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The Average Orientation of Solute Molecules in Nematic Liquid Crystals by Proton Magnetic Resonance Measurements and Orientation Dependent Intermolecular Forces

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Abstract—The average orientation of benzene and some chlorine substituted benzene derivatives in a nematic liquid crystalline solution has been determined. 1,2,3-trichlorobenzene was used to study the influence of a permanent electrical dipole moment. It was measured in different nematic solvents of positive and of negative dielectrical anisotropy. There is no or only little variation in the relative average orientation of the principal molecular axes. It shows that the forces between permanent electrical dipole moments are of minor importance for the average orientation.

A simple relation with two adjustable parameters is assumed for the orientation dependent part of the intermolecular interaction potential between solute molecules and anisotropic solvent. The values of the energy parameters are calculated from the observed average orientation by a simplified statistical treatment. Regarding only the dispersion forces and with some other neglections these parameters for benzene and the different derivatives can be theoretically correlated to each other. The comparison with the experimental results gives an approximate agreement.

Introduction

Nematic liquid crystals differ from normal isotropic liquids only by a spontaneous parallel orientation of their more or less rod-like molecules. The parallel orientation, disturbed by the thermal rotary motion of the molecules, is not complete but good enough to cause a strong macroscopic anisotropy. Nematic liquids behave optically like uniaxial crystals. They can easily be homogeneously oriented in thick layers by a magnetic field. Their optical axis turns parallel to the field.

Nematic liquids are as anisotropic liquid solvents of special interest for nuclear magnetic resonance measurements. It is possible to obtain in nematic solutions highly resolved spectra of partially oriented solute molecules.[1–6] The analysis of proton magnetic resonance (p.m.r.) spectra allows the determination of the average orientation of the solute molecule provided its structure is sufficiently known. Information may be obtained on anisotropic molecular properties that can not be observed in isotropic solutions, so for instance on the anisotropy of the chemical shift. Also some information on the molecular geometry may be obtained. In this work a report is given on a first study about the dependence of the average orientation of the solute molecules on its molecular properties and about the possible dependence on specific properties of the nematic solvent. Measurements have been made with benzene and some chlorine substituted benzene derivatives in nematic liquid 4,4′-di-n-hexyloxy-azoxybenzene. 1,2,3-trichlorobenzene has been measured in five different nematic solvents in search of the influence of electrical dipole-forces on the average orientation. Simplified theoretical relations are used to discuss the experimental results in terms of intermolecular forces.

Average Orientation and Energy

The nematic solution in our p.m.r. measurements was oriented by the magnetic field. We denote by ξ_1, ξ_2 and ξ_3 the axes of a cartesian coordinate system fixed in a regarded solute molecule and with θ_1, θ_2 and θ_3 the angles between these axes and the optical axis of the solution. The average orientation of the solute molecule as far as it is of interest for n.m.r. measurements can be described by a symmetrical matrix[2] defined by the expectation values

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

Here $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. The trace of the S-matrix disappears, so that in general the matrix has five independent elements in certain limits. By a suitable choice of the molecular coordinate system the matrix can always be transformed to diagonal form.

The following molecules have been studied: Benzene (I), 1,3,5- and 1,2,3-trichlorobenzene (II, III) and 1,4-dichlorobenzene (IV). The principal axis are here determined by molecular symmetry so that there remain only two orientation parameters to be experimentally determined. We put ξ_1 and ξ_2 in the molecular plane and ξ_3 perpendicular to it. The position of ξ_1 and ξ_2 is shown in Fig. 4. It is not necessary to define for benzene and 1,3,5-trichlorobenzene the exact position of ξ_1 and ξ_2 because these molecules have a more than twofold symmetry axis, perpendicular to their plane. Here the relations $S_1 = S_2 = -\frac{1}{2}S_3$ hold. It remains only one S-value to be determined experimentally.

We call the diagonal elements the degree of order of the corresponding axis. It may vary between $+1$ and $-\frac{1}{2}$. It is $+1$ if the corresponding axis always shows parallel to the optical axis, $-\frac{1}{2}$ if it always shows perpendicular, and zero for random orientation. In the same way as for the coordinate axis we can define for any molecular axis p its degree of order S_p. It can easily be calculated out of the principal S-values by the relation

$$S_p = \alpha_1^2 S_1 + \alpha_2^2 S_2 + \alpha_3^2 S_3 \tag{1}$$

where α_1, α_2, α_3 are the direction cosines of p in the principal coordinate system.

