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D. F. R. Gilson [a]

[a] Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada

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The Orientational Behaviour of Some Fluorinated Molecules in Nematic Liquid Crystal Solvents

D. F. R. GILSON

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada.

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INTRODUCTION

The analysis of the nmr spectrum of a molecule dissolved in a liquid crystal solvent leads to information about both the geometry of the molecule and its degree of orientation in the solvent[1]. The orientation is often considered as a by-product of the analysis, since it is usually the molecular structure which is of primary interest, but useful information is contained within the orientation matrix and several studies have been reported which attempt to link the orientation to other molecular properties. The early work of Saupe[2,3] showed that, in the absence of specific solvent-solute interactions, a simple bond additive model gave approximate agreement for various fluoro- and chloro-substituted benzene derivatives. Later studies attempted to correlate the orientation with molecular shape,[4] polarizability,[5] moments of inertia,[6] and by empirical relationships involving a form of substituent additivity constant.[7] Very few studies have been reported which specifically examine the molecular orientation of the solute molecule as a function of temperature, concentration, solvent type, etc. Hillenbrand and Yu[8] found that the two orientation parameters required to describe the orientation of fluorobenzene in hexyloxyazoxybenzene were functions of reduced temperature in much the same way that the order of the liquid crystal solvent itself followed a universal curve for either different concentrations of the same solute[9,10] or for a wide variety of solute molecules at the same concentration.[11] A study of the temperature and concentration dependence of the orientation of trichlorobenzene in MBBA showed that the reduced temperature behaviour did depend upon the concentration.[11] More recently it has been claimed that the ability to fit the experimental orientation parameters in phenylcyclohexylcyanide type solvents with a potential based upon the anisotropy of the molecular polarizability determines whether dispersive or repulsive forces[12,13] occur.

The solvent EBBA is one in which the orientation of ortho-difluorobenzene showed marked disagreement between the calculated and experimental behaviour[13] and in the present study we report the results of an examination of the orientation of para-difluorobenzene in this solvent. In addition, two other fluorine containing molecules, fluorobenzene and fluoranil, are considered since the temperature dependence of the orientation has been reported[8,14,15] in these cases.

EXPERIMENTAL

The order parameter information can be obtained easily from the ^{19}F spectra and a 19 mole percent solution of *p*-difluorobenzene in EBBA (nematic to isotropic transition temperature 46 °C) was used with a Varian HR60 spectrometer operating at 56.4 MHz. At the probe temperature and higher the spectra were first order, consisting of two quintets, but at lower temperatures showed second order character and were analysed accordingly. The orientation parameters were obtained from the experimental dipole coupling constants using the geometry determined earlier.[16] The order parameter of the solvent EBBA as a function of temperature was determined from the dipolar splitting in the wide line nmr spectra.[17]

RESULTS AND DISCUSSION

The orientation parameters S_{xx} and S_{yy} can be calculated[2,3] by integration of the appropriate expressions over a general potential function of the form of equation (1).

$$-a_1\cos^2\theta_1 - a_2\cos^2\theta_2 - a_3\cos^2\theta_3 \qquad [1]$$

where θ_i is the angle between the ith molecular axis and the liquid crystal director, the terms a_i are related to free energies for orientation about that axis. From the relationships between the cosine directions and after removal of orientationally independent terms and some rearrangement, the potential function can be written as:

$$-V(\theta, \phi) = Q\sin^2\theta(\cos^2\phi + R\sin^2\phi) \qquad [2]$$

where θ and ϕ are the polar and azimuthal angles, the term R equals $(a_2 - a_3)/(a_1 - a_3)$, and Q is proportional to $(a_1 - a_3)$. For all molecules considered here the y or 2-axis is taken to be the direction of principal orientation and the z or 3-axis (perpendicular to the ring) the least oriented. If the terms a_i reflect both solute and solvent contributions then we require in equation [2] that these can be separated by taking the ratio of differences so that the solvent dependent part cancels, leaving R as a constant for a given molecule and Q as the only term which involves the solvent. Q should include the strength of the intermolecular interaction, the solvent order parameter, and temperature, and will be solvent and solute dependent.

In Figure 1 the orientation parameters S_{xx} and S_{yy} are plotted against each other for fluorobenzene, para-difluorobenzene, and fluor-

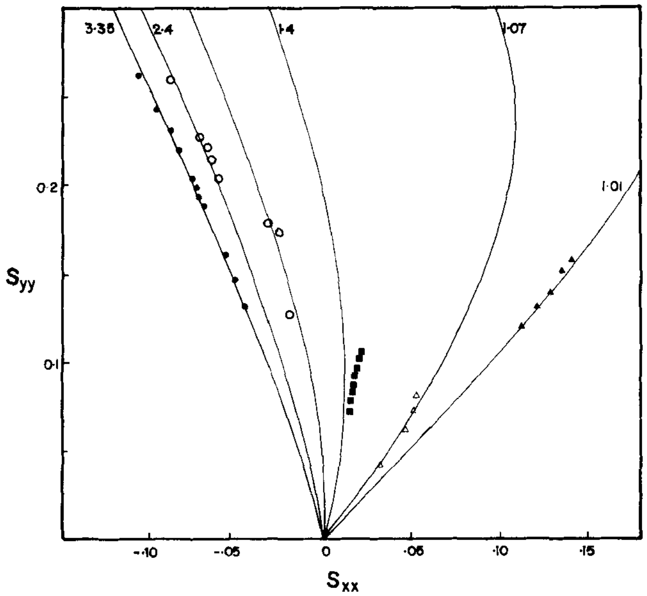

FIGURE 1 S_{yy} versus S_{xx} for fluorobenzene (squares—ref. 8), for para-difluorobenzene (filled circles—present work, empty circles—refs. 2, 3), and fluoranil (filled triangles—ref. 14, empty triangles—ref. 15).

anil, using the present results and those available in the literature. It is apparent that R is not independent of the type of solvent. The results of Hillenbrand and Yu[8] for monofluorobenzene could not be fitted since a constant value for the parameter R could not be obtained.

