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SOLUTION CONFORMATION OF BIS (O-NITROPHENYL) DISULPHIDE

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To date, no precise estimate of the degree of rotational freedom about the C-S bond in model diphenyl disulphide systems has been made by means of dielectric constant measurements since only p derivatives, the dipole moments of which are independent of such rotations, have been investigated[1,2]. On the basis of NMR studies "slow" rotation has been postulated in hindered diaryl disulphides[3].

Recently X-ray crystallographic results have become available[4,5] and we have measured the dipole moment of bis(O-nitrophenyl)disulphide; $\mu = 5.32$ D in benzene at 25° [6]. The structural data allow us to evaluate dipole moments by vector addition for the model shown in Figure 1 according to the relation:

$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$ where the components along each axis are given by.

$\mu_x = \mu_2 \cos \phi' \sin \Phi/2 - \mu_2 \cos \phi \sin \Phi/2 - 2\mu_1 \cos \Phi/2 \cos (\theta - 90^\circ)$

$\mu_y = \mu_2 \cos \phi' \cos \Phi/2 - \mu_2 \cos \phi \cos \Phi/2$

$\mu_z = \mu_2 \sin \phi \cos (\theta - 90^\circ) - \mu_2 \sin \phi' \cos (\theta - 90^\circ)$

with $\mu_1 = 3.98$ and $\cos \alpha$ and $\mu_2 = 1.29 \sin \alpha$ ($\alpha = 41.9^\circ$)

We use the angles $\Phi = 85^\circ$, $\theta = 104^\circ$ [4] and the group moments Ar-NO_2 = 3.98 D[7] and Ar-S- = 1.29 D[1]. We neglect the interaction moment, μ_{int}, since the calculated dipole moment for bis(p-nitrophenyl)disulphide, using the group moments above with $\Phi = 72^\circ$ and $\theta = 106^\circ$ [5], is 4.23 D, in satisfactory agreement, when allowance is made for the solvent,[9] with the measured value of 4.31 D[8]. In fact the interaction S--NO_2 is expected to be almost zero since on passing from p-nitrothiophenol to bis(p-nitrophenyl)sulphide μ_{int} drops from 0.52 to 0.12 D[10], and the longer bridge in the disulphide obviously increases this effect making $\mu_{int} \simeq 0$.

The conformation is defined by the angles of twist ϕ and ϕ', both of which are zero in the sterically favoured rigid skew conformation where each phenyl ring lies in the plane of the C-S-S bonds. Rotation is measured from this position in a clockwise sense.

