

DIPOLE MOMENTS AND CONFORMATION OF α -DISULPHONES. THE *gauche* EFFECT

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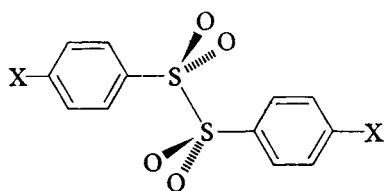
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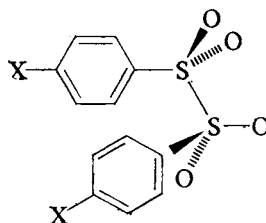
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The dipole moments of substituted diphenyl disulphones *I–III* were measured in benzene solution and interpreted by the previously described graphical method. The results suggest an equilibrium of the *ap* and *sc* conformations in the ratio 3 : 1, at variance with various empirical rules and theories of the so-called *gauche* effect. A statistical treatment of X-ray data of various sulphonyl derivatives revealed essentially two preferred conformations: the more stable *sc*, with a broadened dihedral angle, and the less stable *ap*.

The conformation of diphenyl disulphone *I* is remarkable by the apparent disagreement of the X-ray data in crystal and dipole moment measurement in solution. The conformation in the crystalline state¹ is *ap* (symmetry group C_{2h}) with the dihedral angle C—S—S—C equal to 180° (*I ap*). The non-zero dipole moment in solution was previously interpreted either in terms of the free rotation around the S—S bond², or by an equilibrium of the “*cis*” and “*trans*” forms³. During our systematic investigations of the conformation of sulphonyl derivatives^{4–8} we offered the opinion⁹ that the prevailing conformation in solution might be *I sc* (C_2) in accord with the general rule of *gauche* effect¹⁰. According to this principle, conformations are preferred



ap



sc

- I*, X - H
II, X - CH₃
III, X - Cl

with strongly polar bonds and/or lone electron pairs in mutual *gauche* positions⁷⁻¹³. Our opinion⁹ seemed to be shared by other workers^{14,15} but has been supported only by the dipole moment value^{2,3} of *I*. On the contrary, a 6-31G* calculation of the molecule HSO₂SO₂H suggested the *ap* conformation¹⁶.

In this note we report on a more accurate determination of the solution conformation of α -disulphones. We exploited also the *para*-substituted derivatives *II* and *III*, and evaluated the dipole moment results by the well-tried graphical method¹⁷. In order to explain the different conformation in the crystalline phase, we examined statistically the X-ray data¹⁸ of sulphonic acid derivatives with a SO₂S or SO₂O grouping.

EXPERIMENTAL AND RESULTS

Materials. Diphenyl disulphone (*I*), m.p. 193°C, was prepared from benzenesulphonyl chloride and sodium iodide¹⁹ in a yield of 8% (ref.¹⁹ gives 24%). 4,4'-Dimethyldiphenyl disulphone (*II*) (m.p. 193°C) and 4,4'-dichlorodiphenyl disulphone (*III*) (m.p. 213°C), which could not be prepared in the same way, were obtained by permanganate oxidation of the corresponding arenesulphinic acids²⁰ in the yield 4% and 2%, respectively. Numerous attempts to improve the preparative procedures failed, e.g. oxidation of S-aryl arenethiosulphonates with peracetic acid²¹, or of diaryl disulphide-trioxide with potassium permanganate²². Particular attention was given to the condensation reaction of sodium, potassium, or silver arenesulphinates with arenesulphonyl chloride which could produce unsymmetrically substituted disulphones. In addition to the procedures recommended²³⁻²⁵, different solvents (poly(ethylene glycol)²⁶, dimethylformamide, dimethyl sulphoxide, acetonitrile) and different conditions were tried. Relatively most successful was the condensation of sodium benzenesulphinate and benzenesulphonyl chloride in acetonitrile under reflux (yield 5%). However, the attempts to prepare unsymmetrical disulphones in this way afforded a mixture of products. We can thus only confirm a statement from 1955 that α -disulphones represent a little explored class of compounds²⁷. One can even doubt about the purity of some previously described products. The purity of our samples was checked by TLC and mass spectrometry. By the former method particularly the presence of S-aryl arenethiosulphonate can be detected (solvent benzene).

