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Conformational investigation of diarylsulphides by Kerr effect and dipole moment methods

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Abstract

Molar Kerr constants and electric dipole moments are reported for $(4\text{-}NO_2C_6H_4)_2S$, $(4\text{-}MeOC_6H_4)_2S$, $(4\text{-}MeOC_6H_4)$ $(4'\text{-}NO_2C_6H_4)S$, $(2\text{-}MeOC_6H_4)$ $(4'\text{-}NO_2C_6H_4)S$, $(4\text{-}MeOC_6H_4)$ $(2'\text{-}NO_2C_6H_4)S$, $(2\text{-}MeOC_6H_4)$ $(2'\text{-}NO_2C_6H_4)S$ and $(4\text{-}ClC_6H_4)_2SO$ as solutes in dioxane 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 helical conformers, where both aromatic rings are twisted in the same direction with respect to the C_{Ar}–S–C_{Ar} molecular reference plane. The $(4\text{-}ClC_6H_4)_2SO$ molecule adopts an orthogonal conformation where both aryl rings are approximately perpendicular to the C_{Ar}–S–C_{Ar} molecular reference plane.

INTRODUCTION

The ground state conformations of diaryl derivatives, such as diphenylmethanes, diphenyl-ethers, 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 (i) both aryl rings are twisted in the same direction with respect to the C_{Ar}–Z–C_{Ar} reference plane (form A, Fig. 1) so as to impart a helical arrangement to the molecule, which thus possesses a C_2 point group skeletal symmetry, or (ii) one ring lies parallel to the reference plane and the

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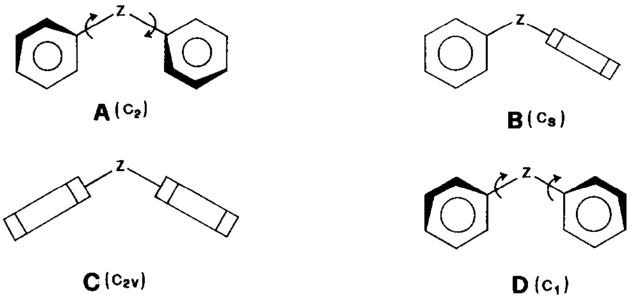

Fig. 1. Possible conformations for a diaryl compound. Point groups of symmetry are indicated.

other is perpendicular to it (form B, hereafter called the planar-orthogonal conformation).

On the contrary, diaryl-sulphones (Z, SO_2), including diphenyl-sulphone, adopt a conformation where both aryl rings are perpendicular to the C_{Ar}–Z–C_{Ar} reference plane [2–4] (form C, hereafter called the orthogonal conformation). This spatial arrangement of the aryl rings is due to the π-conjugative interactions between the rings and the sulphonyl group orbitals, as was inferred from dipole moment measurements on these systems [4]. Nevertheless, form B, as well as an equilibrium between forms B and C, are also feasible structures for diaryl-sulphones. In addition, in molecules where the π-conjugation between the aromatic rings and the SO_2 group is absent, as happens in bis-4-nitrophenyl-sulphone, form A seems to be preferred [4].

Continuing our investigations using Kerr effect and dipole moment methods, we were interested to compare the conformational aspects of diaryl-sulphones with those of their diaryl-sulphide precursors. In fact, in these two classes of compounds steric conditions are nearly the same because the angles C_{Ar}–S–C_{Ar} in sulphones and sulphides are near to each other (104.8° [5] and 109° [6] respectively), but the natures of SO_2 and S bridges in these diaryl compounds are quite different. In fact, the first is a strong π-acceptor whereas the second is a π-donor group. Furthermore, different conformations for diaryl-sulphides were reported in the literature using different techniques. The gas-phase electron diffraction analysis of diphenyl-sulphide [7] can be interpreted in terms of a slightly distorted helical form A, ($\phi = 43°$, $\phi' = 56°$, defined in Fig. 2) as well as in terms of form D ($\phi = 43°$, $\phi' = -56°$), hereafter called the asymmetric conformation. Using the same technique [8] form D was proposed also for di-*p*-mercaptophenyl-sulphide ($(p\text{-}HSC_6H_4)_2S$). In fact, the experimental data are consistent with $\phi = 67.8°$, $\phi' = 4.5°$ and $\phi = 69.5°$, $\phi' = -27°$ respectively. For diphenyl-sulphide as a solute in CCl_4, even the observed molar Kerr constants can be interpreted in terms of form A ($\phi = 42$–$46°$) or B [9]. X-ray

