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DIPOLE MOMENTS OF SOME DIPHENYL THIOETHERS
ABSOLUTE CONFORMATION OF BIS(*O*-NITROPHENYL) SULPHIDE

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Abstract—The electric dipole moments of three diphenyl thioethers have been measured in benzene solution at 25° and the conformational analysis of bis(*o*-nitrophenyl) sulphide has been carried out by vector addition. The results show that this compound exists in a twisted conformation with the phenyl rings considerably rotated from coplanarity with respect to the C–S–C plane and indicate that in *o,o*′-disubstituted derivatives of diphenyl sulphide steric rather than conjugative effects operate in determining the conformational preference.

INTRODUCTION

THE crystal and molecular structure of *para*-disubstituted diphenyl thioethers has been investigated using x-ray diffraction.[1,2] The solution conformation of diphenyl sulphide and of some of its asymmetric derivatives has been previously proposed on the basis of polarization methods such as the molar Kerr constant[3] and dipole moment[4,5] measurements.

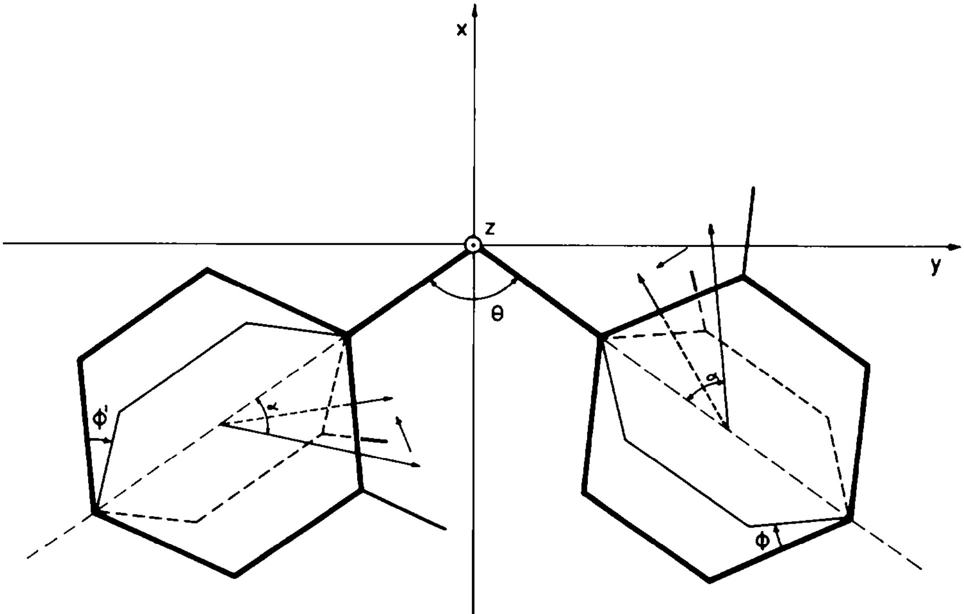

FIG 1. Bis(*o*-nitrophenyl) sulphide oriented along the coordinate system of axis.

A large number of diphenyl thioethers has been the object of NMR,[6–10] UV,[11–15] IR[16, 17] and electric moment[18–21] measurements, but to date the conformational preference of the *ortho* symmetric derivatives has not yet been rigorously determined.

The present paper reports, together with the dipole moment data of the diphenyl thioethers listed in the experimental section, the analysis of bis(*o*-nitrophenyl) sulphide in terms of molecular solute conformation.

RESULTS AND DISCUSSION

The experimental data and the dipole moment values obtained are given in Tables 1 and 2.

