Liquid Crystals

Do the molecules which form discotic liquid crystals have disc-like structures? The conformation of a simple model compound, 1,2-dihydroxydiacetylbenzene, determined from the NMR spectra of samples dissolved in liquid crystalline solvents

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Do the molecules which form discotic liquid crystals have disc-like structures? The conformation of a simple model compound, 1,2-dihydroxydiacetylbenzene, determined from the NMR spectra of samples dissolved in liquid crystalline solvents

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Many discotic mesogens are molecules with a central aromatic ring with adjacent alkylcarboxylate substituents. The simplest such molecule, 1,2-dihydroxydiacetylbenzene, which is not mesogenic, is studied by NMR spectroscopy as a solute in a nematic solvent. The spectra are analysed to give sets of residual dipolar couplings, D_{ij}, which are then used to test models for the conformation adopted by the acetate side groups. The conformations and geometry of an isolated molecule are calculated by the ab initio MP2/6-311G method and also by the DFT approach using the B3LYP functional with the 6-311++G** basis set. The quantum chemical calculations find that the minimum energy conformer has the acetate groups rotated in opposite directions out of the ring plane, and this kind of structure is also consistent with the NMR data.

Keywords: discotic mesogen; NMR; model compound; conformation

1. Introduction

The first reported (*1*) discotic liquid crystal has the structure shown in Figure 1, with R=OCO-*n*-alkyl. The name discotic reflects the idea that such molecules are planar, and hence disc-like in shape, and the discs stack preferentially with their plane normals parallel.

Less crowded structures, such as triphenylenes hexaalkanoates (Figure 2) also form discotic phases. The OCOR group is large, and it seems more probable that these molecules adopt a non-planar structure.

To investigate this possibility we present here a study of the molecule with the structure shown in Figure 3, 1,2-dihydroxydiacetylbenzene (diAcB).

This is the simplest structure of an ortho alkanoate-substituted aromatic compound and our aim is to ascertain the conformation of the acetate groups relative to the aromatic ring. It was studied as a solute in a nematic liquid crystalline solvent. In such an anisotropic solvent the NMR spectrum yields partially-averaged, anisotropic interactions, such as residual dipolar couplings, D_{ij}, and residual quadrupolar splittings, Δv_i, and these may be used to investigate the structure and conformations of the dissolved molecules.

2. Experimental

The proton spectrum of diAcB was recorded on a sample dissolved in the nematic liquid crystalline mixture ZLI 1132, obtained from Merck. Proton spectra were recorded at 200, 300 and 600 MHz, and these are shown in Figure 4. These spectra proved to be unusually difficult to analyse, which in part is because of overlapping of lines from the methyl and aromatic protons.

In practice, the spectrum at 300 MHz was the only one to be eventually analysed. The analysis was achieved by first synthesizing 1,2-dihydroxy-diacetyl[^{13}C, ^{2}H]-benzene (diAcB-C-13) (Figure 5) and recording ^{13}C, ^{2}H and ^{1}H-{^{2}H} spectra on a sample dissolved in ZLI 1132 on a Bruker MSL 200 spectrometer, at approximately the same concentration used to obtain the 300 MHz proton spectrum.

Synthesis of 1,2-dihydroxydiacetylbenzene

Acetic acid (250 mg, 4.17 mmol) was dissolved in dichloromethane (10 ml) in a 50 ml RB flask fitted with a calcium chloride guard tube. Catechol (229 mg, 2.08 mmol) was added, followed by a small quantity (<5 mg) of 4-dimethylaminopyridine. The solution was cooled in an ice-bath, and dicyclohexyl-carbodiimide (857 mg, 4.16 mmol) added. The ice-bath was removed after 5 min, by which time small amounts of a white solid (urea by-product) could be seen in the reaction flask. The reaction mixture was left stirring overnight at room temperature. After this time, removal of the stirrer led to separate layers forming: a clear, colourless bottom layer, and a white top layer. The entire reaction mixture was filtered to

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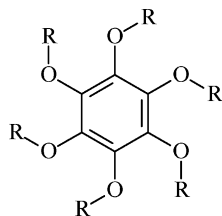
Figure 1. The first reported (*1*) discotic liquid crystal.

give a clear solution. The dichloromethane was removed by rotatory evaporation to give a crude product as an oil. The oil was extracted with hot hexane from which white needles of the required product separated on cooling to room temperature. The needles were filtered off and dried overnight in a vacuum oven (temperature approx. 40°C). M.p, 62–63°C, yield 320 mg (79%).