The S matrix contains all information that n.m.r. measurements can give on the molecular average orientation. As has been shown by Snyder[7] its elements have a simple relation to the coefficients of spherical harmonics of second order obtained by the expansion of the molecular distribution function.

To draw from the observed S-values detailed conclusions on the intermolecular forces we have to make simplifying assumptions:

We assume for the orientation dependence of the interaction potential the relation

$$V = -a_1 \cos^2\theta_1 - a_2 \cos^2\theta_2 - a_3 \cos^2\theta_3 \tag{2}$$

where θ_1, θ_2 and θ_3 refer to the principal coordinate system and a_1, a_2 and a_3 are constants. Since we are only interested in the orientation dependent part of V, we can put $a_3 = 0$ and drop the

last term. Relation (2) is the most simple assumption one can make adequate to an apolar orientation. It can theoretically be derived if only the dispersion forces are regarded and a dipole–dipole approximation is used. The dipole–dipole approximation is only justified for long intermolecular distances. Its use in liquids is therefore very doubtful. In addition it must be assumed for the derivation that the average orientation of the surroundings is independent of the instantaneous orientation of the regarded molecule.

To establish the relation between the observed S-values and the energy parameters a_i we use a simple Boltzmann treatment. It results in

$$S_i = \frac{3}{2}\frac{\int \cos^2\theta_i e^{-V/kT}\, d\Omega}{\int e^{-V/kT}\, d\Omega} - 1 \qquad (3)$$

This statistical treatment is consistent with the above assumption concerning the average orientation of the surroundings.

The two relations are of course a crude simplification of the very complex situation in nematic liquids. No explicit reference has for instance been made to the molecular shape which by many workers is regarded as one of the most important factors in orienting. But the nematic state itself has been treated with some success in a similar way.[8] Many of its properties could at least be qualitatively understood. We can therefore expect that the results derived by the two relations provide a useful basis for the discussion of the intermolecular forces. It is a preposition of course that the regarded molecules should not associate.

The dispersion forces between a solute molecule and the nematic solvent may probably in a good approximation be regarded as the sum of the contributions of its π-electronic-system and of its σ-bonds inclusive the core electrons. The π-electronic-system of benzene does not change much by chlorine substitutions nor will the σ-bonds except of course the substituted one. Analogous to Eq. (2) we assume for the interaction potential of a given σ-bond

$$V = -a_\sigma \cos^2\theta \qquad (4)$$

where θ is the angle between the bond axis and the optical axis. a_σ

will depend on the bond itself, on its position in the regarded molecule and on the nematic solvent. Now let us turn to our special molecules. We neglect the dependents of a_σ on the position of the bond and assume that the molecules have the same nematic surroundings.

We have chosen the axis ξ_3 in all cases perpendicular to the molecular plane. For benzene obviously a_1 is equal to a_2. It follows

$$V(\mathrm{I}) = -a_1(\mathrm{I})\,(\cos^2\theta_1 + \cos^2\theta_2) = a_1(\mathrm{I})\cos^2\theta_3$$

For 1,3,5-trichlorobenzene we have the same relation with another constant $a_1(\mathrm{II})$. If we assume that its difference against benzene is given only by the difference of the interactions of the three C—Cl bonds against that of the corresponding C—H bonds we find

$$a_1(\mathrm{II}) - a_1(\mathrm{I}) = \tfrac{3}{2}\delta; \quad \delta = a_\sigma(\mathrm{C{-}Cl}) - a_\sigma(\mathrm{C{-}H}).$$

In this approximation for (III) the same relation as for (II) should hold, provided the bond angles are the same

$$a_1(\mathrm{III}) = a_2(\mathrm{III}) = a_1(\mathrm{II}).$$

For 1,4-dichlorobenzene we find

$$a_1(\mathrm{IV}) = a_1(\mathrm{I}) + 2\delta; \quad a_2(\mathrm{IV}) = a_1(\mathrm{I}).$$

Later on we shall compare these relations with our experimental results, and next regard the influence of electrical dipole forces.