The rotational configurations can be detected by electric moment data in symmetric derivatives of *ortho*- and *meta*-substituted diphenyl sulphide, i.e., when the bond moments of a C-substituent are not collinear with the C–S axis. For the nitro derivative (**1**), with a planar *ortho* substituent, the total moment can be evaluated by vector addition as a function of the rotation angles about the C—S bonds, ϕ and ϕ', for the model shown in Fig 1 according to the relation

$$\mu = \sqrt{(\mu_x^2 + \mu_y^2 + \mu_m^2)}$$

where the components along each axis are given by

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

$$\mu_y = \mu_2 \cos\frac{\theta}{2} \cos\phi + \mu_2 \cos\frac{\theta}{2} \cos\phi'$$

$$\mu_z = \mu_2 \sin\phi + \mu_2 \sin\phi'$$

with $\mu_1 = \mu_{\mathrm{ph-NO_2}} \cos\alpha$, $\mu_2 = \mu_{\mathrm{ph-S}} \sin\alpha$ and $\alpha = 41{\cdot}9^\circ$.

We used the group moments Ph-NO_2 = 3·98 D,[22] Ph-S = 1·29 D[23] and the C-S-C valency angle $\theta = 109^\circ$ [1]. More precise assumptions can be made now on the mesomeric moment (μ_m) for this compound on the basis of a value of 0·12 D recently found for the analogous *para*-substituted compound.[21] The steric interaction will rotate the *ortho*-nitro group from coplanarity with the phenyl ring;[24] for a twist angle β the mesomeric moment will be lowered according to the expression[25] $\mu_m = \mu_{\max} \cos^2 \beta$ where $\mu_{\max}$ is the mesomeric moment found for the *para*-substituted compound. By considering that the estimate of μ_m for all possible states of rotation of the NO_2 plane does not affect noticeably the results, we assume that the difference between μ_m and $\mu_{\max}$ may be neglected and used in the present calculations the value of 0·12 D for the mesomeric moment.

The possible conformations for bis(*o*-nitrophenyl) sulphide are defined by the rotation angles (ϕ and ϕ') that are described by each Ph ring in a clockwise sense starting from the planar structure (Fig 1) for which $\phi = 0$ and $\phi' = 0$. The results of the calculations are summarized in Fig 2, where the contour 6·89 connects all points for which agreement was found between the calculated and measured dipole moment value.

It is clear that the calculated values for planar *cis* ($\phi = 180^\circ$, $\phi' = 0$: 1·11 D; $\phi = 0$, $\phi' = 180^\circ$: 9·89 D) and *trans* ($\phi = 0$, $\phi' = 0$: 5·88 D) configurations show very poor

TABLE 1. WEIGHT FRACTIONS OF SOLUTE (w_2), DIELECTRIC CONSTANTS (ε_{12}), SPECIFIC VOLUMES (v_{12}) AND REFRACTIVE INDEXES (n_{12}) OF SOLUTIONS IN BENZENE AT 25°C

Bis (*o*-nitrophenyl) sulphide **1**				Bis (*o*-aminophenyl) sulphide **2**				Bis (4-chloro-2-nitrophenyl) sulphide **3**			
100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}
0·2202	2·3156	1·14187	1·49785	0·5123	2·3740	1·14112	1·49830	0·4730	2·3175	1·14006	1·49827
0·3261	2·3364	1·14137	1·49799	0·6191	2·3965	1·14082	1·49841	0·6177	2·3314	1·13946	1·49841
0·4076	2·3517	1·14099	1·49809	0·7957	2·4330	1·14035	1·49858	0·6929	2·3387	1·13906	1·49847
0·5312	2·3756	1·14042	1·49825	0·8802	2·4512	1·14012	1·49866	0·8330	2·3521	1·13840	1·49864
0·6625	2·4008	1·13983	1·49841	1·0937	2·4963	1·13954	1·49888	0·9620	2·3645	1·13777	1·49875
0·7856	2·4245	1·13922	1·49858	1·4524	2·5840	1·13856	1·49923	1·0880	2·3766	1·13720	1·49892

TABLE 2. TOTAL POLARIZATIONS ($P_{2\infty}$ cc), MOLAR REFRACTIONS (R_D cc), DIPOLE MOMENTS (μ) AND OTHER PARAMETERS FOR THEIR EVALUATION