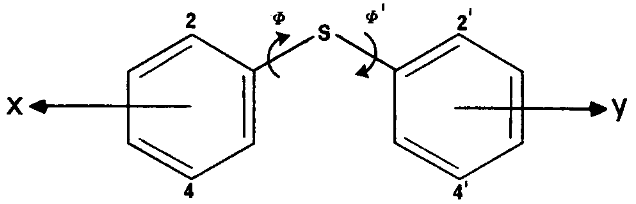

Fig. 2. Diaryl-sulphides examined in this work (Table 1). In the starting conformation ($\phi = \phi' = 0°$) the two aryl rings are coplanar with the C_{Ar}–S–C_{Ar} reference plane.

results, however, indicate that di-*p*-tolyl-sulphide and bis-4-bromophenyl-sulphide have helical conformations A ($\phi = \phi' = 35°$) [6,10]. Vectoral analysis of the dipole moments of the *o,o'*-ditolyl *m,m'*-ditolyl and bis-4-chlorophenyl-sulphides [11] have shown that, if these molecules exist in benzene solutions as single conformers, they should possess twist angles $\phi = \phi'$ ranging between 54 and 86°.

Therefore, these somewhat conflicting data on the conformational aspects of diaryl-sulphides prompted us to reinvestigate in greater detail their static stereochemistry in different substituted compounds (listed in Fig. 2 and Table 1), using as techniques the molar polarisations (${}^{\infty}P_2$), molar

TABLE 1

Physico-chemical data for the diaryl-sulphides investigated

No.^{a}	X	Y	M.p. (°C)	^{1}H-NMR ($CDCl_3$)^{b}
1	4-NO_2	4'-NO_2	158–59 (160–61)^{c}	7.50 (d, 2H, J_{AB} = 9.1 Hz, ArH) and 8.21 (d, 2H, J_{AB} = 9.1 Hz, ArH)
2	4-OCH_3	4'-OCH_3	44–46 (43–45)^{d}	3.80 (s, 3H, OCH_3), 6.82 (d, 2H, J_{AB} = 9.1 Hz, ArH) and 7.30 (d, 2H, J_{AB} = 9.1 Hz, ArH)
3	4-OCH_3	4'-NO_2	66–67 (66–68)	3.86 (s, 3H, OCH_3), 6.98 (d, 2H, J_{AB} = 9.0 Hz, ArH), 7.09 (d, 2H, J_{AB} = 9.0 Hz, ArH), 7.49 (d, 2H, J_{AB} = 9.1 Hz, ArH) and 8.03 (d, 2H, J_{AB} = 9.1 Hz, ArH)
4	2-OCH_3	4'-NO_2	92–93 (93–94)^{f}	3.80 (s, 3H, OCH_3), 7.06–7.48 (m, 4H, ArH), 7.20 (d, 2H, J_{AB} = 9.1 Hz, ArH) and 8.03 (d, 2H, J_{AB} = 9.1 Hz, ArH)
5	4-OCH_3	2'-NO_2	96–97 (97–88)^{g}	3.86 (s, 3H, OCH_3), 6.80–7.45 (m, 3H, ArH), 7.00 (d, 2H, J_{AB} = 8.8 Hz, ArH), 7.50 (d, 2H, J_{AB} = 8.8 Hz, ArH) and 8.23 (m, 1H, ArH)
6	2-OCH_3	2'-NO_2	118–19 (116–17)^{h}	3.78 (s, 3H, OCH_3), 6.80–7.62 (m, 7H, ArH) and 8.23 (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. 12. [d]From Ref. 13. [e]From Ref. 14. [f]From Ref. 15. [g]From Ref. 16. [h]From Ref. 17.

refractions ($^{\infty}R_D$), molar Kerr constants ($^{\infty}({}_mK_2)$), all at infinite dilution, and dipole moments (μ) measured at 298 K in dioxane solution.

In addition we studied the conformation of bis-4-chlorophenyl-sulphoxide because this compound could be regarded as an intermediate reference system between diaryl-sulphones and diaryl-sulphides.

EXPERIMENTAL

General synthetic procedures

Bis-4-chlorophenyl-sulphoxide (**7**) was a high purity commercial sample (Aldrich) which was recrystallised before use. Diaryl-sulphides **3–6** were prepared in high yield ($\geqslant 80\%$) by nucleophilic condensation of the corresponding thiols with the appropriate nitrochlorobenzenes, in refluxing EtOH and KOH. Diaryl-sulphide (**1**) has been prepared according to the method described by Prince and Stacy [12]; compound **2** was obtained by methylation with dimethyl-sulphate of a basic solution of 4,4′-thiodiphenol (Aldrich). Table 1 reports the melting points and the ^{1}H-NMR spectra of the samples synthesized for this work.

