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Conformational investigation of diarylsulphones by Kerr effect and dipole moment methods

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Abstract

Molar Kerr constants and electric dipole moments are reported for $(C_6H_5)_2SO_2$, $(4\text{-}Cl\text{-}C_6H_4)(C_6H_5)SO_2$, $(2,4,6\text{-}Me_3C_6H_2)(4'\text{-}BrC_6H_4)SO_2$, $(4\text{-}NO_2C_6H_4)_2SO_2$, $(4\text{-}MeOC_6H_4)(4'\text{-}NO_2C_6H_4)SO_2$, $(2\text{-}MeOC_6H_4)(4'\text{-}NO_2C_6H_4)SO_2$, $(2\text{-}NO_2C_6H_4)(4'\text{-}MeOC_6H_4)SO_2$ and $(2\text{-}MeOC_6H_4)(2'\text{-}NO_2C_6H_4)SO_2$ as solutes in dioxane solution at 298 K. The data are analysed in terms of the preferred conformations adopted in solution. In most cases these data are consistent with the presence, in dioxane, of orthogonal or planar-orthogonal conformers, or of a mixture of them. In the orthogonal rotamer both aromatic rings are approximately perpendicular to the C_{Ar}-S-C_{Ar} molecular reference plane whereas in the planar-orthogonal conformer one ring is coplanar and the other is orthogonal to the reference C_{Ar}-S-C_{Ar} plane.

INTRODUCTION

The ground state conformations of diaryl derivatives such as diphenylmethanes, diphenyl ethers and diphenyl sulphides, benzophenones and pyridinium ions have been extensively investigated by many techniques [1,2]. The evidence to date indicates that such molecules may adopt one of two conformations: either both aryl rings are twisted in the same direction with respect to the C_{Ar}–S–C_{Ar} reference plane (Fig. 1, form **A**) so as to impart a helical arrangement to the molecule which thus possesses a C_2 point group skeletal symmetry; or one ring lies parallel to the reference plane and the other is perpendicular to it (Fig. 1, form **B**, hereafter called the planar-orthogonal conformation).

In contrast to other classes of diaryl derivatives, the conformational aspects of diphenyl sulphones (Z=SO_2) have received less attention and the existing

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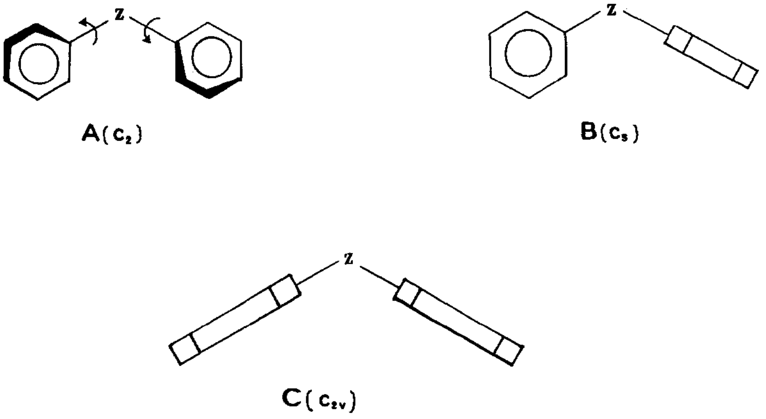


Fig. 1. Possible conformations for a diaryl system. Point group symmetries are indicated.

literature data [2] seem to indicate that the conformation adopted by such molecules is different from that preferred by other diaryl derivatives. In particular, molar Kerr constants indicate that diphenyl sulphone in benzene solution adopts a conformation in which both phenyl rings are approximately perpendicular to the C_{Ar}–S–C_{Ar} reference plane [3] (Fig. 1, form **C**, hereafter called the orthogonal conformation).

The same conformation was found in the solid state for bis-bromophenyl sulphone by X-ray crystal analyses [4]. NMR data on several diaryl sulphones also seem to confirm the existence of such preferred orthogonal conformers in solution [2]. This spatial arrangement, according to theory [5], allows a strong conjugative interaction between the π electrons of both aryl rings and the sulphonyl group; an indication of such conjugation is given by the comparison of the dipole moments of dimethyl sulphone (4.26 D in benzene [6]) and diphenyl sulphone (4.97 D in benzene [3], 5.14 D in dioxane (this work)); in fact, in the latter the significant increase of the experimental dipole moment suggests the presence of quite strong conjugation between the phenyl ring and the SO_2 group; thus, conformation **C** should contribute significantly to the ground state of diphenyl sulphone.