Sulphide	α	ε_{10}	β	v_{10}	$P_{2\infty}$	R_D	μ
Bis (*o*-nitrophenyl **1**	19·23	2·2734	−0·465	1·14289	1053·25	74·5	6·89 D
Bis (*o*-aminophenyl) **2**	21·02	2·2662	−0·272	1·14251	912·07	67·5	6·41 D
Bis (4-chloro-2-nitrophenyl) **3**	9·60	2·2721	−0·471	1·14232	691·20	85·4	5·42 D

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

agreement with the measured dipole moment. On the same basis we may exclude the possible "*butterfly*" conformation in which both Ph rings are perpendicular to the plane of the sulfur valency angle, since calculations for the *cis* ($\phi = 90°$, $\phi' = 90°$) and *trans* ($\phi = 90°$, $\phi' = 270°$) form give values of 8·07 and 4·39 D, respectively.

Recent NMR measurements on *ortho*-substituted diphenyl ethers and thioethers[10] suggested that these compounds may exist in a preferred *skewed* conformation in which the two Ph rings should be placed in planes perpendicular to each other. This asymmetric conformation for the molecule of bis(*o*-nitrophenyl) sulphide, obtained for $\phi = 0$ and $\phi' = 90°$, must be abandoned on the basis of the strong difference found between the calculated (8·14 D) and the observed dipole moment. A further examination of molecular models shows that sterically improbable conformations are obtained when the condition of coplanarity between the ring and the C–S–C plane might be verified by some point of the contour line 6·89 in Fig 2.

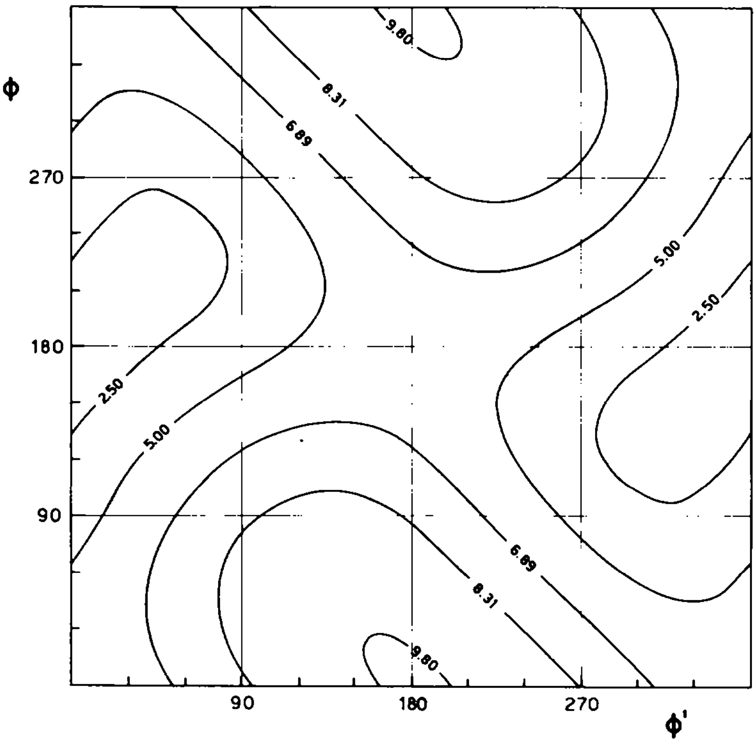

FIG 2. Contour of dipole moment values calculated as a function of the rotation angles ϕ and ϕ' for bis(*o*-nitrophenyl) sulphide

It seems reasonable, however, to consider a preferred conformation in which a Ph ring is perpendicular to the C–S–C plane and the other ring is twisted considerably from coplanarity with this plane, assuming a *distal* position of the *ortho*-groups (as shown by the model below) to be more favoured. The calculations show that we may consider this preferred conformation as arising from the model in Fig 1 by rotation of angles $\phi = 36°$ and $\phi' = 270°$ or, as is the same, $\phi = 90°$ and $\phi' = 216°$, assuming vibration near this position.