Physical measurements

Solute dipole moments μ and electric birefringences (Kerr effect), the latter expressed as molar Kerr constants $^{\infty}({}_mK_2)$, were determined at 298 K. The apparatus, techniques of measurements and symbols have been described elsewhere [18,19]. A He–Ne laser (λ = 632.8 nm) was used as a light source. Benzene was used as the reference liquid. The solvent constants for dioxane were the following: ${}_sK_1 = 12.312 \times 10^{-15}$ e.s.u, $B = 0.6705 \times 10^{-8}$ e.s.u., $n_c = 1.4187$, $d = 1.02687\,\mathrm{g\,cm^{-3}}$, $\varepsilon_1 = 2.209$ [20], $n_D = 1.42025$ [21].

Dielectric permittivities were measured by the heterodyne method on an E-7-5A serial instrument, densities by the hydrostatics method, and refractive indices on a PΦ-23 refractometer. For each compound relative permittivities, densities, refractive indices and Kerr constants (ε_{12}, d_{12}, n_{12}, B_{12} respectively) were measured for a range of solutions having solute weight fractions W_2. Coefficients $\alpha\varepsilon_1$, β, γ and δ were derived, using the linear relations $\varepsilon_{12} = \varepsilon_1(1 + \alpha W_2)$, $d_{12} = d_1(1 + \beta W_2)$, $n_{12} = n_1(1 + \gamma W_2)$ 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 $1.05 \times (^{\infty}R_D)$, where $^{\infty}R_D$ is the experimental refraction for the sodium D-line (in cm^3 mol^{-1}). The Fujita equation [22] was chosen to calculate the molar polarization $^{\infty}P_2$ (in cm^3 mol^{-1}). Solute dipole moments μ are reported in Debye and molar Kerr constants $^{\infty}({}_mK_2)$ 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 Cm = 0.2998×10^{30} D, $1\,m^5V^{-2}mol^{-1} = 0.8988 \times 10^{15}$ e.s.u. mol^{-1}. Experimental results are reported in Table 2.

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 [23, 24] and bond group principal polarisabilities (listed in Tables 3 and 4).

The line of action for dipole moments of diphenyl-sulphide, bis-4-nitrophenyl-sulphide (**1**) and 4-methoxyphenyl-sulphide (**2**) in the helical conformation A (Fig. 1) are straightforward from the molecular symmetry (along the bisector of the C_{Ar}–S–C_{Ar} angle). The geometry of the sulphide group for diaryl-sulphides was chosen according to structural data on bis-4-methyl-phenyl-sulphide [6] (the C_{Ar}–S–C_{Ar} angle is equal to 109°) and it was assumed that the aromatic rings in diaryl-sulphides are ideal hexagons. In the starting conformation ($\phi = \phi' = 0°$) of bis-4-methoxyphenyl-sulphide (**2**), it was supposed that the methoxy groups were coplanar with respect to the aromatic rings and the methyl groups are directed outside the C_{Ar}–S–C_{Ar} valency angle. Actual directions for dipole moments of any other molecule were obtained by vector addition according to the scheme: $\vec{\mu}$ (Ph_2S) plus group dipole moments $\vec{m}$(C–X(Y)). The dipole moment of diphenyl-sulphide $\vec{\mu}(Ph_2S)$ was chosen to be equal to 1.50 [9] and was directed along the bisector of the C_{Ar}–S–C_{Ar} angle from the carbons towards the sulphur atom. For compounds bearing an NO_2 group, a mesomeric interaction between the aromatic rings and the sulphur bridge must be taken into account. In the case of bis-4-nitrophenyl-sulphide (**1**) the mesomeric moment m_{mes} was calculated using the equation

$$\mu(\mathbf{1}) = \mu(Ph_2S) - 2[m(C\text{–}NO_2) + m_{mes}]\cos\theta$$

where θ is half the C_{Ar}–S–C_{Ar} angle. This mesomeric moment is equal to 0.54 and is directed along the C–S bond towards the NO_2 group. For 4-methoxy-4′-nitrodiphenyl-sulphide (**3**) the mesomeric moment was calculated by the vector equation

$$[\vec{\mu}(\mathbf{3})]^2 = [\vec{\mu}(Ph_2S) + \vec{m}(C\text{–}OMe) + \vec{m}(C\text{–}NO_2) + \vec{m}_{mes}]^2$$

where $\vec{m}_{mes}$ belongs to the ring bearing the NO_2 group and also acts along the C–S bond towards the NO_2 group. It was supposed that the methoxy group is coplanar with the aromatic ring, and the vector $\vec{m}$(C–OMe) forms an angle of 72° with the O–C_{sp^2} bond and points towards the aromatic ring

TABLE 2

Molar polarisations and refractions, dipole moments and molar Kerr constants and increase of polarisability of the diaryl-sulphides, measured in dioxan at $T = 298\,\mathrm{K}$

