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SOLUTION CONFORMATION OF BIS(*m*-NITROPHENYL) DISULPHIDE

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Abstract—The electric dipole moment of bis(*m*-nitrophenyl) disulphide has been measured at 25 and 45° in benzene solution and the rotational conformations about C—S bonds have been detected by vector addition. The results have shown that the molecule exists as solute in a preferred rigid conformation in which both the phenyl groups are twisted of an angle of 40° in opposite sense from coplanarity with respect to the sulphur valency plane.

The complete and exact analysis of the PMR spectrum in $CDCl_3$ has been performed and the parameters obtained have been discussed.

The participation of the sulphur 3d-orbitals to the C—S bonds in the disulphide studied has been postulated on the basis of the above proposed molecular conformation.

INTRODUCTION

THE crystal structure of diphenyl disulphide[1] and of some of its substituted derivatives[2–7] has been determined by X-ray diffraction. The solution conformation of a number of substituted diphenyl disulphides has been investigated by using polarization methods such as dipole moments,[8–10] dielectric relaxation[11] and molar Kerr constants.[12]

All these studies have shown that the —S—S— group exists in a rigid non-planar conformation with a dihedral angle of about 90° between the planes of the valencies of adjacent S atoms. However, the problem of the conformational preferences about the C—S bond in diaryl disulphides has not yet been rigorously solved.

The degree of rotational freedom about the C—S bond in bis(*o*-nitrophenyl) disulphide has been previously estimated[13] using dipole moment data. Therefore it has been of interest to investigate the bis(*m*-nitrophenyl) disulphide in which electronic as well as steric effects are less than in the case of *ortho*-substitution.

The present paper thus reports, together with the electric dipole moment of bis(*m*-nitrophenyl) disulphide in benzene solution at 25 and 45°, the complete exact analysis of its PMR spectrum in $CDCl_3$. The data obtained are discussed in terms of molecular solute conformation.

RESULTS AND DISCUSSION

Dipole moment. The experimental data and the dipole moment value of bis(*m*-nitrophenyl) disulphide are reported in Table 1.

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TABLE 1. WEIGHT FRACTIONS OF SOLUTE (w_2), DIELECTRIC CONSTANTS (ε_{12}), SPECIFIC VOLUMES (v_{12}) AND REFRACTIVE INDEXES (n_{12}) OF BIS(*m*-NITROPHENYL) DISULPHIDE IN BENZENE SOLUTION AT 25° AND 45°. LISTED BELOW ARE TOTAL POLARIZATION $P_{2\infty}$ (ml), MOLAR REFRACTION R_D (ml) AND DIPOLE MOMENT μ (DEBYE UNITS) TOGETHER WITH OTHER PARAMETERS FOR ITS EVALUATION

t = 25°				t = 45°			
$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
0·3970	2·3023	1·14151	1·49791	0·4646	2·2474	1·16625	1·48531
0·4812	2·3083	1·14108	1·49802	0·5014	2·2501	1·16606	1·48535
0·5303	2·3118	1·14084	1·49808	0·5611	2·2564	1·16579	1·48541
0·5639	2·3143	1·14066	1·49813	0·6118	2·2580	1·16551	1·48547
0·6158	2·3179	1·14040	1·49819	0·6812	2·2641	1·16518	1·48554
0·7002	2·3240	1·13997	1·49830	0·7223	2·2672	1·16497	1·48559

	α	ε_{10}	β	v_{10}	$P_{2\infty}$	R_D	μ
t = 25°	7·15	2·2739	−0·508	1·14352	472·73	80·2	4·35
t = 45°	7·59	2·2123	−0·496	1·16855	522·05	80·2	4·77

$\alpha = d\varepsilon_{12}/dw_2$; $\beta = dv_{12}/dw_2$; $\varepsilon_{10} = \lim_{w_2 \to 0} \varepsilon_{12}$; $v_{10} = \lim_{w_2 \to 0} v_{12}$.