Physical measurements. The measurement of dipole moments by the Halverstadt-Kumler method²⁸ was described previously in detail²⁹. The molar refractions were calculated from increments as given in our previous paper⁸; corrections for conjugation are immaterial due to the great values of dipole moments. The results are listed in Table I.

The dipole moments anticipated for individual conformations were calculated as previously⁸ by vector addition of standard bond moments: H—C_{ar} 0, C_{ar}—Cl 5.33, C—S 3.0, SO₂ 6.7 (a vector halving the O—S—O angle), correction for the conjugation ArSO₂ 3.33 (all values in 10⁻³⁰ C m). The bond angles were taken from the X-ray work¹ (C—S—S 101.5°, angle of the C—S bond and the SO₂ group moment 132°). The calculated dipole moments are given in Table I and/or plotted in Fig. 1.

DISCUSSION

The squared dipole moments of *I-III* are plotted in Fig. 1 according to our recommended procedure¹⁷. The calculated values are situated always on a straight line

and their position on this line depends on the anticipated dihedral angle C—S—S—C. The experimental points are near to these straight lines within the error limits of the whole approach, confirming the assumptions made in the calculation. The position of the experimental points can be in principle interpreted in two ways: a) by one conformation with the dihedral angle C—S—S—C near to 130° , b) by a mixture of two conformers, *ap* and *sc*, in an approximate ratio of 3 : 1. Since the former explanation would require an eclipsed conformation, there remains only the latter. The ratio 3 : 1 might be somewhat overestimated since the calculation neglected possible mutual induction of near dipoles. Referring to this effect as observed on other compounds³⁰, we may estimate that it does not exceed 10% of the calculated dipole moment in the case under consideration. This would change the population of the *sc* form from 27% to 34%. Considering still its double statistical weight, this form is evidently energetically disfavoured against the *ap* form.

The above result differs from previous qualitative estimates^{9,14,15} and is at variance with the rule of the *gauche* effect¹⁰. In a previous paper⁷ we attempted to formulate this rule with more precision in terms of various theories but none of them was found satisfactory for all cases. The available results on sulphonyl derivatives are summarized in Table II. In order to avoid misunderstanding, we have preferred a classification into more symmetrical and less symmetrical conformations while the nomenclature *ap* and *sc* may refer to different types according to the convention on the preference of substituents. With respect to its double statistical weight, the less symmetrical form is to be considered as energetically preferred if its population exceeds 67%.

TABLE I

Dipole moment data of substituted diphenyl disulphones I—III (benzene, 25°C)

Compound	I	II	III
α^a	6.65	5.73	2.62
β^a	-0.523	-0.423	-0.507
P_2^0 , $\text{cm}^3 \text{mol}^{-1}$	404.9 ^b	400.8	239.6
R_D^c , $\text{cm}^3 \text{mol}^{-1}$	68.5	77.8	78.3
$\mu(5)^d$, 10^{-30}C m	13.5 ^e	13.2	9.2
$\mu(15)^d$, 10^{-30}C m	13.3	13.0	9.0
$\mu(\text{calc})$ <i>ap</i> , 10^{-30}C m	0	0	0
$\mu(\text{calc})$ <i>sc</i> , 10^{-30}C m	25.6	27.3	16.6

^a Slopes of the plots ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; ^b ref.³ gives 400.6; ^c calculated from increments, see Experimental; ^d correction for the atomic polarization 5% or 15% of the R_D value, respectively; ^e ref.^{2,3,14} give 13.2, 13.4, and 13.1, respectively.

According to our previous generalization⁷ the less symmetrical conformations should be always more stable. In Table II there are three indisputable exceptions, *viz.* in addition to the compounds investigated in this paper also the two *N,N*-dimethylsulphonamides, while the 50% population of the *sc* conformer of methyl methane-sulphonate³⁴ is not in accord with the results on other sulphonic esters. A recent LCBO theory developed in terms of bond-antibond interactions on the example of simple fluorine derivatives¹³ is much less satisfactory if applied to sulphonyl derivatives (Table II). We conclude that the conformations of the latter compounds are not controlled by a single factor, and cannot be reliably predicted by a single theory, although the *gauche* effect may serve as a useful generalization. For instance the purely electrostatic effect, usually not decisive, may become sufficiently strong in the presence of two sulphonyl groups as in *I sc*. Hence the generalized curve of potential energy shows the main minimum approximately at 60°, and in addition a secondary minimum at 180°. The latter may become more important in certain derivatives and under special conditions. In order to obtain a semiquantitative picture, we investigated the population of individual conformations of various sulphonyl derivatives in the crystalline phase under variable crystal packing forces. A search in the Cambridge Structural Data Base¹⁸ started with compounds of the types RSO_2OX and RSO_2SX but the latter group contained only three compounds. After eliminating salts and inorganic complexes, the choice was finally restricted to esters of sulphonic acids (76 compounds) as the only available homogeneous set