The isotopically labelled compound was synthesised by the same method, using acetic-1-^{13}C-2-d_3 acid.

3. Analysis of spectra

The analysis of the complex spectra, given by protons of molecules in oriented phases, proceeds by searching in a systematic way for a set of values of the residual dipolar couplings, which are close enough to the correct set so that they can be used in an iterative analysis. This is a relatively easy process for rigid molecules but for flexible cases this search can be very difficult. There is a basic problem: a good set can be obtained only if the conformational distribution is known approximately, but in cases like diAcB there is considerable uncertainty about this distribution. The procedure, which was ultimately successful in analysing the 300 MHz proton spectrum shown in Figure 4,
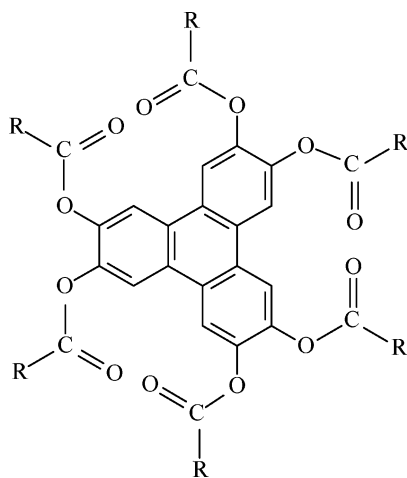

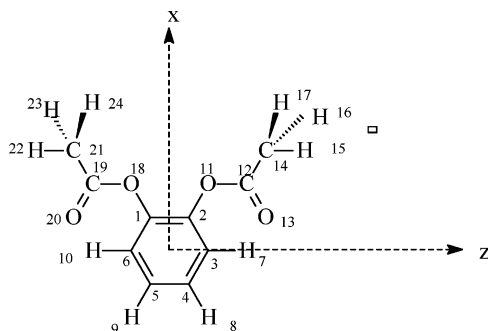Figure 2. Structure of triphenylenes hexaalkanoates.

Figure 3. Structure of the compound investigated, 1,2-dihydroxydiacetylbenzene (diAcB).

was to simplify the spin system by synthesis of isotopically labelled molecules, the spectra of which could be analysed more easily. Thus, the ^{2}H spectrum given by the ^{13}C and ^{2}H labelled isotopomer is a doublet, which yields the quadrupolar splitting, Δv^{methyl}, for the six deuterons. The coupling within the methyl groups, D_{HH}^{methyl}, was estimated from this value by using the approximate relationship:
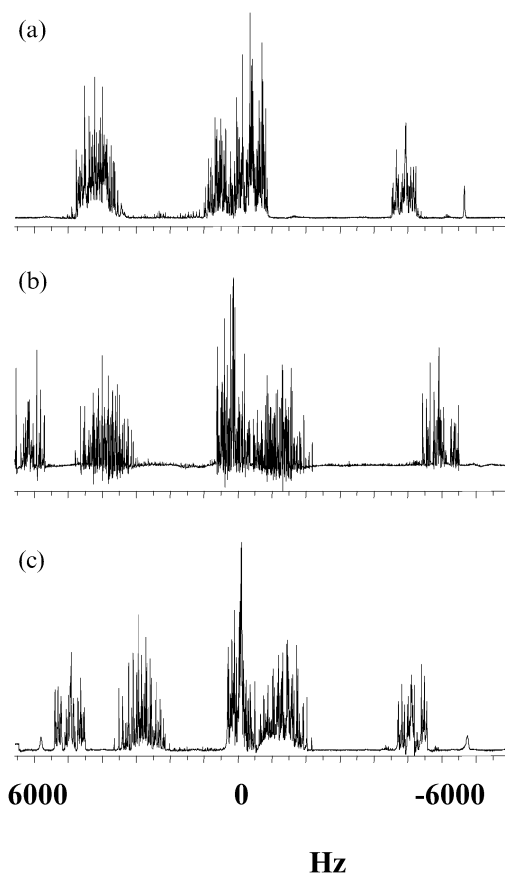
Figure 4. ^{1}H spectra of 1,2-dihydroxy-diacetylbenzene dissolved in the nematic solvent ZLI 1132 recorded at 300 K: 200MHz (a); 300MHz (b) and 600 MHz (c).
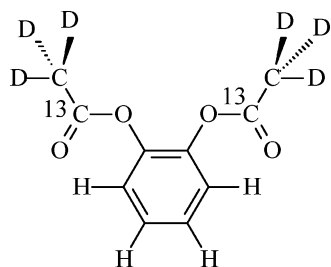
Figure 5. Structure of 1,2-dihydroxydiacetyl-[^{13}C, ^{2}H]-benzene (diAcB-C-13).

$$D_{HH}^{methyl} = k\Delta v^{methyl}, \qquad (1)$$

with the value of $k=-7.5$ obtained from a study of methoxybenzenes (2).

