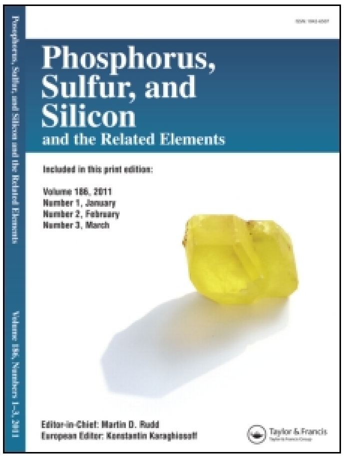

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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE POTENTIAL ANTIBACTERIAL AGENT 2-PYRIDYL-PHENYL SULPHONE

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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE POTENTIAL ANTIBACTERIAL AGENT 2-PYRIDYL-PHENYL SULPHONE

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Crystals of 2-pyridyl-phenyl sulphone are monoclinic, space group $P2_1/c$, with eight molecules in the unit cell of dimensions $a = 11.781$, $b = 5.903$, $c = 29.748$ Å and $B = 94.13°$. The dihedral angles between the best planes of the two aromatic rings are significantly different in two crystallographically independent molecules (88.4° and 71.9° for molecule *A* and molecule *B*, respectively), as well as those between the CSC plane and the pyridine ring (59.4° and 67.4°) and between the CSC plane and the phenyl ring (51.7° and 81.8°). The average bond distances of interest include C—S 1.77(1) and S—O 1.44(1) Å; among the bond angles there are CSO = 108.1(7), CSC = 105.0(6) and OSO = 118.7(6)°. The packing of the molecule in the crystal is determined by the van der Waals interactions and by two intermolecular H···O contacts of 2.43 and 2.49 Å. The observed conformation in the solid state agrees well with results of previous investigations, in the solution state, by means of dipole moment method and theoretical M.O. calculations, for the analogous di-2-pyridyl sulphone.

INTRODUCTION

Diphenyl sulphone‡ derivatives in which one or both phenyl groups are replaced by pyridine rings, i.e. 2-pyridyl-phenyl and di-2-pyridyl sulphone, were recently reported to possess notable and significant *in vitro* antibacterial activity against gram-positive and gram-negative bacteria together with *in vivo* low toxicity indexes.[3] Earlier extensive studies[4–7] of the physical and conformational properties of these compounds were thus made in an effort to elucidate the molecular features that are necessary to elicit biological activity. In particular, theoretical energy calculations using EHT and CNDO/2 approaches together with dipole moment measurements suggest that the energy barrier to internal rotation about Ar-SO_2 bond is high and that di-2-pyridyl sulphone in the solution state oscillates of nearly ±30° about the twisted conformation, with both pyridine planes rotated of *ca.* 60° out from the CSC plane and with the N atoms in a N,N-*inside* position with respect to the CSC angle. In the case of 2-pyridyl-phenyl sulphone a similar conformational arrangement was found for the Py-SO_2 fragment, whereas no information could be obtained on the whole molecule on the basis of dipole moment datum. This is because the component moment of the phenyl group is zero and

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‡ The use of 4,4′-aminodiphenyl sulphone (DDS) in clinical therapeutic practice as antibacterial, antileprotic and antimalarial agent has been known for three decades.[1,2]

thus the resultant total molecular moment is unaffected by the rotational angle about Ph-SO_2 bond. There is now evidence which suggests[3] that the derivatives of this molecule play a more significant role in antibacterial activity than those of diphenyl and di-2-pyridyl analogs, so that it was considered of interest to have unambiguous information on the structure and sterochemistry of 2-pyridyl-phenyl sulphone. An X-ray single crystal analysis of this molecule was therefore performed and the structural details, reported here, were used to provide, *inter alia*, a basis for a comparison with data existing for diaryl sulphone systems.

TABLE I

Crystal parameters (at room temperature) of 2-pyridyl-phenyl sulphone.

a = 11.781(6) Å[a]	Space group: $p2_1/c$
b = 5.903(7)	Z = 8
c = 29.748(18)	Mol. wt: 219.3
β = 94.13(8)°	F(000) = 912
V = 2063.4 Å^3	ρ (calcd) = 1.41 g cm^{-3}
Monoclinic	ρ (obsd) = 1.42 g cm^{-3}
Systematic absences: $h0l$,l odd $0k0$,k odd	$\mu_{MoK\alpha}$ = 2.9 cm^{-1}

[a] The quoted estimated standard deviations are those returned by a least-squares fit of the angular settings of 25 high-order reflections.