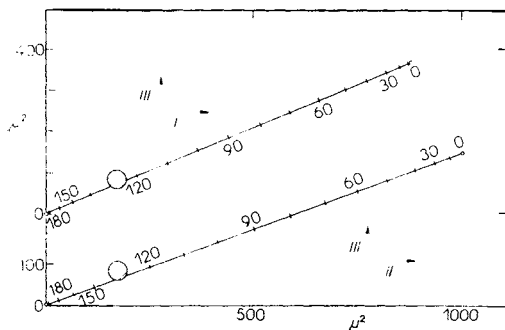


FIG. 1

Graphical comparison of squared dipole moments of substituted diphenyl disulphones *II* and *I* (*x*-axis) vs *III* (*y*-axis). The calculated values are given for the variable dihedral angle C—S—S—C (0–180°), the experimental point is hatched

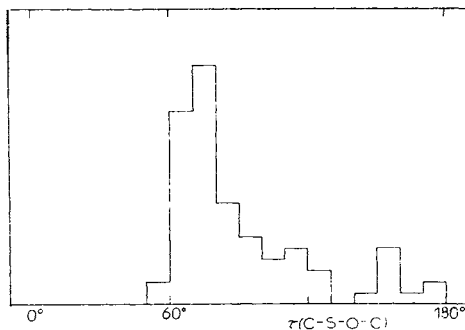


FIG. 2

Histogram of the dihedral angle τ (C—S—O—C) in 76 sulphonic acid esters in the crystalline state. Two values for the same molecule in the same crystal were included only if they differed by more than 10°

TABLE II
Survey of the conformational preference of sulphonyl derivatives^a

Compound	% Less symmetrical form	Reference	Theoretical prediction ¹³	
			preferred form	model
CH ₃ SO ₂ CH ₂ Hal	80–86	31	sym.	F ₂ CHCH ₂ F
ArSO ₂ CH ₂ Hal	~100	8		
ArSO ₂ CH ₂ NO ₂	(~100)	7		
ArSO ₂ CH ₂ CN	~100	32		
ArSO ₂ CH ₂ SO ₂ Ar	(~ 80)	33		
CH ₃ SO ₂ OCH ₃	50	34	sym.	F ₂ CHOH
CH ₃ SO ₂ OAr	80	34		
	75–80	4		
	~100	35		
ArSO ₂ OCH ₃	70–86	36		
ArSO ₂ OAr	60–95	36		
	85–100	4		
ClSO ₂ OCH ₃	~100	37, 38		
ArSO ₂ SC ₂ H ₅	~100	6		
ArSO ₂ SO ₂ Ar	~ 30	this work	unsym.	F ₂ CHCHF ₂
ArSO ₂ NHAr	~100 ^b	39	unsym.	F ₂ CHNH ₂
CH ₃ SO ₂ N(CH ₃) ₂	0(–20) ^b	40, 41		
ArSO ₂ N(CH ₃)NO ₂	~100	8		
ClSO ₂ N(CH ₃) ₂	0	41, 42	sym.	FCH ₂ NH ₂

^a Experimental results in the gas phase or in solution; not included were bifunctional compounds with two axes of rotation at one sulphonyl group; ^b as an alternative, planar configuration on nitrogen was assumed^{4,3}.

of sufficient range. The histogram of the dihedral angle C—S—O—C (Fig. 2) reveals two maxima, corresponding to two minima on the potential energy curve. The population of the *sc* conformation is 88%. Fig. 2 also confirms our previous estimate, made on sulphonic esters⁴ and on other sulphonyl derivatives^{7,8}, that the dihedral angle in the *sc* conformation is larger than 60°. The mean value in Fig. 2 is 83° with a large standard deviation of 17°, revealing that the whole energy curve is relatively flat.

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