The ^{13}C–{^{1}H} spectrum is a septet, which indicates that dipolar coupling is resolved only for the nuclei within single acetate groups, yielding the value of $D_{12,15}^{CD}$, and its symmetrical equivalents. The ^{1}H–{^{2}H} spectrum, shown in Figure 6, is that of an oriented AA′BB′XX′ spectrum, and it was analysed by the Bruker program PANIC to yield the data in Table 1.

4. Conformation analysis using data from the ^{13}C, ^{2}H isotopomer

The difficult residual dipolar couplings to estimate for the analysis of the 300 MHz spectrum of diAcB are those between the ring and methyl protons, which depend on the conformation of the molecule, which at this stage is unknown. The approach taken was to
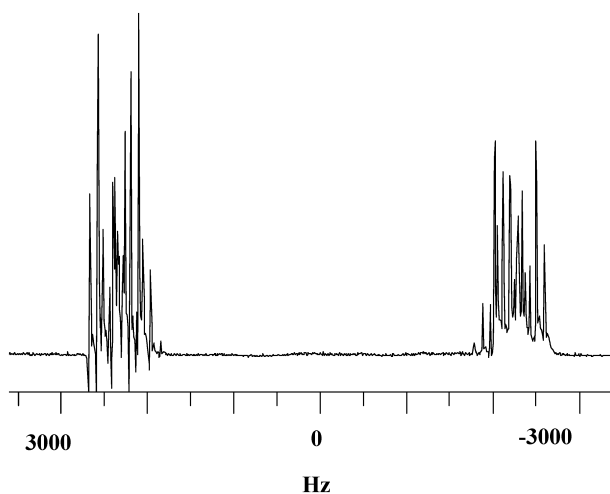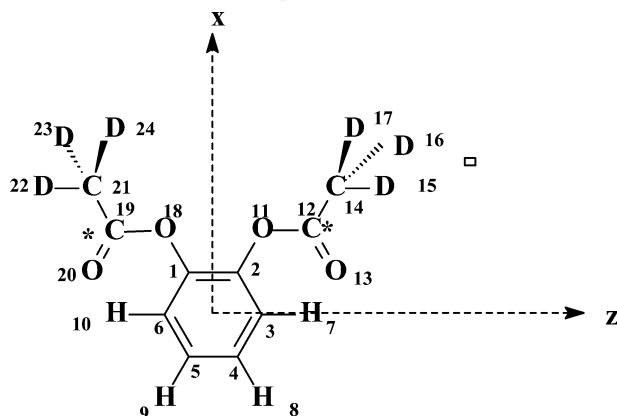

Figure 6. 200MHz ^{1}H – {^{2}H} spectrum of a sample of 1,2-dihydroxy-diacetylbenzene labelled with ^{13}C at positions 12 and 19, and with both methyl groups deuterated and dissolved in the nematic solvent ZLI 1132. The spectrum was recorded at 300 K.

Table 1. Chemical shifts, δ_i, quadrupolar splittings, Δv_i, and dipolar couplings, D_{ij}, obtained from the NMR spectra of a sample of 1,2-dihydroxydiacetyl-[^{13}C, ^{2}H]-benzene dissolved in the nematic liquid crystalline solvent ZLI 1132.

i,j	D_{ij}/Hz	δ_{ij}/Hz
7,8	-1545.7 ± 0.3	
7,9	-108.3 ± 0.3	74 ± 3
7,10	-6.2 ± 0.5	
7,12	-219.3 ± 0.4	
7,18	-19.4 ± 3.0	
8,9	-49.6 ± 0.5	
8,12	-43.3 ± 0.4	
8,18	-28.8 ± 3.0	
12,15	$\pm 57.0 \pm 2.0$	
12,19	0.0 ± 1.0	
15,22	0.0 ± 1.0	
Δv_{methyl}/Hz= $\pm 16\,610 \pm 20$.		

use the data in Table 1 together with a simplified model for the conformational distribution in order to predict initial values for missing residual dipolar couplings. Eventually, data from both the labelled and unlabelled molecules will be used to test more refined conformational models.