However, it is interesting to note that for bis-chlorophenyl sulphone, according to X-ray diffraction studies [7], one aryl ring is twisted by 84.4° with respect to the C_{Ar}–S–C_{Ar} reference plane, whereas the other possesses a dihedral angle equal to 79.5°, with respect to the first one. In other words, one ring is approximately perpendicular, but the other is parallel, to the C_{Ar}–S–C_{Ar} plane, and thus bis-*p*-chlorophenyl sulphone seems to adopt a **B** type conformation in the solid state. By X-ray investigation dimesitylsulphone was found to adopt a helical **A** conformation in the solid state [8].

Therefore, these somewhat conflicting data on the conformational aspects of diaryl sulphones, prompted us to investigate in greater detail the static stereochemistry of different substituted diphenyl sulphones (listed in Fig. 2 and Table 1), using the techniques of molar polarisation (∞P_2), molar refraction (∞R_D) and molar Kerr constants ($\infty ({}_mK_2)$) all at infinite dilution, and dipole moments (μ) measured at 298 K in dioxane solution.

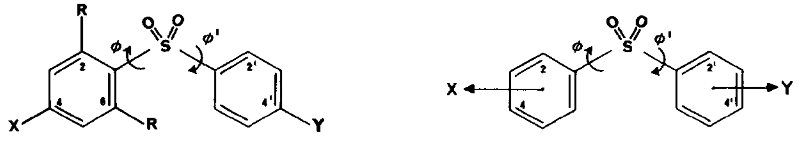


Fig. 2. Diaryl sulphones examined in this work. In the starting conformation ($\phi = \phi' = 0°$) the two aryl rings are coplanar with the C_{Ar}-S-C_{Ar} reference plane.

TABLE 1

Physico-chemical data for the diaryl sulphones investigated

No.[a]	R	X	Y	M.p. (°C)	^{1}H NMR ($CDCl_3$)[b]
1	H	H	H	128	-
2	H	H	4-Cl	95	-
3	H	4-Cl	4'-Cl	148	-
4	Me	4-Me	4'-Br	112-113	2.29(s,3H,CH_3), 2.58(s,6H,CH_3), 6.95(s,2H,ArH), 7.62(s,4H,ArH)
5	H	4-NO_2	4'-NO_2	260	-
6	H	4-OMe	4'-NO_2	166-168 (162-163)[c]	3.86(s,3H,OCH_3), 7.00(d,2H,J_{AB}=9.2Hz,ArH), 7.40(d,2H,J_{AB}=9.2Hz,ArH), 8.13(d,2H,J_{AB}=9.2Hz,ArH) and 8.32(d,2H,J_{AB}=9.2Hz)
7	H	2-OMe	4'-NO_2	138-139	3.79(s,3H,OCH_3), 6.90-7.26(m,3H,ArH), 7.63(m,1H,ArH), 8.15(d,2H,J_{AB}=8.8Hz,ArH) and 8.34(d,2H,J_{AB}=8.8Hz,ArH)
8	H	2-NO_2	4'-OMe	149-150	3.87(s,3H,OCH_3), 7.01(d,2H,J_{AB}=9.2Hz,ArH), 7.75(d,2H,J_{AB}=9.2Hz,ArH), 7.78-8.20(m,3H,ArH), 8.28(m,1H,ArH)
9	H	2-Me	2'-NO_2	155-156	3.77(s,3H,OCH_3), 7.06(m,2H,ArH), 7.72(m,4H,ArH), 8.12(m,1H,ArH), 8.45(m,1H,ArH)

[a] See Fig. 2.

[b] Spectra were recorded on a Bruker WP-80 FT instrument at room temperature in $CDCl_3$ as solvent and TMS as internal reference.

[c] From ref. 9.

EXPERIMENTAL

General synthetic procedures

Diaryl sulphones **1**, **2**, **3** and **5** were high purity commercial products (Aldrich) which were recrystallised before use. Samples **6**, **7**, **8** and **9** were prepared in high yield by oxidation of the corresponding diaryl sulphides in glacial acetic acid with a slight excess of the theoretically required amount of H_2O_2. The precursor diaryl sulphides were synthesised in quantitative yield by nucleophilic condensation of the corresponding thiols with the appropriate nitrochlorobenzenes, in refluxing EtOH and KOH. Diaryl sulphone **4** was synthesised by a Friedel–Crafts reaction in $C_2H_5NO_2$ as solvent and $AlCl_3$ as catalyst reacting *p*-bromosulphonylchloride with a five times molar excess of mesitylene. The crude product, obtained in 85% yield, was recrystallised from AcOH. The melting points and the ^1H NMR spectra of the samples synthesised for this work are reported in Table 1.

