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X-ray Diffraction Study of Mesomeric Plastic Phase of Sulfolane Whose Stability Domain Ranges Within 15.45 and 28.45 C

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The presence of rotational disorder in the plastic phase of sulfolane, stable within 15.45 and 28.45 C, has been demonstrated by X-ray diffraction techniques. Sulfolane forms hexagonal crystals with unit-cell parameters $a = b = 6.05(1)$, $c = 9.75(1)$ Å and two molecules per unit cell. The molecules are randomly oriented about the positions (1/3 2/3 1/4) and (2/3 1/3 3/4) giving rise to a hexagonal close-packed structure. By using a relatively coarse molecular model the experimental diffraction amplitudes are accounted for within an error of 16% by the assumption of a wholly random orientation. Data strongly substantiate the conclusions arising from previous thermodynamic studies.

INTRODUCTION

As already pointed out by one of us[1] sulfolane (tetramethilenesulfone) may be classed among "globular" molecules—substances which solid-

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ify in plastic crystals with a very low decrease of entropy (1.1 e.u. for sulfolane[2]) and undergo, on further cooling, one or more solid-solid transitions with a higher decrease of entropy (9.0 e.u. for sulfolane[2]).

The above thermodynamic properties suggest that on solidification these substances attain merely "positional order" while only at the lower-temperature transition do they gain "rotational order", possibly going through several states with a gradual reduction of disorder. In the mesophase (plastic crystal) the molecules, although positionally ordered in the crystal lattice, would either have several possible discrete orientations or continuously distributed random orientations. Energetically allowed molecular orientations would be among those for which the approximate symmetry elements of the molecule are aligned with the symmetry elements of the lattice.[3]

In the case of sulfolane the orientational disorder in the mesophase, whose stability domain ranges within 15.45 and 28.45 C, is also in keeping with the insensitivity to temperature of the electrical dipole moments calculated from dielectric constant measurements in a wide temperature range (15–80 C) including the mesophase domain.[4] The occurrence of isotropic rotation in the mesophase has been also inferred from wide-line n.m.r. studies.[5]

With the aim of gaining more information on the solid state disorder from the structural point of view we have undertaken X-ray diffraction studies on the crystalline phases of sulfolane. We present herewith the results of such studies carried out on the mesophase at room temperature.

EXPERIMENTAL

Liquid samples of highly purified and dehydrated sulfolane[1,2] were introduced at ~50 C under dry nitrogen atmosphere in glass capillaries for the Debye-Scherrer technique. After sealing, capillaries were let to cool down to room temperature. In one instance a single crystal of sulfolane grew up at one end of the liquid cylinder, as ascertained by recording an oscillating-crystal X-ray diffraction photograph. Subsequently the crystal was studied by using a Philips PW-1100 automated diffractometer with *Mo-Kα* radiation and graphite monochromator ($\lambda = 0.7107$ Å).

The crystal was found to belong to the hexagonal system, Laue group *6/mmm*, with lattice parameters $a = b = 6.05(1)$, $c = 9.74(1)$ Å. The space group resulting from the systematic absences and confirmed by the subsequent analysis was found to be $P6_3/mcc$. The crystallographic density calculated for two $C_4H_8SO_2$ molecules per unit-cell is 1.293 g cm^{-3} in excellent agreement with the experimental value 1.285 at 25 C.[6] Owing to the difficulty in achieving optical alignment of the crystal, diffraction intensities were measured in the whole reciprocal space, the diffraction angle being however confined to $2\vartheta = 27°$ as no appreciable diffracted beams were detected at higher angles. Owing to symmetry, of the 380 diffraction intensities so measured, only 27 were independent. Subsequent analysis was based on the average values within each group of symmetry-related intensities.