The four dipolar couplings between ring protons were used to determine the relative positions of the four protons, using the relationship

$$D_{ij} = -(\frac{\mu_0}{4\pi})\frac{\gamma_i\gamma_j h}{8\pi^2 r_{ij}^3}\Big[S_{zz}^R(3\cos^2\theta_{ijz}-1)$$
$$+(S_{xx}^R - S_{yy}^R)(\cos^2\theta_{ijx}-\cos^2\theta_{ijy})\Big] \qquad (2)$$

where the $S_{\alpha\beta}^R$ are local order parameters for axes fixed in the aromatic ring, μ_0 is the magnetic constant, and γ_i and γ_j are the magnetogyric ratios of nuclei i and j. The distance r_{89} was fixed as 2.48 Å, and the x and z coordinates of protons 7 and 10 varied, together with the two order parameters to give exact agreement with the four, intra-ring,

proton–proton dipolar couplings. The proton positions obtained were kept fixed in all subsequent calculations.

There are six bond rotations in diacetylbenzene (Figure 7).

The dipolar couplings between the ring protons and the two ^{13}C nuclei can be used to explore conformational possibilities produced only by rotation about the two bonds C1–O18 and C2–O11; rotations through angles ϕ_2, $\phi_{2'}$ and ϕ_3, $\phi_{3'}$ do not average these couplings. To do this it is necessary to have an approximate geometry for the molecule, and a reasonable estimate of the positions of the minimum energy conformations. Calculations on the relative energies of selected conformations were done with the program Gaussian 03 (*3*) at the HF/6-311G level. These indicated local minima for conformations with the acetate groups either both in the ring plane, both approximately perpendicular to the ring plane, either on the same or on opposite sides of this plane. More accurate calculations were then done starting from these three positions by the MP2 method with the 6-311G basis, and with the DFT method B3LYP with the basis 6-311++G**, and using full geometry optimization. The vibrational force field was also calculated in each case, which showed that only the up/down conformation with the torsion angles $\beta_{1,2,11,12} = \beta_{2,1,18,19} = 74.5°$ (MP2) or 94.8° (B3LYP) is a true minimum: the acetate groups are on opposite sides of the ring plane, and this conformer is described as up/down. The structures obtained are given in Table 2. The important dihedral angles specifying the out of plane rotations are very different, but the other bond lengths and angles are quite close. Note that similar large differences between dihedral angles calculated by MP2 and B3LYP methods for the rotation of groups out of an aromatic ring plane have been noted (*4–6*).

Conformational averaging of residual dipolar couplings

To calculate the average of residual dipolar couplings over a conformational distribution it is necessary to invoke a model for how the orientational order varies with conformational state. The model used here is
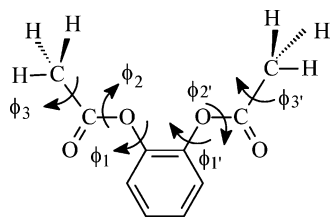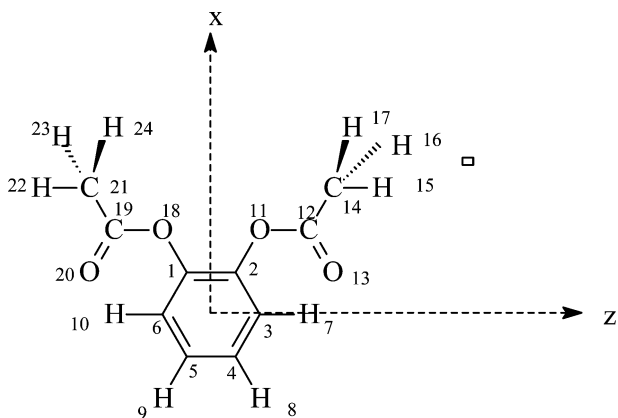
Figure 7. The six bond rotations in diacetylbenzene.

Table 2. Optimised geometries obtained by the MP2/6-311G and B3LYP/6-311++G** methods for the minimum energy structure of 1,2-dihydroxydiacetylbenzene.