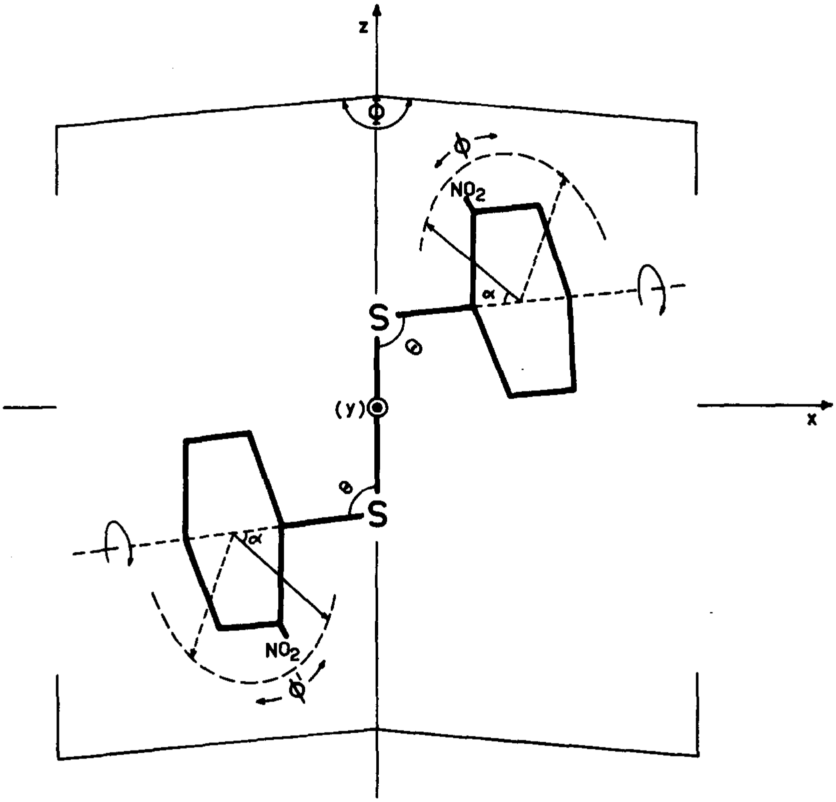

Fig. 1

Thus we consider an essentially rigid structure in which torsional oscillations of the phenyl groups about the C-S bonds are possible. Calculation of μ then shows that many conformations may be excluded because of the large difference between $\mu_{\text{calc.}}$ and $\mu_{\text{exp.}}$ The contour in figure 2 connects all points for which $\mu_{\text{calc.}} = \mu_{\text{exp.}}$ and the favoured conformations are those for which each ring is twisted by the same angle and in the same sense.

U. V. studies[11] have suggested that electronic as well as steric effects contribute to the potential energy barrier hindering free rotation.

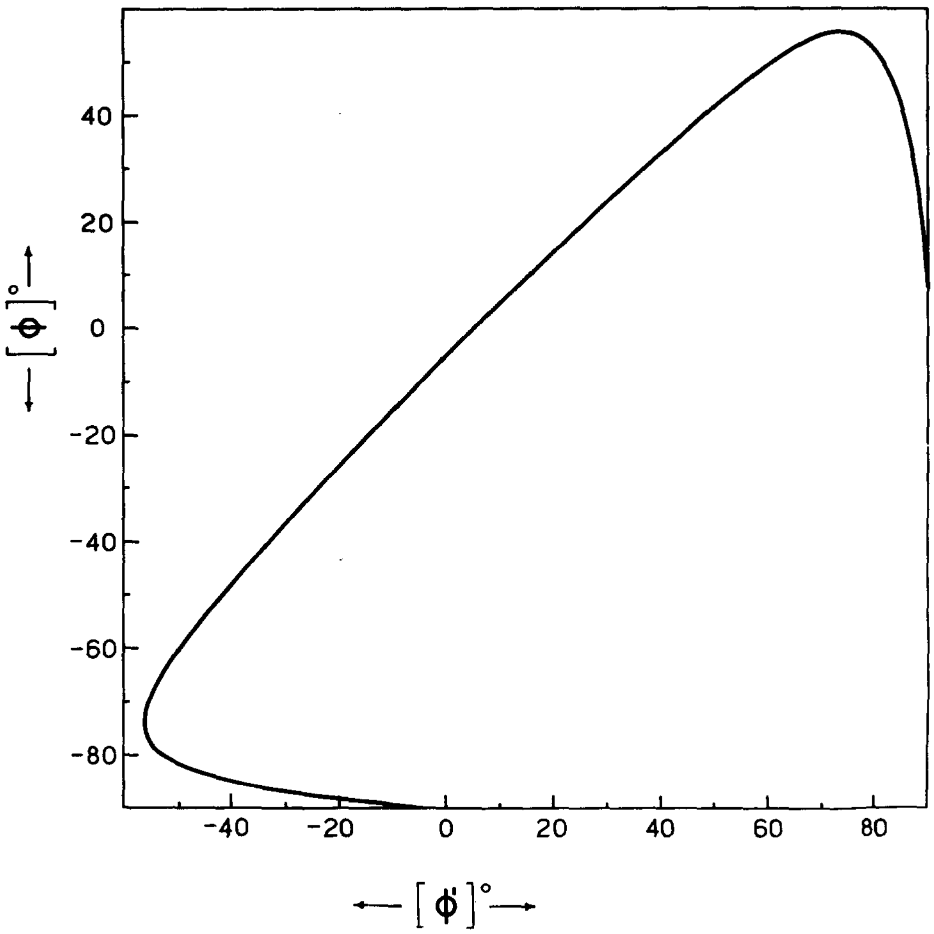

Fig. 2

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