Compound	$W_2 \times 10^{3}$[a]	$\alpha\varepsilon_1$	β	$\gamma^{(b)}$	δ	${}^{\infty}P_2$	${}^{\infty}sR_D$	μ^c	$10^{12} \times {}^{\infty}({}_{m}K_2)^c$	$10^{23}\Delta b^d$
1	4.89–13.90	6.148	0.274	0.160	−33	336.2	81.7	3.50 ± 0.11	−119 ± 8	0.950
2	2.85–15.96	3.623	0.159	0.104	−27	205.6	70.2	2.54 ± 0.09	−85 ± 6	−0.419
3	3.63–16.10	12.554	0.209	0.135	1190	598.7	76.7	5.04 ± 0.04	3813 ± 121	0.347
4	3.70–14.49	11.512	0.199	0.129	1074	550.0	76.2	4.82 ± 0.15	3440 ± 454	0.293
5	4.04–14.11	16.877	0.204	0.135	529	785.4	77.1	5.87 ± 0.04	1678 ± 72	0.397
6	3.71–13.53	15.998	0.239	0.124	291	745.1	72.6	5.72 ± 0.05	915 ± 40	−0.113
7	3.61–13.63	3.095	0.270	0.104	−37	193.8	69.3	24.3 ± 0.09	−127 ± 1	0.031

[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 enjoyed in vector additive calculations of molecular dipole moments

Group or bond and direction of dipole moment	Value of dipole moment m(C–X(Y))
$\overrightarrow{\mathrm{C{-}NO_2}}$	4.01
$\nwarrow\theta$ C–OMe[a]	1.28
$\overrightarrow{\mathrm{C{-}Cl}}$	1.59

[a]The value of angle θ is equal to 72° [23].

[23]. It was supposed also that syn- and anti-orientations of the methoxy groups with respect to the $SC_6H_4NO_2$ fragment are equally populated. For sulphide (**3**) the m_{mes} is equal to 1.35. This value is somewhat higher than m_{mes} for sulphide (**1**), evidently because there are two donor groups in the molecule, i.e. the sulphur bridge and the methoxy group.

It should be noted that the π-conjugative interaction between the sulphur bridge group and phenyl rings in diphenyl-sulphides is rather less than in diphenyl-sulphones. This conclusion comes from the comparison of the dipole moments of dimethyl-sulphide (1.55) [24] and diphenyl-sulphide (1.50) [9], together with dimethyl-sulphone (4.26) [24] and diphenyl-sulphone (4.79) [3], (5.14) [4]. It is easy to see that in the first pair of molecules the difference between dipole moments is very small and, therefore, the π-conjugation

TABLE 4

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

Group or bond	$10^{23} \times b_1$[a]	$10^{23} \times b_2$[a]	$10^{23} \times b_3$[a]	Ref.
C–H	0.065	0.065	0.065	25
C–O	0.089	0.046	0.046	26
$C{-}NO_2$	0.570	0.150	0.190	27
C–Cl	0.430	0.205	0.150	27
C_6H_5	1.056	1.056	0.672	28
C–S (from Me_2S)	0.188	0.169	0.169	29
C–S (from thianthrene)	0.474	0.060	0.106	30

[a]All polarisabilities are in cm^3.

does not play a significant role; on the contrary, in the second pair of molecules this difference is equal to 0.53–0.88 and it indicates a strong π-conjugation between the SO_2 group and the phenyl rings.

Dipole moments of aryl-sulphides (**4**)–(**6**) were calculated as functions of the two internal rotation angles ϕ and ϕ' (see Fig. 2) by vector addition using group moments from Table 3. For the rings bearing nitro groups, $m_{\text{mes}} = 1.35$ or 0.54 (directed along the rotational axis of the NO_2 group) was also taken into consideration. The methoxy group in sulphides (**4**) and (**6**) was supposed to be directed opposite to the sulphur atoms (for steric reasons) and coplanar with the aromatic ring. For sulphide (**5**) syn- and anti-orientations of the *p*-methoxy group to the $SC_6H_4NO_2$ fragment were also assumed to be equally populated. The actual direction of the dipole moment of bis-4-chlorophenyl-sulphoxide (**7**) was calculated by the vector equation

$$[\vec{\mu}(\mathbf{7})]^2 = [\vec{\mu}(\mathrm{Ph_2SO}) + \vec{m}(\mathrm{C{-}Cl})_4 + \vec{m}(\mathrm{C{-}Cl})_{4'}]^2$$

where $\mu(\mathrm{Ph_2SO})$ is the dipole moment of diphenyl-dulphoxide (4.08) [3]. From this equation it was found that the angle between the vector $\vec{\mu}(\mathrm{Ph_2SO})$ and the bisector line of the C_{Ar}–S–C_{Ar} angle is equal to 29°, and $\vec{\mu}(\mathrm{Ph_2SO})$ is directed towards the oxygen atom. The value of the C_{Ar}–S–C_{Ar} angle was taken from literature data [3].