	Bond lengths, r_{ij}/Å	
i,j	MP2/6-311G	B3LYP/6-311++G**
1,2	1.398	1.392
2,3	1.392	1.389
3,4	1.399	1.392
3,7	1.086	1.083
4,8	1.086	1.083
2,11	1.388	1.393
11,12	1.381	1.376
12,13	1.201	1.198
12,14	1.505	1.504
14,15	1.089	1.088
14,16	1.092	1.092

i,j,k	Angles, α_{ijk}/°	
1,2,3	120.289	120.223
2,3,4	119.630	119.682
3,4,5	120.081	120.095
4,3,7	121.665	121.256
3,4,8	119.695	119.678
1,2,11	119.695	119.408
2,11,12	115.198	118.183
11,12,13	123.559	123.464
11,12,14	109.077	109.899
12,14,15	109.373	109.417
12,14,16	109.499	109.909

ijkl	Dihedral angles, β_{ijkl}/°	
1,2,11,12	74.5	94.8
2,1,18,19	74.5	94.8
2,11,12,13	4.0	0.9
1,18,19,20	4.0	0.9
2,11,12,14	183.6	180.7
20,19,21,22	0.5	−0.1
16,14,12,15	121.1	121.0
17,14,12,15	−121.1	−121.0

known as the additive potential model (*7*), and it is briefly described here.

The residual dipolar couplings in flexible molecule are averages over all the allowed conformations.

Thus,

$$D_{ij} = \int P_{LC}(\phi_k)D_{ij}(\phi_k)d\phi, \qquad (3)$$

where $D_{ij}(\phi_k)$ is the dipolar coupling for the molecule in a fixed conformation, and $P_{LC}(\phi_k)$ is the probability that a molecule is in a conformation defined by a set, ϕ_k, of bond rotation angles. The dipolar coupling $D_{ij}(\phi_k)$ is given by [cf. equation (2)]:

$$D_{ij}(\phi_k) = -(\frac{\mu_0}{4\pi})\frac{\gamma_i\gamma_j h}{8\pi^2(r_{ij}^k)^3}\left[S_{zz}(\phi_k)(3\cos^2\theta_{ijz}^k - 1)\right.$$
$$\left. + (S_{xx}(\phi_k) - S_{yy}(\phi_k))(\cos^2\theta_{ijx}^k - \cos^2\theta_{ijy}^k)\right] \qquad (4)$$

The order parameters, $S_{zz}(\phi_k)$, etc, refer to the molecule in conformation k, in principal axes, xyz, and θ_{ijz}^k is the angle between the internuclear vector, $\mathbf{r}_{ij}$ and the axis z when the molecule is in this conformation. The conformation dependence of the order parameters is obtained by introducing a probability, $P_{LC}(\beta, \gamma, \phi_k)$, that the molecule is at an orientation relative to the director specified by the polar angles β and γ, whilst in the conformation described by the set of angles ϕ_k. The order parameter $S_{zz}(\phi_k)$, for example, is given by

$$S_{zz}(\phi_k) = \int\frac{1}{2}(3\cos^2\beta - 1)P_{LC}(\beta, \gamma, \phi_k)\sin\beta d\beta d\gamma. \quad (5)$$

It is convenient to express $P_{LC}(\beta, \gamma, \phi_k)$ in terms of a potential energy function:

$$P_{LC}(\beta, \gamma, \phi_k) = Z^{-1}\exp[-U_{LC}(\beta, \gamma, \phi_k)/k_BT], \quad (6)$$

where

$$Z = \int\exp[-U_{LC}(\beta, \gamma, \phi_k)/k_BT]\sin\beta d\beta d\gamma. \quad (7)$$

The function $U_{LC}(\beta, \gamma, \phi_k)$ can be divided into a part, $U_{ext}(\beta, \gamma, \phi_k)$, which depends on both the orientation of the molecules in the liquid crystal, and on their conformation, and a part, $U_{int}(\phi_k)$, which depends only on the conformation:

$$U_{LC}(\beta, \gamma, \phi_k) = U_{ext}(\beta, \gamma, \phi_k) + U_{int}(\phi_k). \quad (8)$$