Experimental Results

(a) *Electrical Dipole–Dipole Forces*

1,2,3-Trichlorobenzene is a molecule with a permanent electrical dipole moment in the molecular plane and according to the above considerations with little anisotropy in its plane with regard to the dispersion forces. It seemed to use therefore to be a suitable molecule for studying the effect of the interactions connected with a permanent electrical dipole moment. We thought that there might be drastic differences in the average orientation for different solvents, for instance in such a way that in solvents with positive

dielectrical anisotropy $S_1 > S_2$ and in solvents with negative dielectrical anisotropy $S_1 < S_2$, because an electrical dipole moment will tend to show in the direction of the largest dielectrical susceptibility. The result of the measurements did not at all agree with these expectations.

Measurements with 1,2,3-trichlorobenzene were made with the solvents shown in Fig. 1. Solvent A has a negative dielectrical anisotropy. Solvent B differs from A by the substitution of the

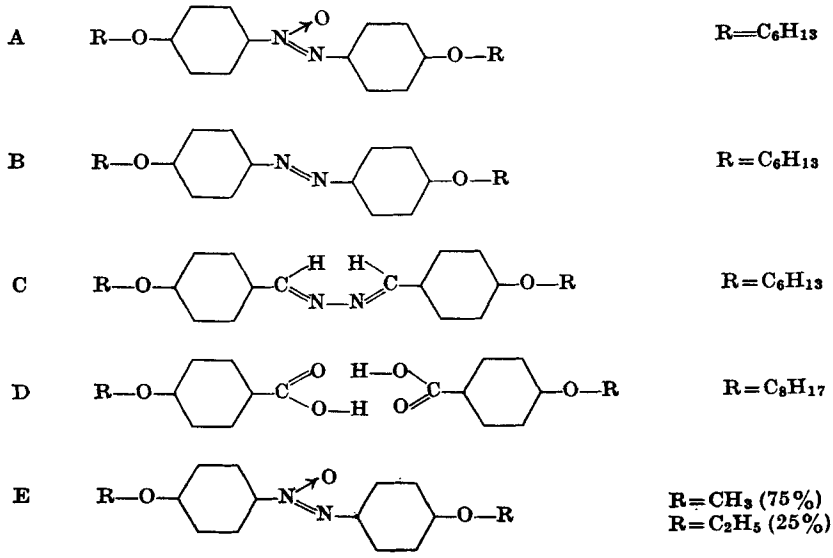

Figure 1. Nematic Solvents.

azoxy-group by an azo-group. B has a positive dielectrical anisotropy. The temperature range of its nematic phase is too small to obtain solutions with a sufficiently high concentration, so we used a mixture of 75% B + 25% A for the measurements. Solvent C has again a negative anisotropy. In D the solvent molecules exist in a dimeric form in the nematic state. But there is of course no conjugation between the π-electrons of the two halves. Its dielectric anisotropy is positive. Solvent E is a mixture of azoxyanisole and azoxyphenetole to increase the temperature range of the nematic

phase. This solvent was used to see whether the reduction of the length of the alkoxy chains has a remarkable effect.

Figure 2 shows as an example the p.m.r.-spectrum of 1,2,3-trichlorobenzene in D together with the calculated lines. The spectrum consists of nine lines. All of them can be observed. Similar spectra have been obtained in all other solvents. We assumed for the determination of the S-values here and with the

