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Orientation Studies on Fluorobenzenes in Nematic Liquid Crystals by NMR‡

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Abstract—The orientation of C_6H_6, 1,2–, 1,3–, and 1,4–$C_6H_4F_2$, 1,3,5–$C_6H_3F_3$, 1,2,4,5– and 1,2,3,5–$C_6H_2F_4$ and C_6F_6 in nematic liquid crystalline solvents has been determined by ^1H and ^{19}F magnetic resonance measurements. Most of these substances have been studied in two solvents, in 4,4′-di-*n*-hexyloxyazoxybenzene and in a mixture (3 : 2) of 4-heptanoyloxy- and 4-hexanoyloxy-4′-ethoxyazobenzene. Orientation parameters (*S*-values) of the solute molecules are given and their free energies are approximately determined as functions of the orientation.

The fluorobenzenes show some correlation in their free energies and in their *S*-values that are theoretically expected by regarding only dispersion forces and assuming localized contributions from the substituted bonds. The results confirm that the influence of permanent electrical dipole moments is relatively small. Although the orientation in the two solvents is similar, a close comparison shows that there are differences, which are assumed to be due to specific interactions.

1. Introduction

Nematic liquid crystals have been found to be excellent solvents for nuclear magnetic resonance spectroscopy on partially oriented molecules.[1] They may be used to study molecular properties such as the molecular geometry and the anisotropy of chemical shifts (see for instance recent reviews ref. 2–5) and also intermolecular

‡ Experimental results from J. Nehring, Thesis, Freiburg 1967.

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interactions may be studied from the orientation of the solute molecule in the liquid crystal.

The orientation is governed in general by three factors: dispersion forces, permanent electrical dipole moments and molecular shape. In our orientation studies a number of different fluorobenzene derivatives are compared. Differences in their orientation should be caused predominantly by dispersion forces and electrical dipole moments, the molecular shape is not much changed by the fluorine substitutions. Similar studies have previously been made with chlorobenzene derivatives.[6] It was concluded that permanent electrical dipole moments have only little influence but that dispersion forces, because of anisotropic properties of the C—Cl bond, are of major importance for the changes of the orientation caused by chlorine substitutions.

2. Definition and Determination of S-Values

The orientation of a molecule in a nematic liquid crystal can be described by a matrix[7] (S) which is defined by the expression:

$$S_{ij} = 1/2\langle 3\cos\theta_i\cos\theta_j - \delta_{ij}\rangle, \quad i,j = 1,2,3 \tag{1}$$

Here θ_i denotes the angles between the axes of a molecule-fixed axis system and the optical axis of the liquid crystal. δ_{ij} is the Kronecker symbol ($\delta_{ij} = 1$ for $i = j$, $\delta_{ij} = 0$ for $i \neq j$). Since (S) is symmetrical and traceless, in general five parameters are required to determine the orientation.

By choice of a proper axis system (principal axis system) (S) can be diagonalized. We denote the diagonal elements obtained in this way by S_1, S_2 and S_3 and call them principal S-values or S-values of the principal axes. The sum of the three principal S-values vanishes and consequently only two of them are required to determine the orientation. In case there is a three- or morefold symmetry axis in the molecule, only one parameter is necessary; for then Eq. (2) holds, where S_3 is the S-value of the symmetry axis.

$$S_1 = S_2 = -S_3/2 \tag{2}$$

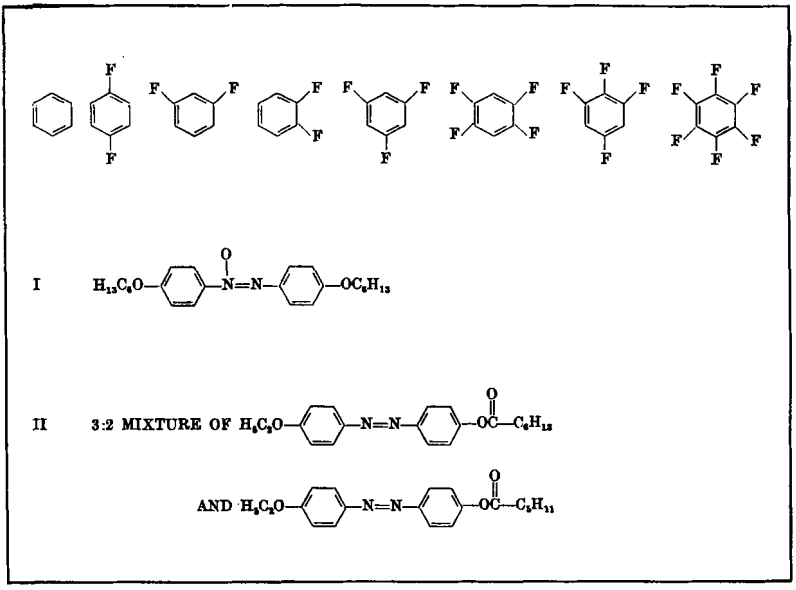


Figure 1 Studied molecules and solvents I and II.