Note that $U_{ext}(\beta, \gamma, \phi_k)$ vanishes when the phase becomes isotropic, whereas $U_{int}(\phi_k)$ does not. $U_{ext}(\beta, \gamma, \phi)$ may be written as:

$$U_{ext}(\beta, \gamma, \phi) = -\varepsilon_{2,0}(\phi_k)C_{2,0}(\beta) - 2R(\varepsilon_{2,2}(\phi_k))C_{2,2}(\beta, \gamma), (9)$$

where $C_{2,m}(\beta, \gamma)$ is a reduced spherical harmonic (8), and the conformationally-dependent coefficients are approximated as a summation of contributions, $\varepsilon_{2,p}(j)$, from sub-molecular fragments, j (7):

$$\varepsilon_{2,m}(\phi_k) = \sum_j\sum_p\varepsilon_{2,p}(j)D^2_{p,m}(\Omega(j)). \quad (10)$$

The Wigner function, $D^2_{p,m}(\Omega(j))$, describes the orientation of j in a set of molecule-fixed reference axes. This additivity of fragment contributions is why this method of parameterising $U_{ext}(\beta, \gamma, \phi)$ is referred to as the additive potential (AP) approach.

There are too many parameters defining both the structure and the conformational distribution, and it is necessary that some are constrained. This is done for the data from the labelled compound by fixing the bond lengths and angles at values calculated by the DFT method. In order to obtain estimates of the ring-methyl residual dipolar couplings it was assumed first that only this single up/down conformer is present. The values of the dihedral angles $\beta_{1,2,11,12} = \beta_{2,1,18,19}$ were varied, and the lowest root-mean-square error was obtained when these are approximately 115°, giving the calculated couplings shown in Table 3. Note that couplings between ^1H and ^2H nuclei were scaled by the ratio of the gyromagnetic constants to give ^1H–^1H couplings. The agreement between observed and calculated couplings shown in Table 3 is good enough that values of all the inter-proton couplings for the fully protonated molecule could be estimated, as given in Table 4, with sufficient precision to act as starting values in a successful, iterative analysis of the 300 MHz proton spectrum shown in Figure 4, producing the final set of couplings, also given in Table 4.

5. Conformational analysis using both sets of residual dipolar couplings

With both sets of residual dipolar couplings it is now possible to examine a more refined conformational model. For molecules in which the k bond rotations are independent, then $U_{int}(\phi_k)$ is often written as a Fourier series, plus a repulsion term to accommodate severe steric hindrance:

$$U_{int}(\phi_k) = \sum_k\sum_n V_{nk}\cos(n\phi) + \sum_{i,j}(A_{ij}/R_{ij})^{12}. \quad (11)$$

The values of n are chosen to reflect the symmetry of the rotation potentials, and the series is often

Table 3. Dipolar couplings, D_{ij} (calculated), calculated assuming that 1,2-dihydroxydiacetyl-[^{13}C, ^{2}H]-benzene exists as a single conformer with the acetyl groups rotated 65° to opposite sides of the ring plane.
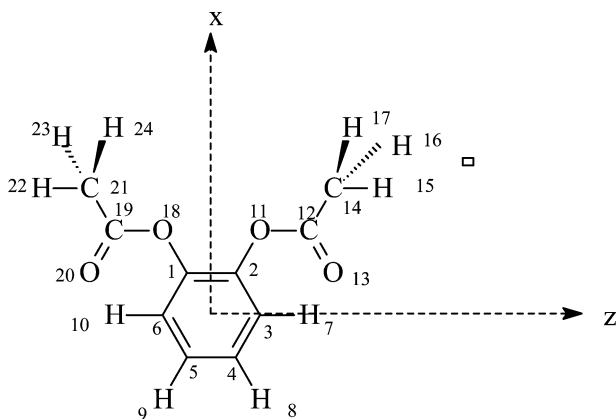
i,j	D_{ij} (observed)	D_{ij} (calculated)
7,8	−1545.7	−1545.6
7,9	−108.3	−106.8
7,10	−6.2	−6.3
7,12	−219.3	−218.5
7,19	−19.4	−16.8
8,9	−49.6	−49.7
8,12	−43.3	−54.1
8,19	−28.8	−25.0
12,19	0.0	−2.1
Order parameters		
S_{zz}	0.0063	
$S_{xx}-S_{yy}$	0.530	
S_{yz}	0.09	

Table 4. Initial starting values and final results from the analysis of the 300 MHz proton spectrum of a sample of 1,2-dihydroxydiacetylbenzene dissolved in the nematic liquid crystalline solvent ZLI 1132.