EXPERIMENTAL

The 2-pyridyl-phenyl sulphone was prepared according to the method described before.[6] Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate/cyclohexane (1:1) solution.

Details of crystal data are given in Table I. The X-ray diffraction experiments were performed using a PW 1100 Philips diffractometer with MoKα (λ = 0.7107 Å) radiation. The observed intensities and their variances were corrected for Lorentz and polarization effects and processed in the normal fashion.[8,9] 1309 unique reflections having a net intensity greater than 3σ were employed in the structure determination and refinement. No significant intensity variation for a given reflection was observed when rotating around the azimuthal angle Ψ. The isotropic temperature factors of the hydrogen atoms were assumed to be those of the bonded atoms. Refinement of the positional, thermal and scale parameters converged after least-squares minimization when the conventional unweighted factor R was 0.059.

The neutral atomic scattering factors used were those of Cromer and Waber,[10] while the H-curve was from Ibers[11] and the anomalous dispersion terms for the S atoms were from Cromer.[12]

The labelling scheme adopted is shown in the Figure 1, drawn with the ORTEP program.[13] All computations were performed on a CDC 6 66/7 6000 System, the major programs used being the X-Ray '72 System.[14]

Final positional and thermal parameters are given in Table II, while atomic parameters for the H atoms are presented in Table III. Interatomic distances and bond angles are shown in Table IV with their estimated standard deviations. Further structural details are presented in Tables V, and VI.

TABLE II

Final fractional atomic co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) for all non-hydrogen atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			Molecule (*A*)						
S	2975(2)	499(4)	−1912(1)	532	606	413	−6	32	−24
0(1)	3014(4)	2403(10)	−2215(2)	831	800	473	−121	83	190
0(2)	3607(4)	−1506(10)	−2009(2)	542	754	704	118	109	−157
			Molecule (*B*)						
S	2544(2)	−3698(4)	558(1)	567	712	380	−49	91	65
0(1)	2665(4)	−1897(10)	246(2)	863	976	438	−153	94	304
0(2)	3094(4)	−5847(10)	485(1)	634	746	633	140	169	−154

	Molecule (*A*)				Molecule (*B*)			
	x	y	z	U	x	y	z	U
C(1)	3427(5)	1491(14)	−1365(2)	476	3028(5)	−2672(13)	1100(2)	440
N	3329(5)	−83(11)	−1042(2)	561	3007(5)	−4228(11)	1428(2)	556
C(2)	3735(7)	615(15)	−620(3)	690	3386(6)	−3524(16)	1845(3)	659
C(3)	4198(7)	2710(16)	−529(3)	697	3776(6)	−1349(15)	1936(2)	612
C(4)	4251(6)	4254(14)	−867(2)	655	3786(6)	170(14)	1595(2)	616
C(5)	3854(5)	3647(15)	−1300(2)	558	3392(6)	−481(14)	1165(2)	590
C(6)	1521(6)	−265(12)	−1882(2)	446	1075(6)	−4212(13)	596(2)	458
C(7)	1172(6)	−2359(14)	−2042(2)	537	317(6)	−2568(14)	438(2)	592
C(8)	19(6)	−2868(14)	−2058(3)	624	−862(7)	−3011(15)	462(3)	713
C(9)	−747(6)	−1302(16)	−1907(2)	670	−1192(7)	−4955(15)	644(3)	737
C(10)	−373(6)	772(15)	−1743(2)	633	−439(7)	−6585(16)	812(3)	770
C(11)	786(6)	1310(14)	−1728(2)	537	732(6)	−6181(14)	789(2)	569