Physical measurements

Solute dipole moments μ and electric birefringences (Kerr effect), the latter expressed as molar Kerr constants ∞ (${}_mK_2$), were determined at 298 K. The apparatus, techniques of measurement and symbols have been described elsewhere [10,11]. An He–Ne laser ($\lambda = 632.8$ nm) was incorporated as a light source. Benzene was used as reference liquid. The solvent constants for dioxane were as follows: ${}_sK_1 = 12.312 \times 10^{-15}$ e.s.u., $B = 0.6705 \times 10^{-8}$ e.s.u., $n_c = 1.4187$, $d = 1.02687$ g cm^{-3}, $\epsilon_1 = 2.209$ [12], $n_D = 1.42025$ [13]. Dielectric permittivities were measured by the heterodyne method on an E-7-5A serial instrument, densities were determined by a hydrostatics method and refractive indices were measured on an *ИРФ*-23 refractometer. For each compound relative permittivities, densities, refractive indices and Kerr constants (ϵ_{12}, d_{12}, n_{12} and B_{12} respectively) were measured for a range of solutions having solute weight fractions W_2. Coefficients $\alpha\epsilon_1$, β, γ and δ were derived using the linear relations $\epsilon_{12} = \epsilon_1(1 + \alpha W_2)$, $d_{12} = d_1(1 + \beta W_2)$, $n_{12} = n_1(1 + \gamma W_2)$ and $B_{12} = B_1(1 + \delta W_2)$ by least-squares analysis. The subscripts 1, 2 and 12 refer to the solvent, solute and solution respectively. The distortion polarisation of the solute, ${}_EP + {}_AP$, was assumed to be equal to $1.05(\infty R_D)$ where ∞R_D is the experimental refraction for the sodium D-line (in cm^3 mol^{-1}). The Fujita [14] equation was chosen in order to calculate molar polarisation ∞P_2 (in cm^3 mol^{-1}). Solute dipole moments μ are given in debye and molar Kerr constants ∞ (${}_mK_2$) in c.g.s. (e.s.u.) units respectively. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are respectively: 1 C m $= 0.2998\ 10^{30}$ D, 1 m^5 V^{-2} mol$^{-1} = 0.8988\ 10^{15}$ e.s.u. mol^{-1}. Experimental results are reported in Table 2.

TABLE 2

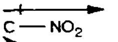
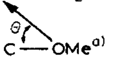
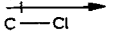
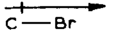
Molar polarisations and refractions, dipole moments and molar Kerr constants and increase of polarisability of the diaryl sulphones, measured in dioxane at $T=298$ K

Compound	$W_2 \times 10^{3a}$	$\alpha\epsilon_1$	β	γ^b	δ	$_\infty P_2$	$_\infty R_D$	μ^c	$10^{12}\times_\infty$ $({}_mK_2)^c$	10^{23} Δb^d
1	3.52-12.57	15.368	0.203	0.110	−405	601.8	60.4	5.14±0.02	−1106±35	0.212
2	3.40-12.57	9.819	0.245	0.105	−247	462.6	66.4	4.39±0.07	−782±24	0.295
3	3.50-11.85	5.244	0.289	0.106	−122	305.5	72.5	3.35±0.04	−440±14	0.397
4	4.44-11.21	8.480	0.263	0.097	−185	544.4	85.7	4.72±0.15	−788±63	0.572
5	2.34-10.31	0.643	0.367	0.102	4.3	86.9	70.8	0.78±0.14	16±12	
6	2.63-14.80	10.681	0.279	0.099	304	575.7	73.3	4.94±0.05	1083±13	0.191
7	2.77-12.56	13.163	0.287	0.095	−191	695.1	71.9	5.51±0.06	−708±15	0.030
8	2.95-13.26	18.010	0.275	0.106	−328	927.5	75.2	6.47±0.08	−1211±80	0.286
9	2.73-13.51	21.487	0.315	0.106	−195	1095.4	72.1	7.07±0.20	−738±57	0.060

[a] Range of concentrations used expressed in weight fractions.
[b] For the sodium D line.
[c] Mean-square deviations are indicated.
[d] Increase of polarisability (see text).

TABLE 3

Group and bond dipole moments employed in vector additive calculations of molecular dipole moments

Group or bond and direction of dipole moment	Value of dipole moment $\vec{m}$(C-X(Y)) (D)
 C — NO$_2$	4.01
 C — OMe[a]	1.28
 C — Cl	1.59
 C — Br	1.57

[a] The value of angle θ is equal to 72° [6].