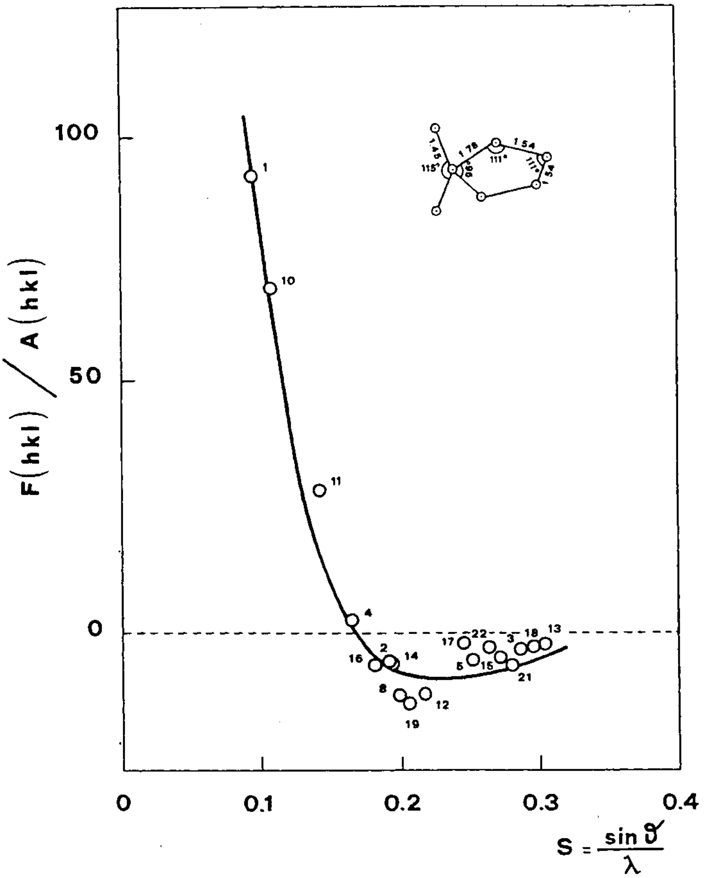

FIGURE 1 $|F(hkl)|/A(hkl)$ ratios vs. $s = \sin \vartheta/\lambda$ (circles). The numbers shown near to the circles correspond to the n values in Table 1. The full line shows the Φ function (see text). The adopted molecular model of C_{2v} symmetry is also indicated.

STRUCTURE ANALYSIS

The Patterson function evaluated from the measured structure factors shows a unique broad peak weighing 38% of the origin-peak and having coordinates (1/3 2/3 1/2) indicating that the centres of sulfolane molecules lie in the (1/3 2/3 1/4) and (2/3 1/3 3/4) positions. This implies an apparent molecular symmetry *at least* D_{3d} whereas the sulfolane molecule may reasonably be assumed to have C_2 symmetry (two-fold axis crossing S atom and the centre of the opposite C—C bond) or, at most, C_{2v} symmetry in the case of a planar five-atom ring. The presence of disorder in the molecular orientation is therefore certain.

In order to calculate the electron density function by Fourier transform of the diffraction pattern, we first attributed to the scattered waves the phase angles consistent with two point-atoms, centered in the above (1/3 2/3 1/4) and (2/3 1/3 3/4) positions. An almost spherical function with its maximum in the centre was obtained. This indication of a substantially spherical random orientation of sulfolane molecules was further investigated by examining the ratios between the structure factors $|F(hkl)|$ and the values $A(hkl) = \cos 2\pi(h/3 + 2k/3 + l/4) + \cos 2\pi(2h/3 + k/3 + 3l/4)$ representing the amplitudes of the scattered waves for a two point-atom structure. If the distribution of

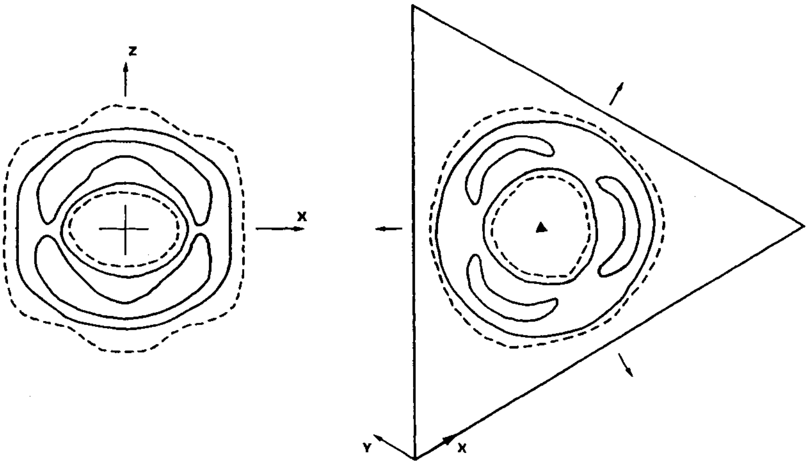

FIGURE 2 Sections of the 3-D electron density maps for sulfolane. *Left*: *x*-*z* section at $y = b/3$; *right*: *x*-*y* section at $z = c/4$. Contours are drawn at 1.2 (broken line), 1.3 and 1.4 electrons/Å.^{3}