In the calculation of ${}_{\mathrm{m}}K_{\mathrm{calc}}$ as a function of the two internal rotation angles (ϕ and ϕ') with use of the tensor additive scheme (Table 4), the increase in polarisability Δb (Table 2) was also taken into account. This increase was determined as the difference between $3b_{\mathrm{exp}}$ and $3b_{\mathrm{calc}}$ ($3(b_{\mathrm{exp}} - b_{\mathrm{calc}})$) where b_{exp} is the average electronic polarisability and was taken to be equal to $0.95^{\infty}R_{\mathrm{D}}\frac{3}{4}\pi N_{\mathrm{A}}$, where N_{A} is the Avogadro number and $3b_{\mathrm{calc}}$ is equal to the trace of the additive calculated molecular tensor polarisability. The increments of $\Delta b/2$ were distributed evenly in the planes of the two aromatic rings or along the rotation axes of each ring for compound **1**; in the case of sulphides **3**–**5** the increase, was distributed in the same way, but only in the ring bearing the NO_2 group (see Table 5). Negative values of this increase were not taken into account.

PREFERRED CONFORMATIONS OF DIARYL-SULPHIDES AND BIS-4-CHLOROPHENYLSULPHOXIDE

Considering thermodynamically unrestricted rotation of the aryl rings in diphenyl-sulphide, diaryl-sulphides (**1**–**6**) and bis-4-chlorophenyl-sulphoxide (**7**) the values (${}_{\mathrm{m}}K_{\mathrm{calc}}$) calculated using the additive scheme are far from the experimental data in most cases. Furthermore, for sulphides **1** and **2** even the signs are different (Table 2, for Ph_2S, ${}_{\mathrm{m}}K_{\mathrm{calc}} = 17 \times 10^{-12}$, this work; ${}^{\infty}({}_{\mathrm{m}}K_2) = 24.7 \times 10^{-12}$ [9]). Therefore, it may be concluded that thermo-

TABLE 5

Calculated torsion angles (ϕ) and dipole moments (μ) which best fit the experimental data of diaryl-sulphides according to the helical structural model (form A, $\phi = \phi'$). Values of ${}_{m}K_{calc}$ and μ_{calc} are also reported for thermodynamically unrestricted rotation of the aryl rings

Compound	X, Y	ϕ^0, C–S polarisabilities from Me_2S (μ_{calc})	ϕ^0, C–S polarisabilities from thianthrene (μ_{calc})	${}_{m}K_{calc} \times 10^{12}$ (μ_{calc}) for free rotation	${}^{\infty}({}_{m}K_2) \times 10^{12}$ (μ) expt.
1	4-NO_2, 4′-NO_2	61[a] 57[b]	58[a] 51[b]	132	−119 (3.50)
2	4-MeO, 4′-MeO	53	55	106 (2.61)	−85 (2.54)
3	4-MeO, 4′-NO_2	roots are absent	13[c]	2810 (5.04)	3813 (5.04)
4	2-MeO, 4′-NO_2	roots are absent	35[c] (5.05) 7[d] (5.15)	1960[c] (4.15) 1655[d] (4.15)	3440 (4.82)
5	4-MeO, 2′-NO_2	37[c] (5.79) 39[d] (5.69)	63[c] (5.79) 52[d] (5.70)	−70[c] (4.99) 277[d] (4.99)	1678 (5.87)
6	2-MeO, 2′-NO_2	60[e] (5.69)	43[e] (5.64)	1152 (4.80)	915 (5.72)

[a] Increase in polarisability is along the rotational axes of the rings.
[b] Increase in polarisability is in the plane of each ring.
[c] Increase in polarisability is along the rotational axis of the ring bearing the NO_2 group.
[d] Increase in polarisability is in the plane of the ring bearing the NO_2 group.
[e] This angle corresponds to ${}_{m}K_{calc} = 1074 \times 10^{-12}$ which is closer to the experimental value.

dynamically unrestricted rotation of the aryl rings is absent for the molecules investigated and, thus, some preferred conformers must be present in solution.

The best condition for π-conjugation between the aromatic rings and the sulphur atom in diaryl-sulphides is the coplanar arrangement of the rings with respect to the C_{Ar}–S–C_{Ar} reference plane. Thus, whenever it is possible on steric grounds, such as in thioanisoles (p–X–C_6H_4–SCH_3), the –SCH_3 is nearly coplanar with the ring, as was inferred for 3-nitrothioanisole, which shows the maximum conjugation [31].

However, for diaryl-sulphides planar conformations ($\phi = \phi' = 0°$) are not feasible structures on steric grounds and, therefore, a skeletal helical arrangement of the aryl rings in sulphides **1**–**6** can be generated; the degree of helicity should arise from a compromise between steric hindrance of the rings and their conjugation with the sulphur bridge.

