

A X-RAY DIFFRACTION STUDY OF THE ADDUCT BETWEEN 1-TOSYLAZOCYCLOHEXENE AND MALEIC ANHYDRIDE

L. Caglioti

Istituto di Chimica Organica della Facoltà di Chimica Industriale
Università di Bologna, Italy

E. Foresti and L. Riva di Sanseverino

Istituto di Mineralogia e Petrografia - Università di Bologna, Italy

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The reaction between 1-tosylazocyclohexene and maleic anhydride in benzene solution gave white crystals of a compound(I) whose analysis gave the elementary composition $C_{17}H_{18}N_2O_5S$. Simultaneously with the chemical investigations (1) an X-ray diffraction study was undertaken: X-ray analysis was thought to be a particularly suitable technique, in view of the stereochemical problems. The attack to the structure solving by "direct methods" was successful at the run.

TABLE I - Statistics for normalized structures factors

Values of	Experimental	Theoretical for	
		Centrosymmetric	Non-centrosymmetric
$\langle E \rangle$	0.813	0.798	0.886
$\langle E^2 - 1 \rangle$	0.984	0.968	0.736
$\langle E^2 \rangle$	1.000	1.000	1.000
$E \geq 1$	26.9 %	32.0 %	36.8 %
$E \geq 2$	4.7 %	5.0 %	1.8 %
$E \geq 3$	0.7 %	0.3 %	0.01%

Crystal data

(I) $C_{17}H_{18}N_2O_5S$, monoclinic prismatic, M.W. 363, M.P. 162°, $a = 18.688$ (9), $b = 7.809$ (4), $c = 11.819$ (7) Å, $\beta = 97.85$ (5)°, $V = 1704$ Å³, (from h0l and hk0 Weissenberg photographs calibrated with Si powder), $P2_1/a$ from systematic extinctions, $Z = 4$, $d_{calc} = 1.41$ gr/cc.

By photographic methods ($\lambda = CuK$) 3250 reflections have been collected along c (0-10) and b (0-1) axes, and measured by visual comparison. A cross layer calculation and a Wilson plot served to reduce the independent data (2990) to the same scale. The programs used were those of the X-ray 63 system (2).

The three-dimensional Patterson synthesis gave coordinates for the sulphur atom ($R = 59\%$); the subsequent Fourier calculation produced most of the peaks in the section where the S was placed [$\bar{y} = 3/30$] a feature strikingly repeating the observed trend of a maxima in section 0 of the Patterson synthesis.

No constitution was assumed, and when 10 highest peaks were chosen, the agreement factor worsened (61%). Two maxima had the very reasonable distance 1.81 Å from S, but the angle formed was of about 180°.

Direct methods^(3a,3b) were then employed. The structure factors were ordered by decreasing value of $|E|$, on which some statistics were calculated (Table 1). \sum_2 relationships for 50 highest E's were listed, three reflections were chosen to fix the origin and three more were used as symbols.

An automatic procedure, using a program mainly developed by S. Motherwell (TANFIZ) for non-centrosymmetric substances, assigned phases to 237 of the 247 reflections used (with $E > 1.75$), on basis of a consistency index, a minimum value of the triple product ($1.25 \sqrt{N}$) and fixed threshold for the change of phase from the previous cycle (in this case equal to π).