TABLE I

Observed structure factors $F(hkl)$ for sulfolane in the mesophase stable at room temperature, in arbitrary units; values of $s = \sin \vartheta/\lambda$ in $Å^{-1}$; point-atom amplitudes $A(hkl)$ and $\Phi(s)$ values (see text). Δ are the differences $F - |kA\Phi|$ ($k = 12.9$ = empirical scale factor). Weak reflections are indicated with *w*. The agreement index $R = \Sigma|\Delta|/\Sigma F$ is 16%

n	*h*	*k*	*l*	$F(hkl)$	$s = \sin \vartheta/\lambda$	$A(hkl)$	$\Phi(s)$	Δ
1	1	0	0	273	.0954	1	21.42	−3
2	2	0	0	17	.1909	1	−.84	6
3	3	0	0	20	.2864	2	−.82	−1
4	1	1	0	16	.1652	2	1.06	−11
5	2	1	0	17	.2524	1	−1.07	3
6	2	2	0	*w*				
7	1	0	1	354	.1082	$\sqrt{3}$	15.83	0
8	2	0	1	64	.1978	$\sqrt{3}$	−1.07	40
9	2	1	1	10	.2577	$\sqrt{3}$	−1.02	13
10	0	0	2	489	.1025	2	18.24	18
11	1	0	2	86	.1403	1	5.42	16
12	2	0	2	36	.2168	1	−1.29	19
13	3	0	2	12	.3041	2	−.73	−7
14	1	1	2	38	.1946	2	−.98	13
15	2	1	2	14	.2726	1	−.91	2
16	1	0	3	32	.1811	$\sqrt{3}$	−.36	24
17	2	0	3	11	.2453	$\sqrt{3}$	−1.13	−14
18	2	1	3	16	.2958	$\sqrt{3}$	−.77	1
19	0	0	4	83	.2054	2	−1.22	51
20	1	0	4	*w*				
21	2	0	4	19	.2803	1	−.85	8
22	1	1	4	16	.2636	2	−.97	9
23	2	1	4	*w*				
24	1	0	5	24	.2739	$\sqrt{3}$	−.90	4
25	2	0	5	*w*				
26	0	0	6	17	.3080	2	−.71	1
27	1	0	6	7	.3224	1	−.61	1

disordered molecules is spherically symmetric, then the F/A ratios should be proportional to the absolute value of the function[7]:

$$\Phi(s) = \sum_j f_j \frac{\sin 4\pi s r_j}{4\pi s r_j} \qquad (s = \sin \vartheta/\lambda)$$

where r_j are the distances of each atom from the centre of rotation and f_j are the atomic scattering amplitudes inclusive of the thermal vibration contribution. A very coarse molecular model is sufficient for evaluating Φ, and we have based our check (see Figure 1) on a model, arbitrarily planar, mainly based on the geometry of $(CH_3)_2SO_2$[8]. In Figure 1 it is shown how, assuming a rotation centre at 1.12 Å from the S atom and a thermal isotropic parameter $U = 11.0$ Å^2, good agreement between F/A and Φ values is obtained.

It is also evident from Figure 1 that beyond the value $\sin \vartheta/\lambda = 0.17$ Å^{-1} Φ function actually changes sign so that the phase angles for all reflections beyond 0.17 Å^{-1} must be the opposite to those assumed above. The electron density function re-evaluated with the corrected phase angles again shows substantial spherical symmetry (see Figure 2) but the function has its maximum value near the surface at about 1.0 Å from the centre. Table I lists, for each measured diffraction intensity, F, A and Φ values and the differences $\Delta = F - |kA\Phi|$ (k = scale factor). The agreement index $R = \Sigma|\Delta|/\Sigma|F|$ for the illustrated fit is 0.16 ($k = 12.9$).

It is worth noting that the distance between the (1/3 2/3 1/4) and (2/3 1/3 3/4) points (5.99 Å) is almost equal to the lattice parameter *a* (6.05 Å) just as is the case of hexagonal close-packed structures (e.g. beryllium, sodium, cobalt, etc.[9]) with coordination number 12. Indeed the "quasi spherical shape" of disordered sulfolane molecules makes this circumstance quite natural.

CONCLUSIONS

Despite the coarseness of the molecular model used, the almost spherical disorder of sulfolane molecule in its mesophase is convincingly proved. It is hardly likely that this conclusion will be altered when the structure of the non-disordered form will be available.

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