Every molecule we investigated (Fig. 1) has a symmetry plane and in addition at least one twofold axis in this plane. The principal axis systems are given here by symmetry: one axis perpendicular to the plane (in all cases called 3-axis) and one of the axes in the plane parallel to the twofold symmetry axis.

Eq. (3) shows how S-values of randomly chosen axes are related to the principal values. Here $\cos \alpha_i$ are the direction cosines of the direction of interest in the molecular coordinate system.

$$S = S_1 \cos^2 \alpha_1 + S_2 \cos^2 \alpha_2 + S_3 \cos^2 \alpha_3 \tag{3}$$

In the case of our planar molecules we are especially interested in S-values of directions through two coupling nuclei p and q and here Eq. (3) simplifies to Eq. (4). For brevity we write now α instead of α_1.

$$S_{pq} = S_1 \cos^2 \alpha + S_2 \sin^2 \alpha \tag{4}$$

To obtain S-values from NMR spectra we have to determine anisotropic coupling constants. Eq. (5) gives the anisotropic coupling part of the Hamiltonian.

$$\mathbf{H}_{\text{anisotr}} = \sum_{p>q} B_{pq}(3I_{pz}I_{qz} - I_pI_q) \tag{5}$$

The coupling constants are composed of two parts ($B_{pq} = B_{pq}^{\text{dir}} + B_{pq}^{\text{indir}}$), one that comes from the direct and another one that comes from the indirect coupling.

The direct coupling between the nuclei p and q depends on the orientation of the connecting axis according to Eq. (6) where r_{pq} is the distance between p and q, and γ_p and γ_q their magnetogyric ratios.

$$B_{pq}^{\text{dir}} = -\frac{h\gamma_p\gamma_q}{4\pi^2}\left\langle\frac{1/2(3\cos^2\theta_{pq} - 1)}{r_{pq}^3}\right\rangle \tag{6}$$

For the determination of S_{pq} we assume that B_{pq}^{indir} can be neglected ($B_{pq}^{\text{indir}} \ll B_{pq}^{\text{dir}}$) and that the relation (7) holds.

$$\left\langle\frac{1/2(3\cos^2\theta_{pq} - 1)}{r_{pq}^3}\right\rangle = \frac{S_{pq}}{r_{pq}^3} \tag{7}$$

For r_{pq} we use values calculated under the assumption that all bond angles are 120° and that the bond distances[8] are: $r_{CC} = 1.394$ Å, $r_{CH} = 1.084$ Å, $r_{CF} = 1.328$ Å.

The assumption $B_{pq}^{\text{indir}} \ll B_{pq}^{\text{dir}}$ is a fairly good one for HH-couplings, but with FF-couplings the neglection of B_{pq}^{indir} may lead to errors of several percent in S_{pq}. When possible we therefore determined S-values from HH-couplings. An estimation of the total errors in our experimental S-values, that includes the errors introduced by the above assumptions and the experimental errors, yields values of several percent (less than 10%).

3. Theory of Orientation and Intermolecular Interactions

The free energy of a solute molecule in a nematic liquid is a function of its orientation. Nematic liquids have an infinite fold symmetry axis C_∞ and we can accordingly write for the average

free energy (averaged over a large number of molecules with the same momentary orientation):

$$F = F(\cos\theta_1,\ \cos\theta_2,\ \cos\theta_3) \tag{8}$$

Or, when we expand into a series

$$F = \sum_{i,k,l} b_{ikl} \cos^i\theta_1 \cos^k\theta_2 \cos^l\theta_3 \tag{9}$$

θ_1, θ_2 and θ_3 are the previously introduced angles. For simplicity they may refer to the principal molecular coordinate system in which (S) has diagonal form.

Any axis normal to C_∞ is a twofold symmetry axis of the nematic solvent. It follows $F(-\cos\theta_1,\ -\cos\theta_2,\ -\cos\theta_3) = F(\cos\theta_1,\ \cos\theta_2,\ \cos\theta_3)$ or in the series $b_{ikl} = 0$ if $i + k + l$ is equal to an odd number. More coefficients in the series disappear when the solute molecules have some symmetry. For instance with the molecules regarded in this paper, where axis (3) is chosen normal to a plane of symmetry and either axis (1) or axis (2) coincides with a twofold symmetry axis, all terms in which i, k or l is an odd number disappear.