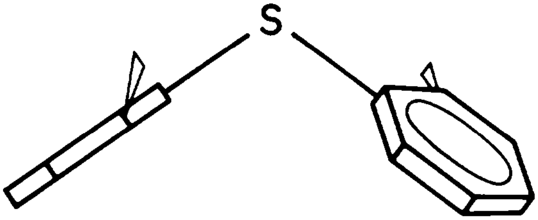

FIG 3

Evidence for lack of coplanarity in the ground state in diphenyl thioethers has been presented in previous papers.[1-3] The present results are in further good agreement with detailed and extensive UV spectroscopic studies[11-13] that pointed out that electron releasing p_π conjugation between the sulphur atom and the rings is sterically inhibited upon increasing the bulk of the *ortho* substituents. Moreover, our results are consistent with NMR data reported,[10] since the diamagnetic shielding exhibited by the *ortho* protons of the molecule and evaluated to be zero,* provide further evidence that a conformation in which a ring is in the C–S–C plane and the other ring is perpendicular to this plane, can be easily excluded.

On this basis, by analogy, the *skewed* conformation previously suggested for bis(*o*-nitrophenyl) ether and *o*,*o*′-disubstituted diphenyl ethers by dipole moments,[26] dielectric relaxation times[27-29] and electron diffraction data[30] seems to be unreliable. To date, only NMR evidence found for such a conformation in the case of the *o*,*o*′-dimethyl substituted compound[31] has been retracted[32] by its authors.

In conclusion, it may be postulated that the presence of *ortho* substituents does change the conformational preferences the steric effect being the more important, and that the solution conformation now proposed for bis(*o*-nitrophenyl) sulphide can be extended to the remaining diphenyl thioethers (**2** and **3**) reported in this paper and whose dipole moment data cannot be analysed by vector addition.

EXPERIMENTAL

Bis(*o*-nitrophenyl) sulphide (**1**) (m.p. 122–3°),[33] bis(*o*-aminophenyl) sulphide (**2**) (m.p. 85–6°),[34] bis(4-chloro-2-nitrophenyl) sulphide (**3**) (m.p. 149–150°),[33] were obtained according to the literature. Each compound was purified by several crystallizations to constant m.p. and $\varepsilon_{\max}$, then dried *in vacuo* before use.

The assessment of purity of samples used for dipole moment determination was made by differential scanning calorimetry[35, 36] using a Perkin-Elmer Mod. DSC-1B instrument. The calculated purities were greater than 99·97%.

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* The magnitude of the shielding effect for *ortho* protons was computed as the difference between the *chemical shifts* of thioanisole and the corresponding thioether. The value given in the paper should be regarded with caution and as approximate, since the *chemical shifts*, although reported to the second decimal figure, were obtained without a complete and exact spectral analysis.

Thiophene-free benzene (solvent), was refluxed over Na and distilled before use: the following solvent constants apply at 25°: $\varepsilon = 2{\cdot}2725$, $v = 1{\cdot}14445$ and $n_D = 1{\cdot}49790$.

The dielectric constant measurements were made using a Dekameter WTW, DM 01 type, previously calibrated with air and standard liquids: the refractive indexes were measured, within ± 0·00001, using the Na_D line, on a Bausch & Lomb precision refractometer of modified Abbe type calibrated with refractometric standards. The specific volumes of the solutions were determined on an Ostwald type pycnometer of about 10 cc capacity, the weight of solution filling the apparatus being reproducible to 0·1 mg.

The total solute polarization $P_{2\infty}$ was obtained by extrapolation at infinite dilution by the Halverstadt and Kumler method:[37] the electronic and atomic polarization, P_e and P_a, was taken to be equal to the distortion polarization assumed to be 1·05 R_D where R_D is the observed molar refraction.

The same dipole moment values were obtained by the use of the Guggenheim procedure.[38]

The probable error in μ is estimated to be ± 0·01 D: where duplicate runs were made, the results were reproducible within 0·01 D.

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