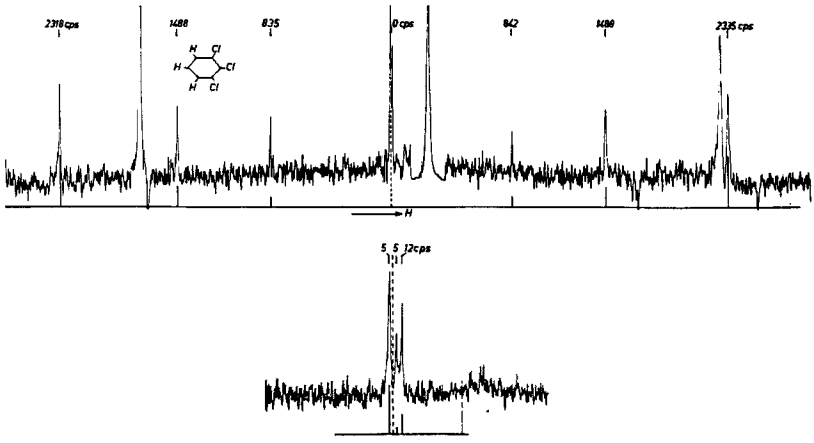

Figure 2. 1,2,3-Trichlorobenzene; p.m.r. spectrum at 60 Mc/s with the completely resolved central part in nematic liquid 4-n-octyloxy-benzoic acid and calculated lines. The very strong line near the centre (the gain was reduced by a factor 10) is due to the acidic proton of the solvent. At a distance of 2016 c/s on both sides of this line are its first side bands.

other molecules that the proton distances are not changed by the substitutions. For proton pairs in *ortho* position we assumed the distance equal to 2.48 Å, for proton pairs in *meta* position 4.30 Å and for *para* position 4.96 Å. For 1,2,3-trichlorobenzene the *ortho* scalar spin–spin coupling constant has to be taken into account. It was put equal to + 8 c/s. The absolute signs of the S-values were determined under the assumption that in all regarded cases the molecular plane orients preferably parallel to the optical axis.

In Table 1 the results are summarized. In any solvent S_2 is much larger than S_1. The values of a_1 and a_2 depend on the temp-

erature and on the concentration. This is probably a consequence of the dependence of the solvents degree of order on these two factors. On the other hand the range of the a-values seems to be nearly independent of the specific nematic solvent. The ratio a_1/a_2 is in a good approximation a constant independent of the temperature, the concentration as well as of the solvent. All variations seen in the table are within experimental errors, except perhaps the value obtained with the mixture 75% B + 25% A that seems to be slightly smaller than the others.

TABLE 1 1,2,3-Trichlorobenzene; S-values and energy parameters.

Solvent	T °C	Conc. mol %	S_1	S_2	S_3	a_1/kT	a_2/kT	a_1/a_2
A	96	6	0.049	0.133	−0.182	1.48	1.81	0.82
	86	6	0.053	0.147	−0.200	1.66	2.05	0.81
	77	>12	0.036	0.106	−0.142	1.07	1.44	0.79
	83	12[a]	0.042	0.133	−0.175	1.39	1.75	0.79
0.75B + 0.25A	85	6	0.035	0.142	−0.177	1.37	1.81	0.76
C	121	6	0.039	0.133	−0.172	1.35	1.72	0.78
D	104	6	0.046	0.145	−0.191	1.66	2.06	0.81
	95	6	0.052	0.153	−0.205	1.74	2.12	0.82
E	91	6	0.041	0.154	−0.195	1.58	2.01	0.79
	86	6	0.048	0.161	−0.209	1.76	2.21	0.80

[a] 8 mol % 1,2,3- and 4 mol % 1,3,5-trichlorobenzene.

We can conclude that the forces between electrical dipole moments are of little importance, else we should observe a more pronounced effect of polar groups. There do not seem to be any important interactions between specific groups at all since there is no remarkable variation of a_1/a_2. We can regard this result in some way as a confirmation of the assumption, that the interaction in nematic liquids can be described in a rather summary way. But the ratio of a_1/a_2 differs from 1 in contrast to our prediction. We shall discuss this fact later on together with the results obtained by the comparative study of molecular orientation.

(b) *Comparative Study*

Relative high solute concentrations are needed to obtain a sufficient high signal-to-noise ratio. Different solutes may react differently on the average orientation of the solvent molecules. We cannot therefore be sure that measurements made on different molecules are really comparable even if they are obtained in the same solvent at the same temperature and at the same molar concentration. This difficulty can be avoided by dissolving the two molecules, we want to compare, together in the same solution. 1,3,5-trichlorobenzene has a simple p.m.r. spectrum of three lines that can easily be observed. We have used this substance therefore as a relative standard and have measured it together with all the other substances.