In the following calculations we neglect all terms in the series for which $i + k + l \geqslant 4$ and can write therefore

$$F = -a_0 - a_1 \cos^2\theta_1 - a_2 \cos^2\theta_2 \tag{10}$$

We used the relation $\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta_3 = 1$ to eliminate $\cos^2\theta_3$. The mixed term of second order disappears generally in this approximation since in the principal coordinate system $\langle\cos\theta_i \cos\theta_j\rangle = 0$ for $i \neq j$.

According to classical Boltzmann statistics we have the following two relations between the S-values and the coefficients a_1 and a_2:

$$S_1 = \frac{3}{2}\frac{1}{R}\int_0^{\pi/2}\int_0^{\pi/2} \cos^2\theta_1 \exp\left(\frac{1}{kT}(a_1\cos^2\theta_1 + a_2\sin^2\theta_1\sin^2\vartheta)\right) \times \sin\theta_1\, d\vartheta\, d\theta_1 - \frac{1}{2} \tag{11}$$

$$S_2 = \frac{3}{2}\frac{1}{R}\int_0^{\pi/2}\int_0^{\pi/2} \sin^2\theta_1 \cos^2\vartheta \exp\left(\frac{1}{kT}(a_1\cos^2\theta_1 + a_2\sin^2\theta_1\sin^2\vartheta)\right)\sin\theta_1\, d\vartheta\, d\theta_1 - \frac{1}{2}$$

with

$$R = \int_0^{\pi/2}\int_0^{\pi/2} \exp\left(\frac{1}{kT}(a_1\cos^2\theta_1 + a_2\sin^2\theta_1\sin^2\vartheta)\right)\sin\theta_1\, d\vartheta\, d\theta_1$$

The functions S_1 and S_2 have been tabulated in the range $0 \leqslant a_1 \leqslant a_2 \leqslant 3kT$ for numerical calculations.

The physical meaning of a_1 and a_2 is easily recognized by regarding Eq. (10). a_1 and a_2 correspond to free energy differences between two molecular orientations: a_1 is the difference between axis (1) parallel to C_∞ and axis (3) parallel to C_∞, a_2 the difference between axis (2) parallel to C_∞ and axis (3) parallel to C_∞.

In the following, additional assumptions are made and some relations for a_1 and a_2 are given which we assume to be approximately valid if a_1 and a_2 essentially result from dispersion forces. This can of course only be true for molecules that do not associate by hydrogen bonds or have some other strong specific interactions.

(A) a_1 and a_2 can be regarded as consisting of two factors, a first factor that depends only on the properties of the nematic solvent and a second one that depends only on the properties of the solute molecule.

(B) a_1 and a_2 can also be regarded as consisting of a number of additive terms. Each σ-bond, especially each C—H and C—F bond in fluorobenzenes, contributes its own term and by fluorine substitution only the term of the substituted bond is affected.

An obvious conclusion from (A) is that the ratio a_1/a_2 is independent of the nematic solvent. For fluorobenzenes, it requires also independence of temperature and solute concentration since the molecular properties of these compounds are independent of concentration and, in the interesting temperature range, practically independent of temperature.

The conclusions following from (B) are less easily obtained. We use an additional more stringent assumption:

(C) The interaction of the CH σ-bond electrons or the CF σ-bond electrons (including the core electrons of F) with the nematic solvent depends only on the angle between bond axis and symmetry axis C_∞ of the solvent.

The contribution of such a σ-bond to the interaction potential is in our approximation accordingly

$$V_\sigma = -a_\sigma^0 - a_\sigma \cos^2 \phi \tag{12}$$

Here a_σ^0 and a_σ are two constants which depend on the bond and on the solvent and ϕ is the angle between bond axis and C_∞. Applying (12) to our fluorobenzenes we find the final relations for the energy coefficients for these compounds

$$\begin{aligned} a_1 &= a_B + b \sum \cos^2 \alpha_i \\ a_2 &= a_B + b \sum \sin^2 \alpha_i \end{aligned} \tag{13}$$

The sum has to be taken over all substituted bonds. α_i is the angle between bond axis (i) and the coordinate axis (1), $b = a_\sigma(CF) - a_\sigma(CH)$ and a_B stands for $a_1 = a_2$ of unsubstituted benzene.