The total moment has been evaluated by vector addition as a function of the rotation angles ϕ and ϕ' according to the relation $\mu = \sqrt{(\mu_x^2 + \mu_y^2 + \mu_z^2)}$. For the molecular model shown in Fig 1, the components along each axis are given by:

$$\mu_x = \mu_3 \cos\phi \cos\left(90^\circ - \frac{\Phi}{2}\right) - \mu_3 \cos\phi' \cos\left(90^\circ - \frac{\Phi}{2}\right) + 2(\mu_2 - \mu_1)\cos\frac{\Phi}{2}\cos(\theta - 90^\circ)$$

$$\mu_y = \mu_3 \cos\phi \sin\left(90^\circ - \frac{\Phi}{2}\right) - \mu_3 \cos\phi' \sin\left(90^\circ - \frac{\Phi}{2}\right)$$

$$\mu_z = \mu_3 \sin\phi \cos(\theta - 90^\circ) - \mu_3 \sin\phi' \cos(\theta - 90^\circ)$$

where $\mu_1 = \mu_{Ar-S}$; $\mu_2 = \mu_{Ar-NO_2}\cos 60^\circ$; $\mu_3 = \mu_{Ar-NO_2}\sin 60^\circ$.

The following assumptions have been made:

(1) We use the group moments $\mu_{Ar-S} = 1·29$ D[12] and $\mu_{Ar-NO_2} = 3·98$ D.[14]

(2) The dihedral angle between the sulphur valencies planes (Φ) is 96°[1] and the C–S–S angle (θ) is 106°.[1]

(3) The mesomeric moment value (μ_m) in bis(*o*-nitrophenyl) disulphide can be neglected.[13] Since in bis(*m*-nitrophenyl) disulphide the interaction S—NO_2 is obviously expected to be smaller than in the analogous *ortho*-substituted compound, we consider in the present calculations $\mu_m = 0$.

The possible rotational conformations of the molecule are defined by the rotation angles ϕ and ϕ' described by each phenyl group in clockwise direction starting from the structure shown in Fig 1. This model in which each phenyl group lies on the *xy* plane and the *meta*-nitro groups are in a *proximal* position is obtained by rotation angles $\phi = \phi' = 0$.

The results of the calculations are shown in Fig 2, where the contours 4·35 connect all points for which $\mu_{exp} = \mu_{calc}$.

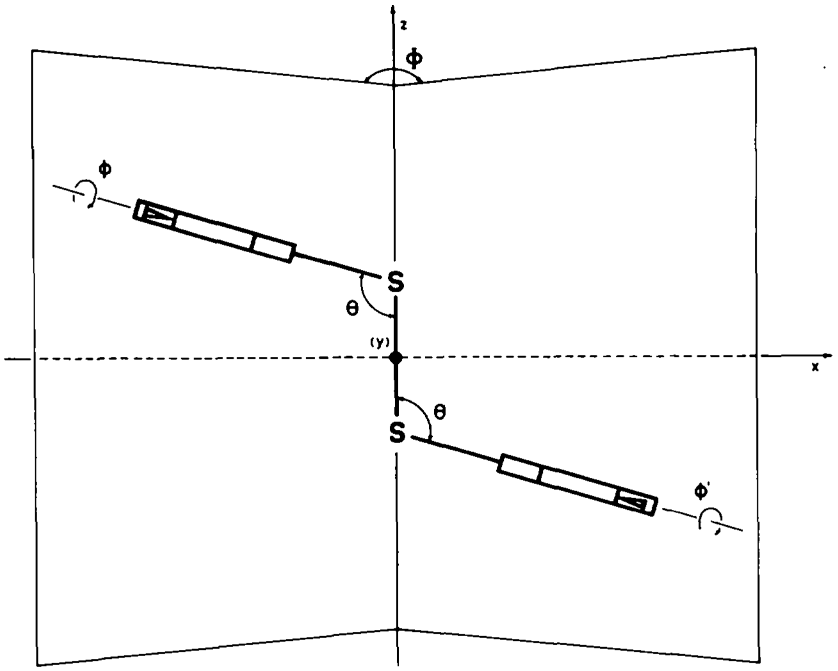

Fig 1. Bis(*m*-nitrophenyl) disulphide oriented along the coordinate system of axes. The configuration in which $\phi = 0^\circ$ and $\phi' = 0^\circ$ is outlined

The points on the diagonal for which $\mu_{calc} = 0{\cdot}90$ D correspond to the possible conformations obtained by concerted rotation (i.e. by angles $\phi = \phi'$) of the phenyl groups in the same sense starting from the model in Fig 1 where $\phi = \phi' = 0$. The poor agreement between this calculated dipole moment and the experimental value (4·35 D) allow us to exclude free rotation about C—S bonds.

On the basis of the large differences between the measured dipole moment and calculated values, we exclude also the possible conformations in which each phenyl group lies on the valency plane of the adjacent S atom ($\phi = \phi' = 90^\circ$ and $\phi = \phi' = 270^\circ$: $\mu_{calc} = 0{\cdot}90$ D; $\phi = 90^\circ$, $\phi' = 270^\circ$: $\mu_{calc} = 6{\cdot}66$ D).