Figure 3 shows for example the especially interesting spectrum of 1,4-dichlorobenzene together with our standard. The inner three lines belong to 1,3,5-trichlorobenzene. It is worth mentioning that the analysis of the spectrum of 1,4-dichlorobenzene shows that the relative proton distances deviate only a little from those in benzene. If we use the latter to calculate the S-values we find

$$S_1 = 0.2945$$

$$S_2 = -0.0866$$

$$S(H_2—H_5) = S(H_3—H_6) = 0.0085 \pm 0.0005$$

The last value should on the other hand be equal to

$$0.25S_1 + 0.75S_2 = 0.0062 \pm 0.0008$$

We can explain that difference if we assume that the angle $H_2—H_5—H_3$ has increased from 30° in benzene to 30°10′ in dichlorobenzene. An increase of the $H_2—H_3$ and $H_5—H_6$ distance of about 0.02 Å corresponds to this if the distances $H_2—H_6$ and $H_3—H_5$ are kept constant. After this excursion let us go back to the orientation problems. Table 2 summarizes the results.

All these measurements have been made in 4,4′-di-n-hexyloxyazoxybenzene (A). The table shows the S-values and the energy parameters. The ratios of the a-values R_1 and R_2 shown in the two

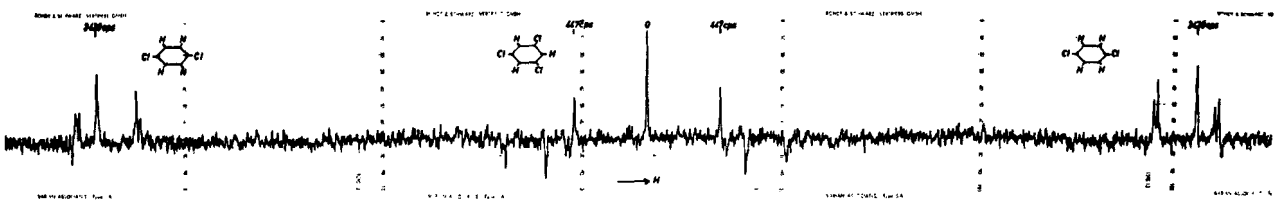

Figure 3. 1,4-Dichloro- and 1,3,5-trichlorobenzene, p.m.r. spectrum at 60 Mc/s in nematic liquid 4,4′-di-n-hexyloxy-azoxybenzene. The lines showing downward are second side bands at distances of 4036 c/s from the main signals.

TABLE 2 Benzene, 1,2,3-trichlorobenzene and 1,4-dichlorobenzene compared with 1,3,5-trichlorobenzene (II); S-values and energy parameters

Q	T °C	$S_1(Q)$	$S_2(Q)$	$S_3(Q)$	S_3(II)	$a_1(Q)$ 10^{-2} eV	$a_2(Q)$ 10^{-2} eV	a_1(II) 10^{-2} eV	$R_1(Q)$	$R_2(Q)$
C_6H_6	88	0.0525		−0.1050	−0.1630	2.69		4.49	1.00	
	79	0.0580		−0.1160	−0.1798	2.93		4.94	0.99	
	68	0.0624		−0.1248	−0.1905	3.09		5.16	1.00	
	68	0.06215		−0.1263	−0.1935	3.13		5.25	1.00	
1,2,3-$C_6H_3Cl_3$	83	0.042	0.133	−0.175	−0.1757	4.26	5.36	4.84	1.48	1.86
1,4-$C_6H_4Cl_2$	78	0.2727	−0.0817	−0.1910	−0.1898	7.01	2.66	5.29	2.22	0.84
	78	0.2733	−0.0817	−0.1916	−0.1900	7.04	2.66	5.29	2.23	0.84
	70	0.2845	−0.0866	−0.1979	−0.1967	7.17	2.72	5.40	2.23	0.84
	70	0.2850	−0.0867	−0.1983	−0.1958	7.17	2.72	5.37	2.24	0.85

$$R_i(Q) = 1.677a_i(Q)/a_1(\text{II}) = a_i(Q)/a_1(C_6H_6)$$

last columns seem to be independent of the temperature. We expect that they will also be approximately independent of the solvent as the ratio a_1/a_2 of 1,2,3-trichlorobenzene proved to be. We regard them therefore as characteristic for the two compared substances. In order to discuss the results more conveniently we have multiplied the ratios $a_i(Q)/a_1(\mathrm{II})$ by the factor

$$a_1(\mathrm{II})/a(\mathrm{C_6H_6}) = 1.677.$$

R_1 and R_2 are therefore related to unsubstituted benzene.