i,j	D_{ij} (initial)/Hz	D_{ij} (final)/Hz	J_{ij}/Hz[a]
7,8	−1545.6	−1610.12 ± 0.04	8.0
7,9	−106.8	−111.44 ± 0.05	2.0
7,10	−6.3	−4.16 ± 0.3	0.0
7,15	−297.9	−290.16 ± 0.08	0.0
7,22	−41.0	−51.03 ± 0.07	0.0
8,9	−50.1	−33.31 ± 0.3	8.0
8,15	−86.9	−92.04 ± 0.09	0.0
8,22	−46.5	−53.32 ± 0.08	0.0
15,16	1985.0	1993.19 ± 0.02	0.0
15,22	−18.8	1.57 ± 0.02	0.0
Chemical shifts			
i,j	δij/Hz		
7,15	1143.8 ± 0.2		
8,15	1296.1 ± 0.2		

[a]The values of Jij are reasonable approximations based on data for similar compounds. They were kept fixed at these values.

truncated at the minimum number of terms necessary to give the correct periodicity. Equation (11) may need modification when the rotors are not independent, and this is the case for the diAcB molecule. For example, the conformations generated by rotating one acetate group through 90° about the bond C2–O11, and the other about C1–O18 by −90° will differ in energy to the case when both groups rotate by 90°. The (90,90) conformer has the acetate groups on opposite sides of the ring plane, whereas for (90,−90) they are on the same side. These two conformations will differ in repulsion energy, but this can be seriously in error when it is assumed that the geometry remains fixed on rotation. It is possible to construct a Fourier series for multiple, dependent rotations, but this contains too many coefficients, which have to be optimised to fit the experimental data. We explore here an alternative approach, which models directly $P_{iso}(\phi_k)$, which is defined as

$$P_{iso}(\phi_k) = Q^{-1} \exp[-U_{int}(\phi_k)/RT], \qquad (12)$$

with

$$Q = \int \exp[-U_{int}(\phi_k)/RT]d\phi, \qquad (13)$$

as a sum of Gaussian probability functions, the position height and widths of which are treated as variables (*9*). The conformationally-dependent order parameters are still obtained using the AP model for $U_{ext}(\beta, \gamma, \phi_k)$.

Both data sets in Tables 1 and 4 were then used to explore in more detail the preferred conformation of diAcB. Calculations of the residual dipolar couplings were done with both MP2 and B3LYP geometries. First, the positions of protons 7 and 10 were adjusted by varying $r_{3,7} = r_{6,10}$ and $\theta_{3,4,7} = \theta_{5,6,10}$ to give values of 1.105 Å and 122.2°, respectively. The next step was to allow for some oscillatory motion about the C1–O18 and C2–O11 bonds. This was done by modelling the probability $P_{iso}(\phi_1, \phi_{1'})$ as a pair of Gaussian functions centred on angles $\phi_1^0 = \phi_{1'}^0$, and a width at half maximum height in each case of h:

$$P_{iso}(\phi_1, \phi_{1'}) = Q^{-1} \exp\left[-(\phi_1 - \phi_1^0)/2h^2 + \exp\left[-(\phi_{1'} - \phi_{1'}^0)/2h^2\right]\right], \qquad (14)$$

with

$$Q = \sqrt{(8h^2\pi)}. \qquad (15)$$

The order parameters will vary over the oscillatory

motion, and this was taken into account by using the AP model for $U_{ext}(\beta, \gamma, \phi_1, \phi_{1'})$.

There is rotation to about the C12–C14 and C19–C21 bonds, and this was assumed to have a threefold symmetry, and a barrier large enough so that the protons occupy only the three positions of equivalent minimum energy. With these approximations the averaging of a residual dipolar coupling constant over the motion of the methyl group is calculated as, for example:

$$\langle D_{7,15}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'})\rangle = \langle D_{7,16}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'})\rangle =$$

$$\langle D_{7,17}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'})\rangle = \frac{1}{3}[D_{7,15}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'}) \quad (16)$$

$$+ D_{7,16}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'}) + D_{7,17}(\phi_1, \phi_{1'}, \phi_2, \phi_{2'})]$$

The aromatic ring requires two fragment coefficients, $\varepsilon_{1,2}$ and $\varepsilon_{1,5}$. Three fragment coefficients were used for the acetate groups: $\varepsilon_{11,14} = \varepsilon_{18,21}$; $\varepsilon_{19,20} = \varepsilon_{12,13}$ and $\varepsilon_{13,20}$. This set of five interaction parameters reflects the five independent, conformationally-dependent order parameters $S(\phi_1, \phi_{1'})$ that are required for conformations generated by the motion. Note that five interaction parameters are required for each data set, making ten in total. The positions of the probability maxima, $\phi_1^0 = \phi_{1'}^0$, and the width h are common to both sets of data, and so the total number of variables is 12, compared with 19 observed residual dipolar couplings. It was found that stable iterations could not be obtained when h was free to vary, and so calculations were done with h in the range 10–20°. The results are shown in Table 5.