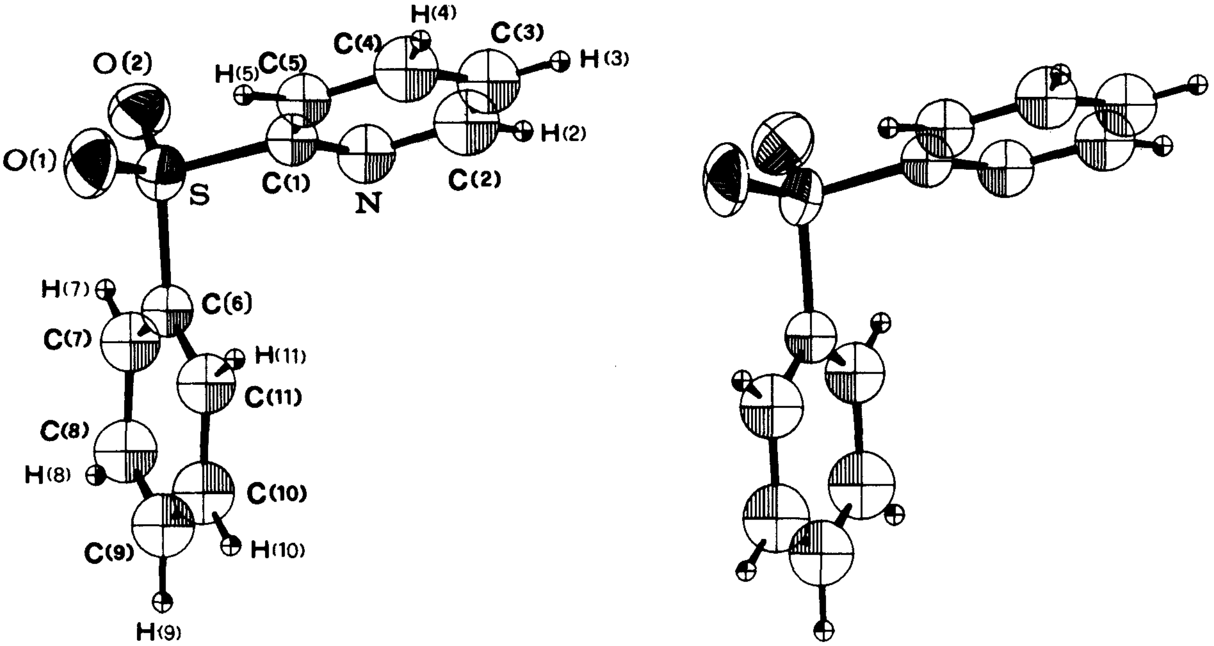

FIGURE 1 [010] projection of *A* (left) and *B* (right) molecules in the asymmetric unit. Numbering scheme holds also for molecule *B*.

RESULTS AND DISCUSSION

The crystal structure determination of 2-pyridyl-phenyl sulphone shows that there are two crystallographically independent molecules in a single asymmetric unit of the crystal. A perspective drawing of the two molecules ([010] projection) is shown in the Figure 1. Both molecules (*A* and *B*) have the same molecular dimensions and almost the same stereochemistry, though some significant differences are discernible in more detail. In both molecules the spatial arrangement of C(1), C(6), O(1) and O(2) about the S atom significantly departs from a regular tetrahedral structure, being the average O(1)—S—O(2) and C(1)—S—C(6) bond angles of 118.8° and 104.9°, respectively (see Table IV). These angle values are in good agreement with previously reported structural data for diaryl sulphones[15–23] and, in particular, for the sulphone group.[22,24,25] The interatomic average distances of the resulting *distorted* tetrahedral configuration are thus: O(1)---O(2), 2.48 Å; C(1)---C(6), 2.81 Å; C---O, 2.61 Å. Accordingly, the intramolecular non-bonded repulsions between the two O atoms will result greater than those involving the C atoms.[26]

TABLE III

Final hydrogen atomic fractional co-ordinates (× 10^3)[a]

	Molecule (*A*)			Molecule (*B*)		
	x	*y*	*z*	*x*	*y*	*z*
H(2)	369	−49	−38	337	−462	209
H(3)	446	309	−22	405	−93	224
H(4)	457	573	−81	405	170	166
H(5)	386	470	−156	334	62	93
H(7)	170	−348	−215	56	−112	31
H(8)	−27	−429	−219	−144	−199	33
H(9)	−156	−169	−191	−200	−527	66
H(10)	−91	182	−162	−73	−791	96
H(11)	106	277	−160	128	−733	90

[a] Hydrogen atoms are numbered according to the atoms to which they are attached.

Table VII compares the important structural features of the sulphone under study with those obtained from crystal structure analysis of other relevant diaryl sulphones. This Table shows that, in general, the nature of the substituent groups of the aromatic fragment does not significantly affect the bond lengths and interbond angles at the S atom. The S—O bond length of 1.44 Å agrees, within the experimental error, with the average of 1.43 Å found for a number of sulphones (see refs. in the table) and for diphenyl

TABLE IV

(a) Bond lengths (Å)[a]

	(*A*)	(*B*)
S—O(1)	1.44	1.43
S—O(2)	1.44	1.45
S—C(1)	1.77	1.78
S—C(6)	1.78	1.77
C(1)—N	1.35	1.34
N—C(2)	1.37	1.35
C—C mean	1.38	1.38
C—H mean	0.98	0.97