RESULTS AND DISCUSSION

Calculation of dipole moments and molar Kerr constants

A vector and tensor additive scheme was employed to estimate theoretical dipole moments (μ_{calc}) and Kerr constants (${}_mK_{calc}$) for various molecular conformations using group dipole moments from substituted benzenes [6] and bond and group principal polarisabilities which are listed in Tables 3 and 4. The calculations of molecular polarisability and theoretical Kerr constants of arylsulphones (**1**)-(**5**) were also performed with use of the non-linear field

TABLE 4

Principal group and bond polarisabilities b_i employed in additive Kerr constant calculations

Group or bond	$10^{23}\ b_1$[a]	$10^{23}\ b_2$[a]	$10^{23}\ b_3$[a]	Reference
C_6H_5	1.056[b]	1.056[b]	0.672[b]	15
1,3,5-$Me_3C_6H_3$ (mesitylene)	1.730[b]	1.730[b]	1.13[b]	16
C_2SO_2	0.355[c]	0.315[c]	0.380	17
C-NO_2[d]	0.570	0.150	0.190	18
C-C	0.099	0.027	0.027	15
C-H	0.065	0.065	0.065	19
C-O	0.089	0.046	0.046	20
C-Cl	0.430	0.250	0.150	21
C-Br	0.620	0.240	0.220	22

[a] All polarisabilities are in cm^3.

[b] Polarisabilities b_1 and b_2 are in the plane of the π system.

[c] Polarisability b_1 is along the bisector of the C_{Ar}-S-C_{Ar} angle, b_2 is in the plane of the O-S-O angle.

[d] For other groups and bonds b_1 is along the C-X(Y), b_2 is in the plane of the aromatic ring connected with the C-X(Y) group.

scheme considering internal-field effects using a point dipole approximation. The details of this scheme and relative parameters have been described before [23–25]. Polarisability parameters of the C_2SO_2 group for the field scheme were taken in this work from molecular principal polarisabilities of dimethyl sulphone [17]. Its geometry was taken from the literature [26] and point polarisabilities of the C_2SO_2 group were centred on the sulphur atom. Unperturbed polarisability parameters of the C_2SO_2 group are: $b_1 = 3.616$ Å^3 (along the bisector of the C–S–C angle), $b_2 = 4.178$ Å^3 (in the plane of the O–S–O angle), $b_3 = 3.084$ Å^3.

The lines of action for dipole moments of diphenyl sulphone (**1**), di-*p*-chlorophenylsulphone (**3**) and di-*p*-nitrophenylsulphone (**5**) are readily apparent from the C_2SO_2 group symmetry (along the bisectors of the C–S–C and O–S–O angles). The geometry of this group for diaryl sulphones was chosen according to structural data on sulphone (**3**) [7] (the C_{Ar}–S–C_{Ar} angle is equal to 104.8°) and it was supposed that the aromatic rings in diaryl sulphones are ideal hexagons. Actual directions for dipole moments of any other molecule were obtained by vector addition according to the scheme: $\vec{\mu}$ (**1**) plus the dipole group moments $\vec{m}$ (C–X(Y)). The dipole moment of diphenylsulphone $\vec{\mu}$ (**1**) was directed along the bisector of the C_{Ar}–S–C_{Ar} plane from sulphur to oxygen atoms. Calculated values of the dipole moment μ_{calc} for sulphones (**2**) and (**3**) are practically equal to the experimental values (μ_{calc} (**2**) = 4.36 D, μ_{calc} (**3**) = 3.20 D; for experimental data see Table 2). For sulphones (**4**)–(**6**) the mesomeric interaction between aromatic rings and the SO_2 group must be taken into account. In the case of mesityl-*p*-bromophenylsulphone (**4**) with use of the vector equation $(\vec{\mu}\,(\mathbf{4}))^2 = [(\vec{\mu}(\mathbf{1}) + \vec{m}(\text{C–Br}) + \vec{m}_{\text{mes}})]^2$ it was calculated that the mesomeric moment of the mesityl ring (to be directed along the C–S bond towards the SO_2 group) is equal to 0.44 D. For di-*p*-nitrophenylsulphone (**5**) the dipole moment $m(C_2SO_2)$ of the C_2SO_2 group (directed from sulphur to oxygens) was calculated by means of the equation