Considering the presence of in solution of the A conformer only ($\phi = \phi'$, Fig. 1), the ϕ angle values were calculated by comparison of ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi)$ and experimental Kerr constants. The results are listed in Table 5. Calculations were performed using the C–S bond polarisability from the dimethylsulphide or thianthrene molecules. Additionally, the distribution of the polarisability increase, among the various directions is indicated in Table 5.

As can be seen from Table 5, the calculated ϕ angle values using different C–S bond polarisabilities from different reference systems and different ways of distributing the increase, are nearly the same for the same sulphide molecules. The ϕ angle values for sulphides **1**, **2**, **5** and **6** are similar to those which were already reported for other diaryl systems, such as diarylmethanes [32,33] and diaryl-silanes [34,35], which adopt a helical conformation, as well as to the value (ϕ = 42–46°) found by Kerr effective investigations [9] on Ph_2S. It should be noted that *ortho*-substituents in compounds **4**–**6** lie on the external region of the C_{Ar}–S–C_{Ar} valency angle and this arrangement reduces steric congestion.

For 4-methoxy-4′-nitrodiphenyl-sulphide (**3**) the roots of the equation ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi) = {}^{\infty}({}_{\mathrm{m}}K_2)$ are absent when the C–S bond polarisabilities are taken from Me_2S. The root exists (ϕ = 13°) when the C–S bond polarisabilities are taken from thianthrene and the increase is distributed along the rotational axes of the rings bearing the NO_2 group. The small degree of helicity in compound **3** arises from the strong conjugation between the ring bearing the NO_2 group and the other molecular moieties which possess strong π-donor groups: the S bridge and the 4-OMe substituent. This is supported by the large value of $m_{\mathrm{mes}} = 1.35$ and by the fact that the C–S bond polarisabilities from thianthrene include the influence of conjugation.

For 2-methoxy-4′-nitrodiphenyl-sulphide (**4**) calculations do not show the existence of roots of the equation ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi, \phi') = {}^{\infty}({}_{\mathrm{m}}K_2)$ using $m_{\mathrm{mes}} = 1.35$ obtained from the results for sulphide (**3**) and C–S bond polarisabilities from Me_2S. However, the above-mentioned equation has solutions at 35° (an increase of polarisability distributed along the rotational axes of the ring bearing the NO_2 group) and at 7° (an increase of polarisability evenly distributed in the plane of the ring bearing the NO_2 group), when using $m_{\mathrm{mes}} = 0.54$ from compound **1** and C–S bond polarisabilities from thianthrene. In the first case the dipole moment (5.05) is sufficiently close to the experimental value (4.82, see Table 5). Roots also exist when using $m_{\mathrm{mes}} = 1.35$ and C–S bond polarisabilities from thianthrene. However, in this case the corresponding calculated dipole moment values are considerably greater than the experimental ones and, therefore, are not reported in Table 5. These arguments allow us to conclude that compound **4** also exists in the helical conformation A, and, relying on the experimental dipole moment value, we prefer to assume a ϕ value of 35°.

For 4-methoxy-2′-nitrodiphenyl-sulphide (**5**) and 2-methoxy-2′-nitrodiphenyl-sulphide (**6**) it should be noted that the best agreement between calculated and experimental values of the dipole moment for conformer A, under the condition ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi) = {}^{\infty}({}_{\mathrm{m}}K_2)$, takes place when the mesomeric moment of the 2′-NO_2 group is zero. In particular, the helicity of compound **5** is close to that of compounds **1** and **2**, when considering all calculated values listed in Table 5 for this compound.

For sulphides **1**–**6**, our experimental data were also used to calculate the population of the B and C conformers (Fig. 1) on the assumption of an equilibrium between them in solution. In the case of bis-4-nitrophenyl-sulphide (**1**) the calculated fraction of orthogonal form C in such an equilibrium is equal to 44% and 49% when using polarisabilities from dimethylsulphide and thianthrene respectively, and for an increae of polarisability distributed along the rotational axes of the rings.

The analysis of the equilibrium between B and C type conformers for other sulphides (**2**–**6**) is more complicated, because in these structures several different steroisomers may exist in solution. Recalling our assumptions on the orientation of the methoxy groups, for bis-4-methoxyphenyl-sulphide (**2**) there is the possibility of two B forms: one with $\phi = \phi°$, $\phi' = 90°$ and the other with $\phi = 180°$, $\phi' = 90°$ (Fig. 2), where the methoxy group of the ring, which is coplanar with respect to the C_{Ar}–S–C_{Ar} reference plane, is disposed in anti- or syn-positions with respect to the other S–C_6H_4OMe fragment. A similar situation exists for the form C. When the ϕ and ϕ' angles are equal to either 90° and 90° or 270° and 90°, the methoxy groups are either in anti- or syn-positions with respect to the C_{Ar}–S–C_{Ar} reference plane. After calculation of the ${}_{\mathrm{m}}K_{\mathrm{calc}}$ and μ_{calc} values of all these forms, it is possible to construct a plot in cartesian coordinates: ${}_{\mathrm{m}}K_{\mathrm{calc}}$ vs. μ^2_{calc}. Such plots were proposed earlier [21]. The points on this plot which relate to different conformers of B and C types are the vertices of the polygon, and the side segments of the polygon relate to equilibrium between the conformers situated on the two vertices, while the points in the interior region of the polygon indicate an equilibrium between all conformers. In other words, when the experimental point $({}^{\infty}({}_{\mathrm{m}}K_2), \mu^2)$ falls on the side line, there is an equilibrium between two forms, but when this point is in the interior region there is an equilibrium between all conformers. If one supposes that the syn- and anti-positions of the methoxy groups in both the B and C structures are equally populated, the population of the C conformer for sulphide **2** is approximately equal to 70%, using different polarisability parameters of the C–S bond.