(b) Valence angles (°) and their estimated standard deviations

	(*A*)	(*B*)
O(1)—S—O(2)	118.3(0.7)	119.2(0.6)
O(1)—S—C(1)	107.1(0.7)	107.2(0.7)
O(1)—S—C(6)	107.6(0.6)	108.3(0.6)
O(2)—S—C(1)	109.3(0.7)	108.5(0.6)
O(2)—S—C(6)	108.4(0.7)	108.0(0.7)
C(1)—S—C(6)	105.3(0.6)	104.6(0.6)
S—C(1)—N	113.0(1.1)	113.9(1.1)
S—C(1)—C(5)	121.1(1.1)	121.6(1.1)
C(5)—C(1)—N	125.8(1.2)	124.5(1.2)
C(1)—N—C(2)	113.8(1.3)	115.7(1.3)
N—C(2)—C(3)	123.9(1.5)	123.2(1.5)
S—C(6)—C(7)	118.3(1.1)	118.0(1.2)
S—C(6)—C(11)	118.6(1.2)	119.4(1.1)
C—C—C mean	119.6	119.6

[a] Their estimated standard deviations average 0.01 Å.

TABLE V

Angles (°) between the mean planes for molecules *A* and *B*. Plane *1*: pyridine ring; plane *2*: benzene ring; plane *3*: C(1)—S—C(6); plane *4*: SO$_2$ group.

	A	*B*	*A B*	
1 – 2	88.4	71.9	*1 – 1*	3.6
1 – 3	59.4	67.4	*2 – 2*	48.7
1 – 4	61.0	56.7	*3 – 3*	4.7
2 – 3	51.7	81.8	*4 – 4*	2.8
2 – 4	66.0	53.0	*2 – 1*	90.0
3 – 4	89.5	89.5	*3 – 2*	80.3

TABLE VI

Intermolecular distances less than 3 Å

H(2A)---O(1B)	2.43	H(4B)---O(2A$^{\mathrm{III}}$)	2.88
H(5B)---O(2B$^{\mathrm{I}}$)[a]	2.49	H(4B---O(2B$^{\mathrm{III}}$)	2.86
H(5A)---O(2A$^{\mathrm{I}}$)	2.60	H(9A)---C(4B$^{\mathrm{IV}}$)	2.98
H(2B)---O(1A$^{\mathrm{II}}$)	2.71	H(9B)---C(4A$^{\mathrm{IV}}$)	2.83
H(2B)---O(2A$^{\mathrm{II}}$)	2.77	H(10A)---N(B$^{\mathrm{IV}}$)	2.94
H(3B)---O(2A$^{\mathrm{II}}$)	2.79	H(3B)---O(1A$^{\mathrm{V}}$)	2.96

[a] Roman numeral superscripts refer to molecules in the following position relative to the reference molecule at x,y,z

(I)	x,	$1 + y$,	z
(II)	x,	$-\frac{1}{2} - y$,	$\frac{1}{2} + z$
(III)	$1 - x$,	$-y$,	$-z$
(IV)	$-x$,	$-y$,	$-z$
(V)	x,	$\frac{1}{2} - y$,	$\frac{1}{2} + z$

TABLE VII

Comparison of molecular dimensions[a] in sulphones of the type Ar$_1$—SO$_2$—Ar$_2$

Compound	Ref.	Interatomic distances		Interatomic angles ( )		Dihedral angles (°)			
		S—O	S—C	O—S—O	C—S—C	CSC—Ar$_1$	CSC—Ar$_2$	Ar$_1$—Ar$_2$	OSO—CSC
4,4′-dichlorodiphenyl[b]	15	1.43	1.76	120.4	104.8	84.4		79.5	89.9
4,4′-dichlorodiphenyl[b]	16	1.43	1.77	119.7	104.6	84.6		79.0	89.8
4,4′-dibromodiphenyl[b]	16	1.45	1.76	120.1	104.3	83.8		78.5	89.9
4,4′-diiodiodiphenyl[b]	16	1.44	1.76	119.4	105.6	86.9		74.5	88.9
diphenyl	17	1.44	1.77	119.2	104.1	81.1	88.3	76.8	89.7
4,4′-difluorodiphenyl	17	1.44	1.77	119.9	104.4	72.6	88.9	79.5	89.4
3,3′-dinitro-4,4′di-fluorodiphenyl	17	1.43	1.77	120.7	104.2	89.0	85.2	77.7	89.6
4,4′-diaminodiphenyl	18	1.44	1.76	119.4	105.9	85.0	75.0	77.3	89.5
dimesiytl	19	1.41	1.79	117.2	104.5	55.6	54.5	77.0	86.5
phenyl-mesityl[c]	20	1.43	1.77	117.3	106.1	36.0	67.0	87.2	89.3
		1.44	1.78	117.3	105.4	34.6	68.2	86.9	89.7
2-pyridyl-phenyl[c]	this	1.44	1.77	118.3	105.3	59.4	51.7	88.4	89.5
	work	1.44	1.77	119.2	104.6	67.4	81.8	71.9	89.5

