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A Crystallographic Study of the Diphenyl Sulphoxide–Diphenyl Sulphone System

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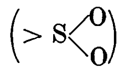
The diphenyl sulphoxide–diphenyl sulphone system has been studied crystallographically, using both the powder and the single-crystal methods. Diphenyl sulphoxide is shown to dissolve in diphenyl sulphone in all concentrations up to a limit of about 91% diphenyl sulphoxide, without producing any major structural changes in the diphenyl sulphone crystal. At 92% diphenyl sulphoxide, the structure of the solid solution undergoes a transition to that of diphenyl sulphoxide.

Introduction

A knowledge of the stereochemistry of the sulphoxide (> S–O) and sulphone  $\left(>\mathrm{S}\genfrac{}{}{0pt}{}{\diagup\mathrm{O}}{\diagdown\mathrm{O}}\right)$ groups is important for a fundamental understanding of the electronic configuration of sulphur in its 3- and 4-covalent bonded states. The crystal structure of diphenyl sulphoxide has now been established in detail by Abrahams & Grenville-Wells (1955), who showed the sulphur atom to have a pyramidal configuration, with the two C–S–O bond angles of 106° and a C–S–C bond angle of 97½°.

Rheinbolt & Giesbrecht (1946) studied the phase diagram of the diphenyl sulphoxide–diphenyl sulphone system by the method of thermal analysis, and established the formation of a continuous series of solid solutions of the minimum type. In case the formation of the continuous series of solid solutions was due to isomorphism, which would permit a rapid determination of the crystal structure of diphenyl sulphone, the diphenyl sulphoxide–diphenyl sulphone system was examined crystallographically.

Study of the diphenyl sulphoxide–diphenyl sulphone system

It is apparent from the measurements collected in Table 1 that while the crystals of diphenyl sulphoxide and diphenyl sulphone belong to the same space group,* there is no obvious simple relation between the two sets of cell constants and no indication of isomorphism. Powder photographs confirmed the two crystal structures to be essentially quite different, and the corresponding spacings and intensities are given in Table 2.

Powder photographs of nine intermediate compositions were recorded, and the spacings and intensities for two selected compositions, as well as for pure diphenyl sulphoxide and diphenyl sulphone, are included in Table 2. It may be seen from Table 2 that for compositions between 100 and 9% by weight of diphenyl sulphone the structure of the solid solution remains essentially that of pure diphenyl sulphone. At 8·4% sulphone, the crystal structure undergoes a transition almost entirely to that of diphenyl sulphoxide, as indicated by the abrupt intensity changes, although traces of the sulphone structure are still present. At 5% sulphone (not given in Table 2) the only structure present is that of the sulphoxide. The powder patterns indicate a gradual decrease in the size of the diphenyl sulphone-type unit cell as the diphenyl sulphoxide content increases, but accurate cell constant measurements could not be made owing to the

Table 1. *Single-crystal data for the diphenyl sulphoxide–diphenyl sulphone system*

Sulphoxide (% w/w)	100	92	88	0
Sulphone (% w/w)	0	8	12	100
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	8·90 ± 0·02	8·92 ± 0·02	11·98 ± 0·03	12·21 ± 0·03
b (Å)	14·08 ± 0·03	14·13 ± 0·03	7·64 ± 0·02	7·82 ± 0·02
c (Å)	8·32 ± 0·02	8·37 ± 0·02	11·46 ± 0·03	11·31 ± 0·03
β	101° 7′ ± 10′	100° 55′ ± 10′	99° 35′ ± 10′	98° 25′ ± 10′
U (Å^3)	1022·9	1035·8	1034·2	1070·5
D_m	1·304	1·305	1·306	1·355
Z	4	4	4	4
D_X	1·313	1·305	1·311	1·353
Space group	$P2_1/n$–C_{2h}^5	$P2_1/n$–C_{2h}^5	$P2_1/c$–C_{2h}^5	$P2_1/c$–C_{2h}^5
M.p. (°C.)	70	62–64*	61–66*	124

* The m.p. range gives the difference between the thaw and the true m.p.

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* Although the unit cells are differently oriented, the similarity in external morphology of the two crystals suggests that the present choice of a and c axes should be retained

Table 2. *Powder data for the diphenyl sulphoxide–diphenyl sulphone system*

Sulphoxide (% *w*/*w*)	100		91·6		91		0	
Sulphone (% *w*/*w*)	0		8·4		9		100	
	d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
	6·60	3	6·33	5	6·30	10	6·39	10
	5·99	3	5·79	2	5·79	4	5·87	3
	5·47	10	5·44	10	5·45	7	5·37	5
	4·12	10	4·51	5	4·53	10	4·57	10
	3·82	7	4·11	9	4·10	5	4·04	6
	3·59	1	3·83	5	3·93	6	3·84	1
	3·47	6	3·60	4	3·82	5	3·68	6
	3·26	5	3·48	7	3·62	6	3·53	7
	3·10	3	3·37	2	3·49	7	3·35	2
	3·00	5	3·25	4	3·37	4	3·18	2
	2·85	1	3·08	3	3·27	1	3·02	3
	2·69	5	2·98	4	3·14	3	2·92	1
	2·57	1	2·80	3	2·98	5	2·81	4
	2·49	2	2·68	4	2·87	2	2·68	1
	2·33	3	2·57	2	2·81	4	2·55	1
	2·27	1	2·49	1	2·66	1	2·45	1
	2·14	1	2·39	2	2·58	2	2·37	1
	2·10	1	2·33	3	2·49	1	2·28	1
	2·01	2	2·26	2	2·40	3	2·10	3
	1·92	2	2·15	1	2·34	2	2·03	1
	1·83	2	2·10	3	2·27	2	1·97	2
	1·72	1	2·02	2	2·14	1	1·90	1
	1·63	1	1·96	1	2·11	3	1·85	1
			1·91	2	2·02	1	1·83	2
			1·81	2	1·96	2		
					1·90	2		
					1·85	1		
					1·83	2		
					1·80	2		

lack of diffraction data at Bragg angles greater than about $\theta = 26°$.

Single crystals of composition close to, but on either side of, the transition composition enabled single-crystal data to be measured. These results, included in Table 1, confirm the sudden change in crystal structure, already noted, as the diphenyl sulphoxide composition is increased from 88 to 92% by weight. At the transition composition, the volume of the unit cell is a maximum, and the density of the solid solution is a minimum. It is of interest that the density at the transition is lower than that of either pure component.

Discussion

The foregoing observations indicate that at a composition of about 90% diphenyl sulphoxide 10% diphenyl sulphone, the crystal structure remains that of pure diphenyl sulphone in which nine molecules in every ten possess an electron pair in the space normally occupied by an oxygen atom of the sulphone group. Since either of the two sulphone group oxygen atoms may be replaced by an unshared pair of electrons, the structures of the solid solutions will be disordered. It is possible that single crystals in this system may possess interesting electrical properties, as a covalent analogue of an ionic crystal with ion vacancies present.

Experimental

The materials used were Eastman Kodak Company, Rochester, U.S.A., diphenyl sulphoxide and British Drug Houses Ltd, London, diphenyl sulphone. The diphenyl sulphone was recrystallized from methanol and the single crystals of intermediate composition from 60–80 petroleum ether. The powders of intermediate composition were prepared by melting the components together for about 90 sec., followed by cooling with stirring and grinding to pass an 80 mesh sieve. The intensities in Table 2 were estimated visually.

The single-crystal photographs were recorded using a precession camera, with Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation, the powder patterns were recorded with a Philips 114·59 mm. powder camera and Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation.

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