$$\mu(\mathbf{5}) = m(C_2SO_2) - 2m(\text{C–NO}_2)\cos\theta \tag{1}$$

where θ is half the C_{Ar}–S–C_{Ar} angle. When the actual direction of the molecular dipole moment $\mu(\mathbf{5})$ is from sulphur to oxygens, $\vec{m}(C_2SO_2)$ is equal to 5.67 D which is greater than the dipole moment of diphenyl sulphone itself ($\mu(\mathbf{1}) = 5.14$ D). If this is the case one must suppose that the conjugation between the rings and the SO_2 group in di-*p*-nitrophenylsulphone is greater than in diphenyl sulphone, but this seems unrealistic considering that the NO_2 and SO_2 groups are both strong electron-acceptor groups. However when $\vec{\mu}(\mathbf{5})$ was considered to be oppositely directed, $\vec{m}(C_2SO_2)$ became equal to 4.11 D, a value very near to the dipole moment of dimethyl sulphone [6] ($\boldsymbol{\mu} = 4.26$ D). This means that the conjugation between the aryl rings and the SO_2 group in di-*p*-nitrophenylsulphone is absent. A final decision about the value of the group moment $m(C_2SO_2)$ was possible from the dipole moment calculations of *p*-methoxy-*p'*-nitrodiphenylsulphone (**6**) by the vector equation,

$$(\vec{\mu}(\mathbf{6}))^2 = (\vec{m}(C_2SO_2) + \vec{m}(\text{C–OMe}) + \vec{m}_{\text{mes}} + \vec{m}(\text{C–NO}_2))^2 \tag{2}$$

where $\vec{m}_{\text{mes}}$ is the mesomeric moment of the methoxy group acting along the O–C_{sp^2} bond. It was supposed that the methoxy group is coplanar with the aromatic ring and the $\vec{m}(\text{C–OMe})$ forms an angle of 72° with the bond to the ring [6]. It was also suggested that syn and anti orientations of the methoxy group to the $SO_2C_6H_4NO_2$ fragment are equally populated. When $m(C_2SO_2) = 4.11$ D, m_{mes} is equal to 0.81 D and directed towards the ring, but for $m(C_2SO_2) = 5.67$ D the $\vec{m}_{\text{mes}}$ has the opposite direction and therefore does not possess any physical meaning. The mesomeric moment for the aromatic ring can also be calculated by means of the equation

$$\mu(\mathbf{1}) = m(C_2SO_2) + 2m_{\text{mes}}\cos\theta \tag{3}$$

When $m(C_2SO_2) = 4.11$ D, m_{mes} is equal to 0.84 D and is very close to the result obtained from sulphone (**6**). It follows that the value of $m(C_2SO_2)$ for NO_2 substitution in phenyl sulphones is equal to 4.11 D and the mesomeric conjugation between the ring bearing the *p*-NO_2 group and the SO_2 moiety is absent, considering that the values of the dipole moments for Me_2SO_2 and $\vec{m}(C_2SO_2)$ in sulphone (**5**) are practically equal.

Dipole moments of aryl sulphones (**7**)–(**9**) were calculated as a function of the two internal rotation angles ϕ and ϕ' (see Fig. 2) by vector addition using group moments from Table 3 and $\vec{m}(C_2SO_2) = 4.11$ D. For the rings with a methoxy group, $\vec{m}_{mes} = 0.81$ D (directed along the rotational ring axis) was also taken into consideration. The methoxy group in sulphones (**7**) and (**9**) was supposed to be oppositely directed to the SO_2 group (for steric reasons) and coplanar to its ring. For sulphone (**8**) syn and anti orientations of the p'-methoxy group to the $SO_2C_6H_4$ fragment were also supposed to be equally populated.

In calculation of $_{m}K_{calc}$ as a function of the two internal rotation angles ϕ and ϕ' with use of a tensor additive scheme (Table 4), the increase of polarisability Δb (Table 2) was also taken into account. Increase of polarisability was determined as the difference between $3b_{exp}$ and $3b_{calc}$, $3(b_{exp} - b_{calc})$, where b_{exp} is the average electronic polarisability and was taken equal to $0.95 \infty R_D\ 9/4\ \pi\ N_A$, where N_A is the Avogadro number and $3b_{calc}$ is equal to the track of additive calculated molecular tensor polarisability. The increments of $\Delta b/2$ were distributed evenly in the planes of each ring in the cases of sulphones (**1**)-(**4**). For the sulphones (**6**) and (**8**) the increase Δb was distributed along the rotation axes of the rings possessing the methoxy group. Different methods of distribution of Δb gave calculated values ($_{m}K_{calc}$) far from the experimental ones. In the case of sulphones (**7**) and (**9**) the increase was not taken into account because of its low value.