In the case of 4-methoxy-4′-nitrodiphenyl-sulphide (**3**), among the possible B and C conformers only one B form ($\phi = 0°$, $\phi' = 90°$, Fig. 1) has

${}_{m}K_{calc} = 3704 \times 10^{-12}$ which comes close to the experimental value (3813×10^{-12}, Table 2). For this form the ring bearing the NO_2 group is orthogonal to the C_{Ar}–S–C_{Ar} reference plane. However, as was shown above, the dipole moment of this molecule indicates a considerable conjugation between the ring bearing the NO_2 group and the rest of the molecule, and we know that the best condition for conjugation is the coplanarity of this ring with respect to the C_{Ar}–S–C_{Ar} reference plane. Thus this kind of conformation for sulphide **3** is not realistic. The plots on coordinates ${}_{m}K_{calc}$ vs. μ^2_{calc} for different kinds of B and C conformers for 2-methoxy-4′-nitrodiphenyl-sulphide (**4**) and 4-methoxy-2′-nitrodiphenyl-sulphide (**5**) do not contain, inside the polygon, the experimental points (${}^{\infty}({}_{m}K_2)$, μ^2). This means that the idea of an equilibrium between B and C forms for these molecules is not realistic.

However, for 2-methoxy-2′-nitrodiphenyl-sulphide (**6**) the experimental point (${}^{\infty}({}_{m}K_2)$, μ^2) is in the interior region of the polygon, and lies very near to the line connecting the vertices which relate to the orthogonal form C ($\phi = \phi' = 90°$) and the planar-orthogonal form B ($\phi = 90°$, $\phi' = 0°$, Figs. 1 and 2). The content of the form C is about 80%, using both sorts of polarisability data for the C–S bond (Table 4). The ortho-substituents in this form lie in the anti-position with respect to the C_{Ar}–S–C_{Ar} reference plane. In the form B, the 2′–NO_2 group is outside the C_{Ar}–S–C_{Ar} valency angle.

The possibility of the presence in solution of asymmetric conformations, $\phi \neq \phi'$, (Fig. 1) for sulphides (**1**–**6**) was also considered.

The coincidence of the calculated ${}_{m}K_{calc}(\phi,\phi')$ value with the experimental one reported in Table 2 occurs for bis-4-nitrophenyl-sulphide (**1**) when ϕ and ϕ' angles vary in the ranges: $50° \leqslant \phi \leqslant 90°$, $45° \leqslant \phi' \leqslant 72°$ or $30° \leqslant \phi \leqslant 90°$, $28 \leqslant \phi' \leqslant 72°$, for increase in polarisability distributed along the rotational axes or in the planes of the rings respectively. These angle ranges include, of course, the roots of the helical form A ($\phi = \phi'$).

In the case of bis-4-methoxyphenyl-sulphide (**2**) the roots of the equation ${}_{m}K_{calc}(\phi,\phi') = {}^{\infty}({}_{m}K_2)$ under the condition $\phi \neq \phi'$ are $\phi = 72°$, $\phi' = 138°$ and $\phi = 51°$, $\phi' = 93°$ respectively. The polarisabilities of the C–S bond were taken from Me_2S for sulphide **1** as well as for sulphide **2**.

For 4-methoxy-4′-nitrodiphenyl-sulphide (**3**) the coincidence of ${}_{m}K_{calc}(\phi,\phi')$ with ${}^{\infty}({}_{m}K_2)$, when $\phi \neq \phi'$, takes place for $\phi = 0°$, $\phi' = 41°$ or $\phi = 0°$, $\phi' = 25°$ (C–S bond polarisabilities from thianthrene). However, they do not represent realistic structures for sulphide **3** because the best condition for conjugation, as indicated by the dipole moment of this molecule, is coplanarity of the ring bearing the NO_2 group and not of the ring with the methoxy group.