We shall use Eqs. (11) and (13) to calculate a_B and b starting from the experimental S-values of a suitable fluorobenzene. Using the same relations and the obtained values for a_B and b we then calculate S-values for other fluorobenzenes in the same nematic surroundings. The comparison with the observed S-values provides a test for the assumptions (B) and (C). We assume in such calculations again that the bond angles are 120°.

Of special interest are 1,2- and 1,3-difluorobenzene. We choose the twofold symmetry axis in the first molecule as axis (2) and in the second molecule as axis (1). The axis (3) is, as in all cases, normal to the plane. For both molecules we find now the same values for a_1 and a_2

$$a_1 = a_B + \tfrac{1}{2}b; \quad a_2 = a_B + \tfrac{3}{2}b$$

We expect accordingly similar S-values for both molecules. This is indeed confirmed experimentally as will be shown in the next section. We have here another example showing that the electrical dipole moment—it lies in (1)-direction in 1,3-difluorobenzene ($\mu = 1.6\ D$) and in (2)-direction in 1,2-difluorobenzene ($\mu = 2.4\ D$)—is of minor influence for the orientation in nematic liquids. This fact has been demonstrated earlier in another way: no significant differences were found in the orientation of 1,2,3-trichlorobenzene[6] in nematic liquids with opposite signs for the dielectric anisotropy.

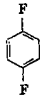
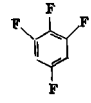
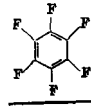
4. Experimental Results and Comparison with the Theory

In Table 1 a selection of S-values is shown, observed with benzene and fluorobenzene derivatives in two different solvents I and II (Fig. 1), and their energy coefficients derived from these S-values. S_3 is assumed to be negative in all cases; that means the molecules are assumed to orient preferably with their planes parallel to the optical axis. For monofluorobenzene the data reported by Snyder[9] were used. His solvent was not pure but contained p-methoxy derivatives of azoxybenzene.

The values in parentheses were calculated using Eqs. (13) and (11) and two different sets of values for a_B and b: $a_B/kT = 0.81$, $b/kT = 0.44$ in solvent I and $a_B/kT = 0.55$, $b/kT = 0.56$ in solvent II. These values were obtained by adapting to 1,4-difluorobenzene.

Table 1 shows that the molecules orient similarly in the two solvents but fluorine substitution causes strong changes in their orientation. The agreement between the experimental and the calculated values is fairly good, except perhaps for 1,2,4,5-tetrafluorobenzene and hexafluorobenzene. Table 1 shows also that 1,2- and 1,3-difluorobenzene orient nearly equally as has been already mentioned. Both facts are a strong justification for our assumptions (B) and (C). However, the experimental S-values in Table 1 can be used only for a rough qualitative comparison since they have been determined in different samples

TABLE 1 Typical experimental S-values and Energy Coefficients. The values in parentheses were calculated with a_B and b in each solvent adapted to 1,4-difluorobenzene. The position of the molecular coordinate system is indicated in the first column.

	solvent I				solvent II			
	S_1	S_2	a_1/kT	a_2/kT	S_1	S_2	a_1/kT	a_2/kT
	0.05	0.05	0.82	0.82	0.05	0.05	0.82	0.82
	(0.05)	(0.05)	(0.81)	(0.81)	(0.04)	(0.04)	(0.55)	(0.55)
	0.10‡	0.01‡	1.09	0.70				
	(0.11)	(0.01)	(1.25)	(0.81)	(0.12)	(− 0.01)	(1.11)	(0.55)
	0.18	− 0.03	1.68	0.81	0.20	− 0.06	1.66	0.55
	(0.18)	(− 0.03)	(1.68)	(0.81)	(0.20)	(− 0.06)	(1.66)	(0.55)
	0.02	0.10	0.83	1.17	0.00	0.14	0.88	1.47
	(0.02)	(0.13)	(1.03)	(1.46)	(0.00)	(0.13)	(0.83)	(1.39)
	0.03§	0.11§	1.03§	1.36§	0.03	0.11	1.03	1.36
	(0.02)	(0.13)	(1.03)	(1.46)	(0.00)	(0.13)	(0.83)	(1.39)
	0.08	0.08	1.41	1.41	0.08§	0.08§	1.41§	1.41§
	(0.08)	(0.08)	(1.46)	(1.46)	(0.08)	(0.08)	(1.39)	(1.39)
	0.00	0.18	1.23	1.95	0.01	0.17	1.28	1.92
	(− 0.02)	(0.21)	(1.24)	(2.12)	(− 0.04)	(0.23)	(1.11)	(2.22)
	0.14§	0.04§	1.82§	1.42§	0.15	0.04	1.95	1.52
	(0.15)	(0.04)	(1.90)	(1.46)	(0.16)	(0.02)	(1.94)	(1.39)
	0.14	0.14	3.10	3.10	0.14	0.14	3.10	3.10
	(0.11)	(0.11)	(2.12)	(2.12)	(0.11)	(0.11)	(2.22)	(2.22)