Preferred conformations of diaryl sulphones

Diphenyl sulphone (1)

Considering thermodynamic unrestricted rotation of the aryl rings in (**1**) the calculated value ($_{m}K_{calc}$) with use of the additive scheme is equal to 110×10^{-12}, a value far from the experimental one (-1106×10^{-12}); furthermore, even the sign is different. Therefore, it may be concluded that for this molecule, as well as for the other examined sulphones (**2**)-(**9**) of Table 5, thermodynamic unrestricted rotation of the aryl rings is absent and thus some preferred conformers must be present in solution. The calculated ($_{m}K_{calc}$) minimum with use of the additive scheme for (**1**) as a function of the two internal rotation angles ϕ and ϕ' (Fig. 2) is equal to -1083×10^{-12} when $\phi = \phi' = 90°$, a value which comes very close to the experimental one. For conformer **B** ($\phi = 90°, \phi' = 0°$), $_{m}K_{calc}$ is equal to 104×10^{-12}, very far from the experimental value. The same result was obtained from calculations of polarisability, and $_{m}K_{calc}$ of (**1**), considering the internal-field effects (field scheme), is $_{m}K_{calc} = -1054 \times 10^{-12}$ when $\phi = \phi' = 90°$. Thus, it may be concluded that for (**1**) the orthogonal conformer **C** is present in dioxane solution, as already found in benzene [3]. It must be pointed out that stereospecific solvations with benzene as solvent [27] do not play any role considering that the molar Kerr constant of this compound in benzene (-1115×10^{-12}) [3] is very close to the value in dioxane obtained in this work.

TABLE 5

Experimental and calculated values of Kerr constants and dipole moments for the diaryl sulphones investigated; calculated values are reported for different possible conformers and for the thermodynamic unrestricted rotation of aryl rings (free rotation)

Compound	∞ $({}_{\mathrm{m}}K_2)\times 10^{12}$ (μ_{exp})	${}_{\mathrm{m}}K_{\mathrm{calc}}$[a] (μ_{calc})	${}_{\mathrm{m}}K_{\mathrm{calc}}\times 10^{12}$ (additive scheme)			${}_{\mathrm{m}}K_{\mathrm{calc}}\times 10^{12}$ (field scheme)[c]			Additive scheme, weight fraction of form **C**	Field scheme, weight fraction of form **C**
			Form **C** $(\phi=\phi'=90°)$	Form **B** $(\phi=0°, \phi'=90°)$	Form **B**′ $(\phi=90°, \phi'=0°)$	Form **C**	Form **B**	Form **B**′		
1	−1106 (5.14)	110 (5.14)	−1083	104	104	−1054			1.00	1.00
2	−782 (4.39)	−52 (4.34)	−1002	−518	399	−880	−476	251	0.54(**C**⇌**B**) 0.84(**C**⇌**B**′)	0.76(**C**⇌**B**) 0.91(**C**⇌**B**′)
3	−440 (3.35)	112 (3.35)	−535	103	103	−448	41	41	0.85	0.98
4	−788 (4.72)	−68 (4.72)	−1082	−415	263	−1178		148	0.56(**C**⇌**B**′)	0.71(**C**⇌**B**′)
5	16 (0.78)	31 (0.78)	−12	27	27	−9	34	34	0.28	0.42
6	1083 (4.94)	602 (4.94)	−5	125	1032				0.00	
7	−708 (5.51)	−77 (5.31)	−708[b]	−290	526				1.00	
8	−1211 (6.47)	1143 (7.04)	−1211[b]	584	5358				1.00	
9	−738 (7.07)	1562 (7.26)	506(syn)[c] −1029(anti)[c]	355	4918				1.00 0.81(anti)	

[a] Free rotation additive scheme.

[b] Values calculated for form with $\phi=90°$, $\phi'=117°$ (compound **7**) and $\phi=107°$, $\phi'=91°$ (compound **8**).

[c] Prefixes syn and anti refer to forms in which the *o*-methoxy and *o*′-nitro groups either lie on the same side or are in opposite directions with respect to the reference plane.

[d] For compounds (**6**)-(**9**) calculations by the field scheme were not performed due to lack of polarisability parameters.