The equations ${}_{m}K_{calc}(\phi,\phi') = {}_{\infty}({}_{m}K_2)$ and $\mu_{calc}(\phi,\phi') = \mu_{exp}$ have no simultaneous solutions for 2-methoxy-4′-nitrodiphenyl-sulphide (**4**) and 4-methoxy-2′-nitrodiphenyl-sulphide (**5**). However, for 2-methoxy-2′-nitrodiphenyl-sulphide (**6**) there are roots which are: $\phi = 160°$, $\phi' = 110°$, using polarisabilities from Me_2S and $\phi = 110°$, $\phi' = 139°$, using polarisabilities from thianthrene. Once again, these solutions seem unrealistic because the substituents in the 2 positions are disposed in the interior region of the C_{Ar}–S–C_{Ar} valency angle, making the steric requirements more demanding than in forms A, B or C.

Let us now compare the results achieved under the three approximations: existence of helical form A; equilibrium between B and C forms; existence of asymmetric forms D. The distinctive peculiarity of the form A is the presence of solutions to the conformational problem for all examined sulphides (**1**–**6**), including sulphide **3**. Moreover, the positions of the *ortho*-substituents in sulphides **4**–**6** occupy the less hindered positions in space. On the contrary, the solution to conformational problems in terms of D forms or in terms of an equilibrium between B and C structures, is achieved only for half of the compounds examined. It follows that the existence in solution of helical forms A for the examined sulphides (**1**–**6**) is a more acceptable solution. If one compares the conformations of diaryl-sulphides **1**–**6** with those of diaryl-sulphones exampled by us previously [4], it is easy to see the difference between them. The first group of compounds has a helical arrangement of the rings but the second class adopts, in most cases, the orthagonal C or planar-orthogonal B conformation, or a mixture of both. This difference is due to the strong conjugation between the sulphone group and the aromatic rings.

Bis-4-chlorophenyl-sulphoxide (*7*)

The difficulty of solving the conformational problem for this molecule is connected with the absence of data for the sulphoxide group polarisability ellipsoid. Following Aroney et al. [3], we used for the SO group the polarisabilities of the sulphonyl group. The K value so calculated in a free-rotation model is equal to -172×10^{-12}, which is far off from the experimental value (-127×10^{-12}). It was calculated that the roots of the equation ${}_{\mathrm{m}}K_{\mathrm{calc}}(\phi,\phi') = {}^{\infty}({}_{\mathrm{m}}K_2)$ are the following: $\phi = 40$–$70°$, $\phi = 82$–$90°$. Therefore, one can conclude that this sulphoxide has a non-coplanar arrangement of the aryl rings with respect to the C_{Ar}–S–C_{Ar} reference plane. According to X-ray crystal analysis [36] and Kerr constant examination [3], the diphenyl-sulphoxide molecule exists in the orthogonal form C only. It is quite possible that this is also the case for bis-4-chlorophenyl-sulphoxide (**7**), and the divergence between our experimental angles with respect to this ideal form is probably due to inaccuracy of the polarisability ellipsoid used for the sulphoxide group, and to the inexact direction of the molecular dipole moment calculated by the vector additive scheme.

In the paper of Aroney et al. [3] the dependence of ${}_{\mathrm{m}}K_{\mathrm{calc}}$ of diphenyl-sulphoxide on the α angle was also calculated (α is the angle between the molecular dipole moment direction and the bisector of the C_{Ar}–S–C_{Ar} angle for the form C). We have also calculated these dependences for forms A and B for sulphoxide (**7**). Full agreement between $_mK_{calc}$ and experimental Kerr constants occurs for conformation C when α is equal to 13° and for conformation B when α is equal to 55°. The additive direction of the dipole moment of this molecule is equal to 29° (see p. 8) relative to the bisector of the C_{Ar}–S–C_{Ar} angle. The first value calculated for α is closer to the additive one and the direction of dipole moment inclination may be attributed to the mesomeric interaction of the rings with the sulphoxide group. Thus, the orthogonal conformation is the most realistic form for bis-4-chlorophenyl-sulphoxide (**7**), as a solute in dioxane. Therefore, the preferred conformation of sulphoxide **7** is similar to that adopted by sulphones [4], but it is different from that of the diaryl-sulphides (**1**–**6**) investigated in this work.

CONCLUSIONS

From the foregoing work it can be concluded that the infinite-dilution molar Kerr constants and dipole moments of the examined diaryl-sulphides are consistent, in most cases, with the presence in dioxane of helical conformers, where both aryl rings are equally twisted in the same direction with respect to the C_{Ar}–S–C_{Ar} reference plane. In these conformations the *ortho*-substituents of the aryl rings are disposed outside the interior part of the C_{Ar}–S–C_{Ar} valency angle.

4-Chlorophenyl-sulphoxide exists in dioxane in an orthogonal conformation, where both aryl rings are perpendicular to the C_{Ar}–S–C_{Ar} reference plane.

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