Väänänen *et al.*[13] proposed that if the observed behaviour of S_{xx} and S_{yy} followed that calculated for a function similar to R, in which the terms a_i are replaced by the molecular polarizabilities, α_i, then the orientation was due to dispersion forces. An acceptable fit was obtained in the case of ortho-difluorobenzene dissolved in phenylcyclohexyl type solvents, but the available data on the orientation in other solvents did not agree with the calculated behaviour. It was suggested that, in such cases, either the solvent-solute interaction was repulsive rather than attractive, and the constant R should be calcu-

TABLE I

Orientation parameters for *p*-difluorobenzene and EBBA as functions of reduced temperature

T^*	S_{xx}	S_{yy}	S_{EBBA}
.869	−.105	.263	.729
.884	−.099	.253	.717
.902	−.094	.243	.700
.919	−.087	.231	.679
.929	−.082	.221	.665
.939	−.078	.212	.648
.944	−.075	.204	.637
.955	−.072	.200	.615
.958	−.071	.195	.607
.963	−.068	.189	.595
.975	−.062	.175	.554
.981	−.056	.161	.529
.987	−.051	.147	.497
.993	−.045	.132	.455

TABLE II

Comparison of the ratios R based on polarizabilities and on molecular size with experimental values

	Solvent	Rpol	RvdW	Rexp	Ref.
Fluorobenzene	HBAB	1.113	1.350	1.3–1.4	8
p-difluorobenzene	EBBA	1.215	1.476	3.35	Present work
	Mixed			2.40	2.3
Fluoranil	M1132	1.435	1.171	1.01	15
	Phase IV			1.07	14

lated for molecular dimensions instead of polarizabilities, or that specific interactions occurred. In Table II the experimental values of R are compared with those calculated using the polarizabilities[18] and van der Waals radii. The change in the value of R does not imply a change from an attractive to a repulsive potential since the *sign* of the potential is unaltered. Even if allowance is made for the large uncertainties in these parameters there is only very qualitative agreement. Fluoranil shows little difference in the value of R for the phenylcyclohexyl and azoxy-type solvents, however both S_{xx} and S_{yy} are quite sensitive to the value of R at low R, and in both solvents there is little preferred orientation in the xy plane which is surprising in view of the polarizability of the quinoid structure. If specific intermolecular interactions do exist then the most obvious possibility, the presence of charge transfer interactions between fluoranil and solvent molecules, does not seem to influence either the orientation or the molecular structure.[14,15] Thus the term R is neither independent of the solvent nor is it attributable to a specific molecular property.

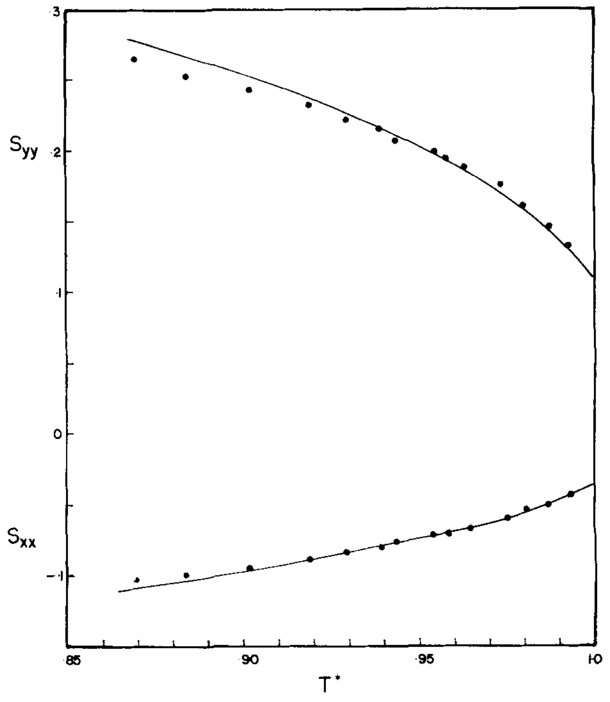

FIGURE 2 S_{xx} and S_{yy} versus reduced temperature T^* for para-difluorobenzene in EBBA. Solid line is the calculated curve.

It is possible, however, to extend the application of equation [3] a little further. If the order parameter of the solvent is known as a function of temperature then this can be included in the variable Q, which should be reduced to a constant for the particular system. To do this we take advantage of the fact that the order parameter for the solvent is a function of reduced temperature, $T^* = T/T_N$, and is therefore independent of the solute or its concentration.[9-11] The calculated and experimental dependence of S_{xx} and S_{yy} for *p*-difluorobenzene, as functions of reduced temperature, are compared in Figure 2 with a value of 0.984 for the "reduced" constant, Q^*. The agreement is quite good. However the system is still incompletely described since Q should probably include solute-solute as well as solute-solvent interactions, and should therefore reflect the solute concentration, and it neglects the temperature dependence of the volume.

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