However, inspection of the contour map shows* that the possible conformations of bis(*m*-nitrophenyl) disulphide are given by the marked points A, B, and A', B' on the contours 4·35. Scale molecular models indicate that the conformation in which $\phi = 40^\circ$, $\phi' = 320^\circ$ (A) or $\phi = 320^\circ$, $\phi' = 40^\circ$ (A') is unfavoured because of steric and electrostatic repulsions between the *meta*-nitro groups.

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* The conformation in which the angles are $\phi = \phi' = 0$ results unchanged if we consider a further rotation of 360° for a phenyl group. Therefore the model in Fig 1 can be assumed as corresponding on the map to the point in which the angles are $\phi = 0$, $\phi' = 360^\circ$ or, as is the same, $\phi = 360^\circ$, $\phi' = 0$. We now consider concerted rotation, i.e. by the same angles, of the phenyl groups about the C—S axes, but in opposite sense to each other starting from the above stated molecular model: any of the possible conformations obtained corresponds on the map to a point that lies on the diagonal line given by the relation $\phi + \phi' = 360^\circ$. Thus A, B, A', B' are the crossing points of this line with the contours for which $\mu_{exp} = \mu_{calc}$ (4·35 D).

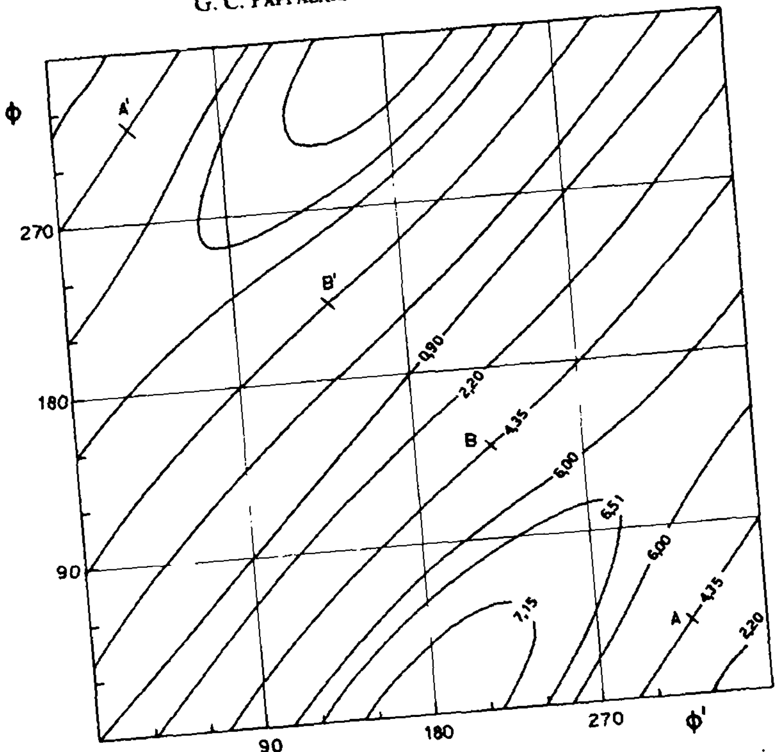


FIG 2. Contour of dipole moment values calculated as a function of the rotation angles ϕ and ϕ' for bis(*m*-nitrophenyl) disulphide

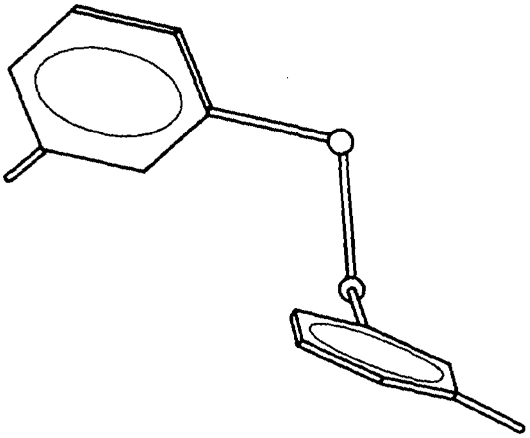


FIG 3. Molecular solute configuration of bis(*m*-nitrophenyl) disulphide

Thus we consider the molecule to exist as a solute in the twisted conformation (Fig 3) arising from the model in Fig 1 by rotation angles $\phi = 140°$, $\phi' = 220°$ or, as is the same, $\phi = 220°$, $\phi' = 140°$ (marked points *B* and *B*').