We can now compare the experimental a-values with our theoretical predictions. From comparison of benzene and 1,3,5-trichlorobenzene we can derive

$$\delta = a_\sigma(\mathrm{C—Cl}) - a_\sigma(\mathrm{C—H}) = 0.45\, a(\mathrm{C_6H_6}).$$

For 1,2,3-trichlorobenzene we expected the same a-values as for the symmetrical substance, that gives $R_1 = R_2 = 1.68$. Experimentally R_1 turns out to be 12% smaller, R_2 to be 11% higher. For 1,4-dichlorobenzene we obtain with the δ-value derived with symmetrical trichlorobenzene $R_1 = 1.9$ and R_2 should be equal to 1. The observed value of R_1 is here 2.23 and R_2 is 0.84. The comparisons show that there is only a rough approximate agreement, but that is all we could really expect.

One reason for the observed deviations is that the interaction of a bond with the neighbouring molecules depends on how near the neighbouring molecules may approach it. An obvious fact which has not been accounted for in our approximation. If we regard the shapes of the molecules (Fig. 4) we recognize with 1,2,3-trichlorobenzene for instance that the middle C—Cl bond is more shielded than the C—Cl bonds in 1,3,5-trichlorobenzene. Of course this will reduce the value of R_1. The other two C—Cl bonds are perhaps also more strongly shielded which should mainly lead to a reduction of R_2 but this effect is counteracted since the C—C bonds opposite to the Cl-atoms are less shielded than in the symmetrical substance. The angles between neighbouring C—Cl bonds in 1,2,3-trichlorobenzene are very likely larger than 60° because of the repulsion of the Cl-atoms. This may be a further important cause for the observed value of R_2 to be larger than expected and for R_1 to be smaller.

In 1,4-dichlorobenzene the C—C bonds parallel to direction ξ_1 are less shielded than the C—C bonds in 1,3,5-trichlorobenzene and therefore R_1 will be larger than the calculated value, while the C—C bonds stabilizing mainly orientation 2 (ξ_2 || optical axis) are less effective than in benzene and R_2 becomes smaller than 1.

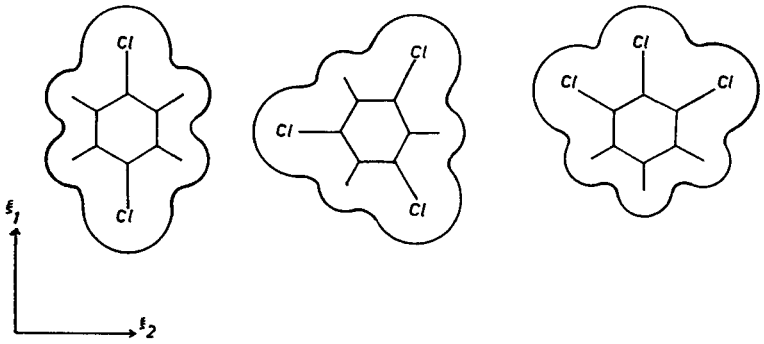

Figure 4. Solvent molecules; coordinate system and shape.

Our qualitative considerations show that we may get better results when we take into account in addition to the direction of the bonds that they are more or less strongly shielded. But it seems advisable to wait for more experimental results before additional shielding parameters are introduced. For instance measurements with monochlorobenzene are of special interest. We expect here using the results of 1,4-dichlorobenzene that R_1 will equal 1.61 and R_2 will equal 0.92. If experiments give no good agreement it cannot be explained by shielding effects and shows that we missed some important factor.

On the whole our results are encouraging. They stress the importance of σ-bonds in orienting. A direct experimental demonstration of their importance is the good orientation observed with methylene chloride, which is a small molecule without any double bonds. We found in a nematic solution of 4,4′-di-n-hexyloxy-azoxybenzene for the H—H axis absolute S-values between 0.06 and 0.08. We suppose that the two C—Cl bonds are mainly responsible for the orientation of this molecule. Accordingly we can estimate using

the observed S(H—H) that the S-values of the Cl—Cl axis range from 0.08 to 0.10 and are only by a factor near 3 smaller than the S-values obtained for the *para* axis of 1,4-dichlorobenzene.

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