*Diaryl sulphones (**2**)-(**6**)*

In Table 5 the calculated Kerr constants (${}_{\mathrm{m}}K_{\mathrm{calc}}$) for different conformations are reported and compared with the experimental data. Inspection of this table indicates that all conformers corresponding to forms **C**, **B** and **B**′ are populated for the diaryl sulphones (**2**)–(**5**) as solutes. The weight fractions obtained by means of the additive and field scheme calculations are internally consistent (Table 5). In the case of *p*-methoxy-*p*′-nitrodiphenylsulphone (**6**) only form **B**′ is present in solution (the ring bearing the OMe substituent is orthogonal and that containing the NO_2 group is coplanar with the C_{Ar}–S–C_{Ar} reference plane). Such a preferred conformation accounts for the strong π conjugation between the ring bearing the methoxy group and the sulphonyl group; in order to relieve steric congestion, the ring with the nitro group becomes coplanar with the C_{Ar}–S–C_{Ar} reference plane and, in this case, this would be possible considering that, for this ring, conjugation with the SO_2 group does not play a significant role. It should be noted that in this compound the Kerr constant calculations are very sensitive to small variations of the torsional angle ϕ' and therefore the experimental results obtained for sulphones (**6**) can be interpreted unambiguously in favor of conformer **B**′.

Our experimental data were also used to calculate the torsional angles ϕ and ϕ' which gave the best fit ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi) = \infty$ (${}_{\mathrm{m}}K_2$) (Table 6), according to a conrotatory motion which generates helical **A** conformers ($\phi=\phi'$). The indications obtained are realistic for sulphones (**2**) and (**3**) for which an orthogonal **C** form is found once again, and for sulphone (**5**) in which lack of strong conjugative π interactions between the rings and the sulphonyl group should be expected. By contrast, values of $\phi=\phi'=61$–$64°$ for compound (**6**) are not realistic, considering steric and conjugative interactions, as was discussed before. For sulphone (**4**) an equilibrium between forms **C** and **B**′ should be more palatable considering the steric requirement of the mesityl ring which is forced to assume a perpendicular position with respect to the reference plane, whereas

TABLE 6

Calculated torsional angles ϕ which best fit the experimental data of diaryl sulphones, according to a helical structural model (form **A**)

Compound	ϕ (deg)	
	Additive scheme	Field scheme
1	90	90
2	70	76
3	74	87
4	61	64
5	51	57
6	20	

for sulphone (**6**) conjugative π interactions strongly support conformer **B**′, as was discussed before.

Diaryl sulphones (7)-(9)

The best fit between the experimental and calculated values of ${}_{m}K_{calc}$ and μ_{calc} (see Table 5) is achieved when $\phi = 90°$, $\phi' = 85°$ or 117° in the case of *o*-methoxy-*p*′-nitrodiphenylsulphone (**7**), and $\phi = 107°$, $\phi' = 91°$ for *o*-nitro-*p*′-methoxydiphenylsulphone (**8**). These values therefore strongly support orthogonal **C** conformers as would be expected if conjugative and steric interactions are taken into consideration.

For *o*-methoxy-*o*′-nitrodiphenylsulphone (**9**), in principle different conformations are conceivable, but as can be inferred from Table 5 the best fit between calculated and experimental data is obtained only when a mixture of syn and anti forms of structure **C** are considered. Prefixes syn and anti refer to forms in which the *o*-methoxy and *o*′-nitro groups lie on the same side as or are in opposite directions with respect to the reference C_{Ar}–S–C_{Ar} plane respectively.

The calculated values for syn and anti forms of **C** are ${}_{m}K_{calc} = 506 \times 10^{-12}$ ($\mu_{calc} = 7.76$ D) and ${}_{m}K_{calc} = -1029 \times 10^{-12}$ ($\mu_{calc} = 6.85$ D) respectively. The weight fraction of the anti form **C** is equal to 0.81 from data obtained by the Kerr constants, and equal to 0.77 from dipole moment data; these two values are very close to each other confirming that sulphone (**9**) exists preferentially in the anti form **C**.

CONCLUSIONS

From the foregoing it can be concluded that the infinite-dilution molar Kerr constants and dipole moments of the examined diaryl sulphones are consistent, in most cases, with the presence in dioxane of orthogonal **C** or planar-orthogonal **B** conformers, or with a mixture of them.

In particular, diphenyl sulphone, *o*-nitro-*p*′-methoxydiphenylsulphone and *o*-methoxy-*o*′-nitrodiphenylsulphone exist preferentially as orthogonal **C** forms. In contrast, *p*-methoxy-*p*′-nitrodiphenylsulphone has a planar-orthogonal **B** conformation in which the ring bearing the methoxy group is perpendicular to the C_{Ar}–S–C_{Ar} reference plane. For *p*-chlorodiphenylsulphone and mesityl-*p*-bromophenylsulphone an equilibrium between orthogonal **C** and planar-orthogonal **B** conformers exists in solution, with a bias towards form **C**. For di-*p*-nitrophenylsulphone the conrotatory molecular helical conformation **A** in which the two rings are equally twisted with respect to the C_{Ar}–S–C_{Ar} plane seems a more realistic explanation. The conformation of *o*-methoxy-*p*′-nitrodiphenylsulphone is in between planar-orthogonal **B** and helical **A** forms: the ring containing the *o*-methoxy substituent is perpendicular to the reference plane whereas the ring bearing the p'-NO_2 group is rotated by approximately 117° (53°).