A further inspection of the contour map shows that the measured dipole moment is also in satisfactory agreement with the calculated for a skew *distal* conformation in which the aromatic rings are in planes perpendicular to each other ($\phi = 180°$, $\phi' = 270°$), one group being in the C–S–S plane and able to accomodate the sulphur *p*-electrons. This asymmetric conformation is to be abandoned on the basis of the unlikely non-equivalent position of the two phenyl groups with respect to the C–S–S planes. Moreover, we may exclude rapid interconversion between the phenyl rings in this conformation, since oscillations of such amplitude would give rise to an average dipole moment value very different from that of 4·35 D. However, further precise choice will be made in favor of the conformation given by the point *B* on the basis of the PMR spectral analysis discussed in the following section.

The measured dipole moment at 45° is 4·77 D. The small temperature coefficient shows that the increase in the amplitude of oscillation about C—S bonds which should accompany the rise of temperature agrees with the average dipole moment. On this basis, bis(*m*-nitrophenyl) disulphide exists in an essentially rigid conformation in which small torsional oscillations (up to *ca* 2°) about C—S bonds are possible.

Now it is clear that in aromatic disulphides hindered rotation about C—S bonds is either due to partial double bond character (resonance effects) or due to the steric effects of bulky *ortho*-substituents. In the present case of *meta*-substitution steric effects are unlikely to be important in determining the potential energy barrier hindering free rotation. On the other hand, in the above proposed favoured conformation each aromatic ring as a whole is twisted 40° from coplanarity with respect to the valency plane of the adjacent S atom. This lack of coplanarity involves lack of overlap between the sulphur 3p orbital and the 2p orbitals of the π system. This view also agrees with a previous UV study[15] in which evidence was presented of inhibited resonance interaction of the unshared *p* electrons of the S atoms with the π electrons of the phenyl groups in bis(*m*-nitrophenyl) disulphide.

Thus it appears that electronic effects arising exclusively from the participation of the sulphur 3d orbitals to the C—S bond are significant, and perhaps dominant, in determining the preferred conformation as well as the potential barrier hindering free rotation. Therefore in bis(*m*-nitrophenyl) disulphide the interaction between the full p_Z orbital on the C atom (part of the aromatic π bond) with an empty *d* orbital on the S atom is present to the extent that both C—S bonds contain partial double bond character.

The above conclusion is supported by the values of the rotation angles ϕ and ϕ' we have obtained for which one of the favourable positions for extensive $p_\pi - d_\pi$ overlap occurs.

PMR spectrum. Reasonable trial values of the *chemical shifts* have been estimated assuming additivity of substituent effect[16] in benzenethiol.[18] Trial parameters for the coupling constants have been taken from the analysis cited for benzenethiol and, partly, on the basis of splitting patterns.

Table 2 gives the final parameters obtained by iteration of all the resolved lines. Fig 4 shows the observed spectrum compared to the calculated one.

Theoretical Lorentz-shape pattern exhibits all the resonance lines of the observed

TABLE 2. ^{1}H-NMR SPECTRAL PARAMETERS FOR BIS(m-NITROPHENYL) DISULPHIDE (IN Hz) (RMS error of the final iteration 0·038.)

Coupling constants						Chemical shifts			
J_{24}	J_{25}	J_{26}	J_{45}	J_{46}	J_{56}	2H	4H	5H	6H
2·303 (0·006)	1·447 (0·035)	1·993 (0·012)	8·159 (0·016)	1·042 (0·011)	7·831 (0·024)	493·797 (0·020)	486·788 (0·018)	453·286 (0·031)	471·035 (0·023)

The probable errors of all the parameters iterated are given in parentheses.

spectrum and the computed intensities in satisfactory agreement with the experimental. Moreover, it can be observed that the hydrogen *chemical shifts* values are in the order $H_2 > H_4 > H_6 > H_5$ as might have been expected for a *meta*-substituted benzenethiol. Thus, in agreement with the assumption on which the analysis has been based, in the present case of bis(m-nitrophenyl) disulphide the phenyl groups are not rendered distinct by the restricted rotation about C—S bonds above elucidated by dipole moment considerations.