‡ Snyder[9] § Added in proof.

with varying concentrations (5–20 mole%) and temperatures. Table 2 gives an example of the temperature dependence of the orientation. For a reliable comparison of the orientation of two compounds one should measure them together in the same sample. This is difficult with fluorobenzenes since the spectra may become rather complicated. Fortunately, there is still another way for testing our theory.

TABLE 2 Temperature Dependence of S_1, S_2, a_1 and a_2 of 1,4-difluorobenzene in solvent II. a_1/a_2 is constant within experimental error limist

T (°C)	S_1	S_2	a_1 (10^{-2} eV)	a_2 (10^{-2} eV)	a_1/a_2
40	0.260	− 0.086	5.75	1.85	3.11
45	0.228	− 0.070	5.20	1.76	2.95
48	0.223	− 0.067	5.16	1.78	2.90
52	0.215	− 0.064	5.04	1.74	2.90
59	0.204	− 0.060	4.89	1.68	2.91

According to our first assumption (A) we expect that the ratio a_1/a_2 are independent of temperature, concentration and solvent. The last column of Table 2 and additional results confirm the independence on temperature and concentration within the investigated ranges as a good approximation. The ratios measured in the same solvent can therefore be compared without reservations. The conclusion of our theory about the independence on solvent is, as Table 3 shows, not a good approximation for fluorobenzenes in our two solvents. The largest variation is found with 1,4-difluorobenzene where the ratio is about 2 in solvent I and about 3 in solvent II. This result differs from the observations with 1,2,3-trifluorobenzene[6] where, within the limits of experimental error, no variation in five solvents was found.

We use again the experimental results found for 1,4-difluorobenzene and calculate the ratios for the other molecules in the same solvent. Of course, only the molecules without a threefold axis are of interest, since otherwise necessarily $a_1/a_2 = 1$. From

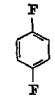
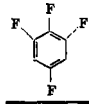
Eq. (13) follows

$$a_1/a_2 = \frac{1 + (b/a_B) \sum \cos^2 \alpha_i}{1 + (b/a_B) \sum \sin^2 \alpha_i}$$

Only the ratio b/a_B enters the calculations. In solvent I we find $b/a_B = 0.52$, in solvent II $b/a_B = 0.98$.

Table 3 shows the results of the calculations together with the experimental data. The agreement is very good in solvent I. In solvent II some deviations are larger than the experimental error. The largest deviation of 27% is found here for 1,2,4,5-tetrafluorobenzene. The same compound in solvent I behaves as expected.

TABLE 3 Ratios of Energy Coefficients. The experimental values (except for monofluorobenzene) are average values of several spectra. For the calculation the parameter ratio a_B/b was adapted again to 1,4-difluorobenzene in both solvents.

	solvent I		solvent II	
	$(a_1/a_2)_{exp}$	$(a_1/a_2)_{calc}$	$(a_1/a_2)_{exp}$	$(a_1/a_2)_{calc}$
	1.55	1.52		1.97
	2.04	2.04	2.95	2.95
	0.71	0.71	0.60	0.60
	0.76‡	0.71	0.74	0.60
	0.61	0.59	0.68	0.50
	1.26‡	1.29	1.28	1.40

‡ Added in proof.

5. Conclusions

It can be stated that differences in the orientation of different fluorobenzenes are mainly caused by localized contributions of the substituted bonds to the intermolecular interactions. Similar conclusions were obtained earlier with chlorobenzene derivatives.[6] With fluorobenzenes we expected to find a better agreement with the theory, which uses "localized contributions" as a basic assumption, since fluorine is a less bulky atom. Substitutions with fluorine cause considerably smaller changes in the molecular shape and in the screening of other bonds than chlorine substitutions. In solvent I we did find a better agreement but not in solvent II. There are differences between the two solvents which we did not expect to find. They probably indicate that in solvent II some specific interactions are of importance but for more detailed statements additional measurements, also in other solvents, are necessary. Electric dipole moments do not seem to have much influence on the orientation which confirms an earlier result.[6]

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