In diaryl sulphones the perpendicular orientation of the aromatic rings with respect to the C_{Ar}–S–C_{Ar} reference plane is due to the π-conjugative interactions between the aromatic rings and the sulphonyl orbitals. In di-*p*-nitrophenylsulphone such conjugative forces between the aromatic rings and the SO_2 group were found to be absent.

REFERENCES

1 D. Gust and K. Mislow, J. Am. Chem. Soc., 95 (1973) 1535.
2 G. Montaudo, P. Finocchiaro, E. Trivellone, F. Bottino and P. Maravigna, J. Mol. Struct., 16 (1973) 299, and references cited therein.
3 M.J. Aroney, L.R. Fisher and R.J.W. Le Fevre, J. Chem. Soc., (1963) 4450.
4 J. Toussaint, Bull. Soc. Chim. Belg., 54 (1945) 319.
5 H.P. Koch and W.E. Moffitt, Trans. Faraday Soc., 47 (1951) 7.
G. Cilento, Chem. Rev., 60 (1960) 147.
6 O.A. Osipov, V.I. Minkin and A.D. Garnovskii, in Vicshaya Schcola, (Ed.), Spravochnic po dipolnym momentam, Moscow, 1971.
V.I. Minkin, O.A. Osipov and Yu.A. Zhdanov, Dipole Moments in Organic Chemistry, Plenum Press, New York, 1970.
7 J.G. Sime and S.C. Abrahams, Acta Crystallogr., 13 (1960) 1.
8 S.A. Chawdhury and A. Hargreaves, Acta Crystallogr., Sect. B, 27 (1971) 548.
9 J.B. Hyne and J.W. Greidanus, Can. J. Chem., 47 (1969) 803.
10 C. Le Fevre and R.J.W. Le Fevre, J. Chem. Soc., (1953) 4041.
11 S.B. Bulgarevich, V.N. Sheinker, O.A. Osipov, A.D. Garnovskii and A.A. Kushjarov, Zh. Obshch. Khim., 44 (1974) 1944.
12 R.J.W. Le Fevre and S.C. Solomon, Aust. J. Chem., 21 (1968) 1703.
13 A.N. Vereschagin, in K. Nauka (Ed.), Polarizability of Molecules, Moscow, 1980, (in Russian).
14 T. Fujita, J. Am. Chem. Soc., 79 (1957) 2471.
15 C.G. Le Fevre and R.J.W. Le Fevre, Pure Appl. Chem., 5 (1955) 261.
16 M.J. Aroney and S.J. Pratten, J. Chem. Soc. Faraday Trans., 80 (1984) 1201.
17 B.A. Arbuzov, S.G. Vul'fson, A.A. Butenko, O.A. Samazina, A.B. Teitel'baum and A.N. Vezeshchagin, Izv. Acad. Nauk SSSR, Ser. Khim., (1976) 86.
18 R.J.W. Le Fevre and B.P. Rao, J. Chem. Soc., (1958) 1465.
19 R.J.W. Le Fevre, B.J. Orr and G.L.D. Ritchie, J. Chem. Soc. B, (1966) 273.
20 R.J.W. Le Fevre, A. Sundaram and R.K. Pierens, J. Chem. Soc., (1963) 479.
21 R.J.W. Le Fevre and B.P. Rao, J. Chem. Soc., (1958) 1465.
22 R.J.W. Le Fevre, Adv. Phys. Org. Chem., 3 (1965) 1.
23 D.Ya. Movshovich, S.B. Bulgarevich, S.E. Filippov and O.A. Osipov, Zh. Obshch. Khim., 52 (1982) 1620.
24 S.E. Filippov, D.Ya. Moshovich and S.B. Bulgarevich, Zh. Obshch. Khim., 57 (1987) 1624.
25 D.Ya. Moshovich, S.E. Filippov, S.B. Bulgarevich and T.A. Horol'skaya, Zh. Obschch. Khim., in press.
26 M. Hargittai and I. Hargittai, J. Mol. Struct., 20 (1974) 283.
27 R.J.W. Le Fevre, D.S.N. Murthy and P.J. Stiles, Aust. J. Chem., 22 (1969) 1421.