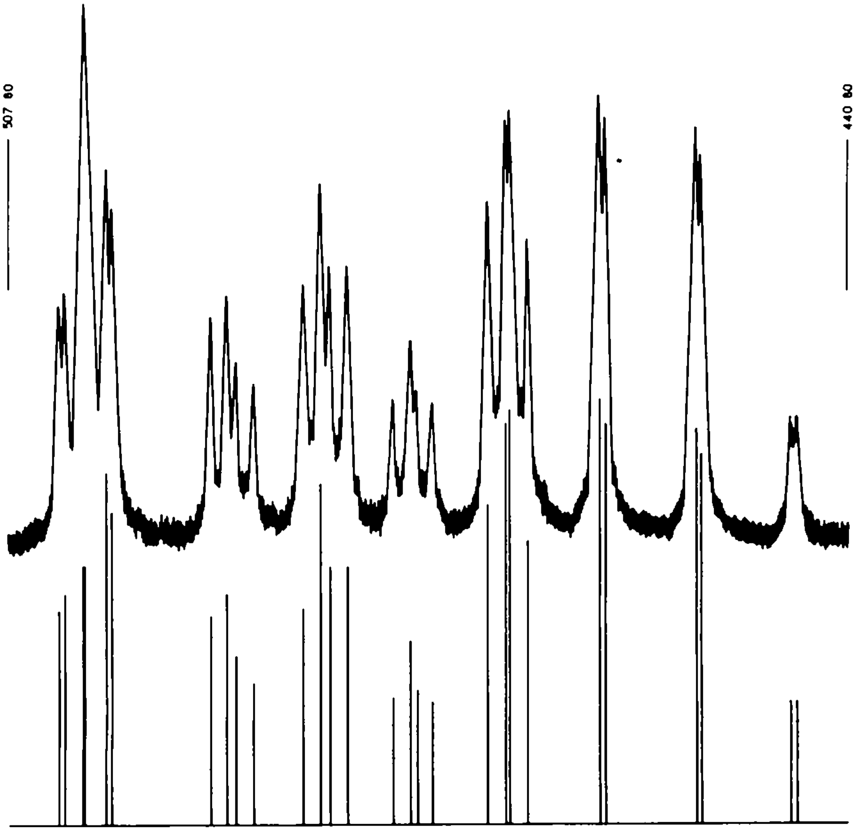


FIG 4. The observed and calculated 60 MHz ^{1}H spectrum of bis(m-nitrophenyl) disulphide in CDCl$_3$ (frequency markers in c/sec from tetramethylsilane)

The equivalence between the aromatic groups is due to the equal charge densities close to the corresponding hydrogens of the rings. It can be also simply due to equal shieldings from the S atoms. However, both hypotheses are consistent with the proposed molecular conformation in which the rotation angles ϕ and ϕ' have equal values with opposite signs with respect to each sulphur valency plane, since in this position electronic as well as steric equivalence occurs between the phenyl groups of the molecule.

These results confirm that a skew conformation can be excluded because of the strong difference observed between the rotation angles of the aromatic rings.

In the course of our experiments it has been tested that solvent effects on the *chemical shifts* are absent and that the spectral pattern is unaffected by the change of the solvent. Consequently, the conformational preference of the disulphide studied is independent of the medium.

EXPERIMENTAL

Bis(*m*-nitrophenyl) disulphide was a commercial Aldrich Chemical Co. product, purified to 99·96% by several recrystallizations from alcohol to constant m.p. (78°) and ε_{max}.

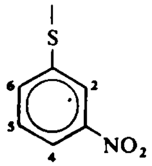
The dipole moment was determined at 25° and 45° ± 0·01° in benzene soln using the apparatus, technique of measurement, solvent constants and method of assessment of purity of the same described in detail elsewhere.[10] The dipole moment value was evaluated by the Halverstadt and Kumler[18] and the Guggenheim[19] methods. The probable error in μ has been estimated to be ±0·01 D at 25° and ±0·02 D at 45°.

The PMR spectrum has been recorded on a Varian Ass. Model A60-A nmr spectrometer at a probe temp of *ca* 38°. TMS as an internal reference was added to the 15 mol% soln of the disulphide in $CDCl_3$*.

The sweep linearity of the spectrometer was initially tested and the spectrum calibrated using the usual side-band method. The transition frequencies were measured averaging the results of three recordings (forward and backward) of the spectrum. The r.m.s. error over a resonance line has been estimated to be 0·05 Hz.

The iterative LAOCOON III computer program[20] (run on a CDC 6600 computer) was used to analyse the 60 MHz hydrogen resonance spectrum of bis(*m*-nitrophenyl) disulphide.

The analysis has been based on the assumption that the compound could be regarded as a disubstituted benzene:



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* $CDCl_3$ was chosen because of solubility difficulties in other solvents.

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