[a] Averaged over all the crystallographically inequivalent, but chemically equivalent, bonds and angles

[b] Only one crystallographically independent aromatic ring

[c] Two crystallographically independent molecules in one asymmetric unit.

disulphone (1.43 Å).[25] This value also indicates that S—O bond has, according to Cruickshank's views,[27] comparable and high π-bond character that can be considered as $> 50\%$. The C—S bond distances (1.77 Å) lie between those suggested for a pure single bond (1.82 Å) and a double bond (1.62 Å)[28]. This would imply participation of the sulphur 3*d* orbitals to the Ar-S bond to the extent of approximately 25% of double bond character[28] (the use of Pauling's relation,[29] however, would indicate a somewhat smaller π-bond order). In the Table VI of Ref. 31 many examples are given of aromatic $C(sp^2)$—S distances ranging from 1.75 Å to 1.80 Å.

Further inspection of Table VII shows that solid state conformation of the sulphones listed, in general, agrees well with previous theoretical views,[30] since the observed structures are characterized by dihedral angles between the aromatic rings and CSC plane between 72.6° and 88.9° (refs. 15–18). The dimesityl[19] and phenyl mesityl sulphone[20] are exception, the strong departure from perpendicularity between aromatic and CSC planes being clearly attributable to the sizeable steric interactions between the SO_2 and methyl groups. In the present case, it should be thus stressed the peculiar departure from 90° of the dihedral angle between aromatic and CSC planes, that is higher than the expectable for a sterically not-hindered diaryl sulphone. The found conformations thus appear rather unusual, the above distortion from the "diphenyl sulphone type" arrangement being also in fairly good agreement with results of conformational studies in the solution state for di-2-pyridyl and 2-pyridyl-phenyl sulphone by using dipole moment analysis and theoretical calculations of conformational energy.[6] These findings indicate that the molecule examined may act as a solute molecule with a *quasi*-rigid conformation in which torsional oscillations of $\sim \pm 30°$ can take place about the minimum energy conformation. The torsion angle of the pyridine ring plane can be reasonable accounted for on energetic grounds, i.e. as a result of a compromise between the tendency to the perpendicularity with respect to the CSC plane owing to conjugative effects, and the repulsion between non-bonded N···O interactions between pyridine and sulphonyl groups. The torsional angle taken by the phenyl ring may be thus interpretated as arising from a balance of repulsion energies between its hydrogen atoms and those of the pyridine ring.

This distortion from a perpendicular arrangement, as shown by the present structure determination, does not seem to be accompanied by any significant changes in the bond lengths and angles with respect to diphenyl sulphone-type systems.

A further question arises as to why the two types of molecules *A* and *B* have different orientation in the crystal. At first thought, it would seem a simple matter to arrange them so as to satisfy molecular close packing requirements. Indeed, the different orientation may be influenced by the H(2*A*)···O(1*B*) and H(5*B*)···O(2*B*) at x, $1 + y$, z contacts (2.43 and 2.49 Å, respectively), although these contacts are slightly longer than the value of 2.4 Å below which significant interaction may exist between H and O atoms.[32] In both molecules the S atom is displaced from the aromatic planes by different amounts but in the same direction, the largest (0.16 Å in *A*) from the phenyl ring which makes the smallest dihedral angle (51.7°) with the CSC plane.

The dihedral angle between the best planes of the two rings is significantly different in the two independent molecules (88.4° and 71.9° in *A* and *B*, respectively), whereas there is no significant difference between corresponding distances in the two molecules.

Finally, there are no intermolecular contacts less than van der Waals distances, except for those reported in Table VI, and the crystal packing has been determined essentially by van der Waals forces.

In conclusion, the present results primarily bear out the findings reached for diaryl sulphones and derivatives in the solution state and, in addition, suggest that there is a conformational aspect peculiar for these systems which could play important roles in their transport, binding and antibacterial activity. In particular, a high degree of molecular complementarity with the receptor could be predicted for diaryl sulphones having a "diphenyl sulphone-like" conformation with a limited amount of conformational flexibility.

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