TABLE 2 - Fractional positional and thermal parameters

	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>B</u>		<u>X</u>	<u>Y</u>	<u>Z</u>	<u>B</u>
S	0.4668	0.4020	0.7422	3.04	C13	0.3873	0.3823	0.6454	2.78
C1	0.5015	0.1844	0.7682	2.75	C14	0.3889	0.4172	0.5316	3.47
C2	0.5048	0.0947	0.6512	3.55	C15	0.3256	0.4054	0.4540	3.82
C3	0.5275	0.0948	0.6748	4.08	C16	0.2621	0.3566	0.4917	3.40
C4	0.6015	0.1056	0.7512	4.00	C17	0.2607	0.3179	0.6059	3.90
C5	0.5970	0.0137	0.8643	3.69	C18	0.3227	0.3274	0.6843	3.09
C6	0.5748	0.1798	0.8462	2.83	C19	0.1934	0.3450	0.4053	5.30
C7	0.5785	0.2855	0.9574	2.62	C20	0.6067	0.0831	1.1155	5.51
C8	0.6228	0.4402	0.9362	3.17	C21	0.6805	0.3064	1.1021	4.19
C9	0.6576	0.3930	0.8318	3.48	C22	0.7262	0.5617	1.0587	6.28
C10	0.6328	0.2629	0.7836	3.26	C23	0.4482	0.4651	0.8480	4.73
C11	0.6215	0.2049	1.0630	4.16	C24	0.5182	0.4990	0.6889	4.11
C12	0.6827	0.4451	1.0375	4.48	\bar{C}	0.0005	0.0012	0.0007	0.40

The first E map revealed the SO₂ group and rings A, B and C. It is worth noticing the low value of the ratio number of reflections used to number of atoms in the cell (2.37). A further cycle structure factor-Fourier including all observed reflections produced the rest of the structure.

The sulphur position corresponds to that found from the Patterson synthesis, but the two named peaks resulted in fact spurious. The SO₂ oxygens were really present in that first Fourier calculation, but much lower than the ten highest peaks.

Two cycles of full matrix least squares isotropic refinement reduced R from

26% to 15.3%. Atomic parameters are given in Table 2, distances and angles in figure 1, while the torsional angles in the rings are given in figure 2. A list of observed and calculated structure factors is available from the third author on request.

The position of the azo group was confirmed by both peak heights and the short N=N distance. Interatomic distances are normal within the standard deviation, evaluated as $\sigma = 0.007$ for S-O and as $\sigma = 0.013$ Å for other bonds. Some angles, e.g. the external ones at C1, C6, C7 and C11, are slightly higher, denoting steric hindrance. Their average standard deviation is $\sigma = 0.5^\circ$.

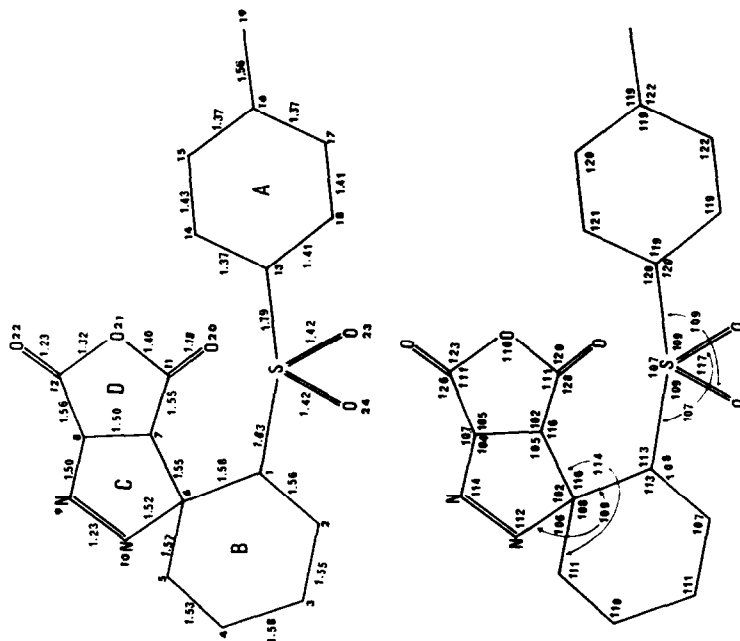


FIGURE 1 - Distances in Å and angles.

In ring D good agreement is found with results by Marsh et al.⁽⁴⁾ on maleic anhydride and by Ehremberg⁽⁵⁾ and Biagini and Cannas⁽⁶⁾ on succinic anhydride. The benzene plane contains also C19 and S. Geometrical calculations for rings C and D show that C7 is out of the plane formed by C6, N10, N9 and C8 of 0.23 Å, while ring D contains in its plane O20 and O22.

A noticeable compact packing, foreseen by the high value of the density, is demonstrated by 13 intermolecular distances less than 3.5 Å, and by 6 distances less than 3.2 Å without possibility for hydrogen bonds.

