angle between the planes to the ring normals is now 58° , compared with $50^\circ \pm 1^\circ$ for the *syn*-form in the liquid crystalline phases, and 57° for the same form from the molecular orbital calculations.

The question arises as to whether the difference found for the position of the *syn*-form in the solid and liquid crystalline phases is significant. This is tantamount to deciding how accurate are the rotational potentials determined by the NMR method. This is a difficult question to answer since there are no other methods of obtaining the rotational potential in a liquid phase. Palke *et al.* [14] have attempted an assessment of the precision by which the Additive Potential method can obtain $P_{\text{LC}}(\phi)$ from a set of dipolar couplings. They simulated a set of dipolar couplings for biphenyl dissolved in a liquid crystalline solvent by the molecular dynamics method. The simulated data were then treated by the AP method (and also a maximum entropy method) so see how well the original bond rotational potential was obtained. The results were very encouraging in that $P_{\text{LC}}(\phi)$ obtained by the AP method was close in form to the true potential, and in particular the maximum was found to be within 2° of the correct value. This is a test of the AP method, but not of the importance of the other approximations in the model. The inclusion of a steric term in the potential does not affect the positions found for the two maxima in $P_{\text{LC}}(\phi)$, and so this aspect of the model is not critical. The remaining, significant approximation is the neglect of small amplitude vibrational motion, and this might bring the liquid crystal and X-ray results into closer agreement. It is not safe, therefore, to conclude that the difference of 8° between

Table 12. Results of bringing observed and calculated D_{ij}^{HF} and D^{HH} obtained for the samples in ZLI 1132 and ZLI 1167 into agreement by varying ϵ_{zz}^{R} , $\epsilon_{xx}^{\text{R}} - \epsilon_{yy}^{\text{R}}$, $\epsilon_{aa}^{\text{CF}}$, V_1 , V_2 and V_4 . An estimate for D^{FF} was used, and the repulsion term was included in the internal potential.

i, j	Weight ^a	ZLI 1132		ZLI 1167	
		$D_{ij}(\text{obs})/\text{Hz}$	Δ_{ij}/Hz	$D_{ij}(\text{obs})/\text{Hz}$	Δ_{ij}/Hz
13,14	1	-3155.2	2.7	1377.9	-1.8
13,15	1	-342.8	-0.3	153.3	-1.5
13,16	0	38.8	5.5	-12.6	-0.4
13,17	0	222.3	-13.3	-97.6	-4.8
13,18	1	-63.3	-0.7	27.5	0.8
14,15	1	252.5	-0.3	-95.9	0.4
14,16	0	279.3	-8.5	-114.9	-10.2
14,17	0	5.8	-10.7	-2.9	-5.9
14,18	1	-269.6	2.0	117.2	-2.4
15,16	0	24.6	-75.5	-12.6	-43.6
15,17	0	-485.9	0.1	212.3	-3.1
15,18	1	-201.7	1.6	89.0	-2.5
16,17	1	-3758.0	2.5	1636.9	2.0
16,18	1	-212.1	0.7	96.5	-1.1
17,18	1	-180.1	0.2	80.9	-0.2
$\epsilon_{zz}^{\text{R}}/\text{kJ mol}^{-1}$		1.112 ± 0.003		-6.25 ± 0.002	
$\epsilon_{xx}^{\text{R}} - \epsilon_{yy}^{\text{R}}/\text{kJ mol}^{-1}$		1.6 ± 0.6		-0.24 ± 0.002	
$\epsilon_{aa}^{\text{CF}}/\text{kJ mol}^{-1}$		-0.102 ± 0.008		0.045 ± 0.002	
$V_1/\text{kJ mol}^{-1}$		-0.73 ± 0.09		-0.61 ± 0.010	
$V_2/\text{kJ mol}^{-1}$		-3.9 ± 0.2		-3.20 ± 0.2	
$V_4/\text{kJ mol}^{-1}$		0.4 ± 0.2		1.48 ± 0.2	
$\phi(\text{syn})/^\circ$		48 ± 1		49 ± 1	
%syn		60 ± 1		58 ± 1	
$\phi(\text{anti})/^\circ$		135 ± 1		133 ± 1	
%anti		40 ± 1		42 ± 1	

^aDipolar couplings were included in the calculation if weight = 1, and excluded if weight = 0.

the position of the *syn*-form in the solid and liquid crystalline phases is significant.

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