The maxima in the probability distributions obtained when the geometry is either that calculated by MP2 or B3LYP are not significantly different ($70 \pm 10°$ and $62 \pm 6°$. respectively, the error limits reflecting the fits to the data, and including the range of h from 5–20°) and close to that obtained by the MP2 calculation of 75°. These values are, however, significantly smaller than the value of 95° obtained by the B3LYP calculation.

6. Conclusions

The safest conclusion is that both the analysis of the residual dipolar couplings and the quantum chemical calculations support the up/down conformation as the global minimum, and with the two acetate groups arranged as shown in Figure 8.

In discotic liquid crystals the alkyl groups are larger, and have their own internal flexibility, which may have a large effect on the minimum energy conformation. It is still probable, however, that an

Table 5. The interaction parameters, ε/RT, and the positions of the maxima, $\phi_1 = \phi_{1'}$, in the Gaussian probability functions that bring residual dipolar couplings, calculated with MP2/6-311G and B3LYP/6-311++G** geometries, $D_{ij}(\text{calc})$/Hz, into best least-squares agreement with those observed, $D_{ij}(\text{obs})$ for 1,2-dihydroxydiacetylbenzene dissolved in the nematic liquid crystalline solvent ZLI 1132. The data set 1 is for the double ^{13}C, double CD_3 compound and set 2 is for the unlabelled compound.

|	$D_{ij}(\text{calc})-D_{ij}(\text{obs})$			
	MP2/6-311G Geometry		B3LYP/6-311++G** Geometry	
i,j	Set 1	Set 2	Set 1	Set 2
7,8	0.2434	3.0075	0.0914	−0.0394
7,9	0.4393	0.4575	−0.4247	0.4467
7,10	0.0769	0.3813	0.1231	0.0610
7,12	0.1073		−0.0069	
7,19	3.3046		−2.3550	
7,15		0.7841		−0.4210
7,22		7.2987		−0.4759
8,9	0.0399	0.3276	0.1008	−0.0841
8,12	3.0610		−3.1991	
8,19	4.2375		4.3901	
8,15		1.2850		1.5982
8,22		3.9818		0.0658
12,19	0.9159		0.4488	
15,16		0.2880		−0.0019
15,22		0.1964		0.0126
Interaction parameters/RT				
ε_{zz}	2.1 ± 0.3	1.8 ± 0.2	1.8 ± 0.1	1.78 ± 0.05
$\varepsilon_{xx} - \varepsilon_{yy}$	4.2 ± 0.3	3.6 ± 0.2	-1.44 ± 0.06	2.9 ± 0.1
$\varepsilon_{11,14}$	-1.2 ± 0.2	-0.83 ± 0.03	-1.44 ± 0.06	-0.59 ± 0.05
$\varepsilon_{12,13}$	-0.1 ± 0.4	-1.6 ± 0.2	-0.3 ± 0.1	-0.67 ± 0.05
$\varepsilon_{13,20}$	0.7 ± 0.4	1.0 ± 0.4	0.1 ± 0.3	0.2 ± 0.3
$\phi_1/°$	70 ± 1		62 ± 6	
$\phi_{1'}/°$	70 ± 1		62 ± 6	
$h/°$(fixed)	10		10	
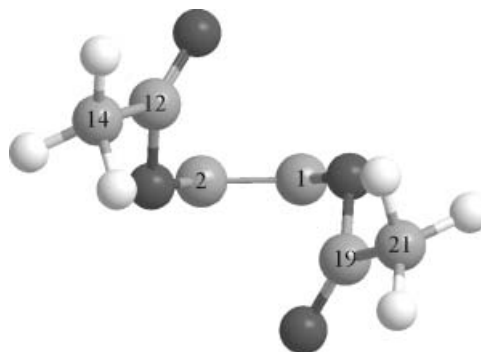
Figure 8. The arrangement of the two acetate groups relative to the ring plane in 1,2-dihydroxydiacetylbenzene.

up/down arrangement of adjacent alkylcarboxylate groups will be the preferred conformation.

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