

Structure of the *o*-Sulfobenzimidide (Saccharin)–*N,N*-Dimethyl-*p*-toluidine (1/1) Molecular Complex

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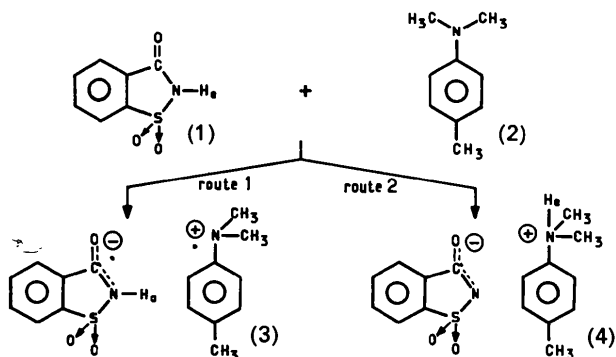
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Abstract. 1,2-Benzisothiazol-3(2*H*)-one 1,1-dioxide–*N,N*-dimethyl-*p*-toluidine (1/1), $C_7H_5NO_3S \cdot C_9H_{13}N$, $M_r = 318.4$, monoclinic $P2_1/c$, $a = 7.857(1)$, $b = 11.554(2)$, $c = 17.874(2)$ Å, $\beta = 92.59(1)^\circ$, $V = 1621.0$ Å³, $Z = 4$, $D_x = 1.304$ g cm⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54056$ Å, $\mu = 17.8$ cm⁻¹, $F(000) = 672$, $T = 295$ K, $R = 0.074$ for 2384 independent reflections with $I > 2\sigma(I)$. The structure contains an *N,N*-dimethyl-*p*-toluidinium *o*-sulfobenzimidate ion pair with a strong N(toluidinium)–H \cdots N(*o*-sulfobenzimidate) hydrogen bond. The dihedral angle between the ions is 41°.

Introduction. The possibility of initiating the free-radical polymerization of acrylic monomers by *o*-sulfobenzimidide (saccharin) (1)–*N,N*-dimethyl-*p*-toluidine (DMPT) (2) systems has been known for a long time (Lal, Green & Ellis, 1957). However, the mechanism of the initiation process is not understood; thus, no theoretical approach can definitely establish whether the interaction between (1) and (2) results in a charge-transfer complex (3) (route 1) or in the provisional formation of an amine salt (4) (route 2, involving the actual transfer of a proton).



In embarking upon a study of the free-radical polymerization mechanism of alkyl methacrylates,

we examined the behaviour of the (1)–(2) system (equimolecular amounts) in various solvents and noted that a solid crystallizes from concentrated solutions in acetone.

Since the crystals may be isolated, although they are sensitive to air degradation, we were prompted to study them by X-ray diffraction. Our aim was to determine the relative positions of the imide (1) and tertiary amine (2) in the crystal as well as to locate the amino proton H_a . As H_a should be closer to the imide part than to the amine if the charge-transfer complex (route 1) is involved, and closer to the amine moiety in the amine salt *via* route 2, it should be possible to establish the behaviour of (1)–(2) systems in concentrated solutions by solving the crystal structure.

Experimental. Crystals of the compound were prepared (with difficulty) by the vapor diffusion method. Single crystals were grown from microspots of 80 μ l containing 0.3 *M* saccharin in acetone, 0.4 *M* DMPT in ethanol and 10% 2-methyl-2,4-pentanediol (2-MPD) with equilibration to 80% acetone and 20% 2-MPD.

Unstable brown prismatic crystals appeared after two weeks. A crystal measuring 0.1 \times 0.2 \times 0.45 mm was mounted in a glass capillary and sealed with a droplet of mother liquid inside. Space group and preliminary unit-cell parameters determined from Weissenberg photographs. Accurate cell parameters obtained by least-squares refinement of the θ values of 25 reflections ($12 < \theta < 31^\circ$) measured on an Enraf–Nonius CAD-4 diffractometer. The intensity data were collected to $(\sin \theta / \lambda)_{\max} = 0.61$ Å⁻¹ using graphite-monochromated Cu $K\alpha$ radiation and an ω -2 θ scan technique (maximum scan time of 90 s per reflections). A total of 3239 measurements collected with $-9 < h < 9$; $0 < k < 14$; $0 < l < 21$; $\Delta\omega = (2 + 0.15 \tan \theta)^\circ$. Three reference reflections measured after every 3 h of X-ray exposure time; overall varia-

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors for non-H atoms ($\times 10^3$) with *e.s.d.*'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S(1)	384 (2)	2512 (1)	1674 (1)	46 (1)
N(2)	1500 (7)	3621 (4)	1439 (3)	47 (5)
C(3)	3157 (8)	3373 (5)	1471 (3)	42 (6)
C(4)	5161 (10)	1614 (6)	1787 (4)	50 (7)
C(5)	5193 (12)	446 (7)	1987 (4)	59 (8)
C(6)	3700 (12)	-153 (6)	2100 (4)	61 (8)
C(7)	2126 (11)	376 (6)	2038 (4)	56 (7)
C(8)	2104 (8)	1540 (5)	1830 (3)	41 (6)
C(9)	3579 (8)	2146 (5)	1710 (3)	38 (5)
O(11)	-703 (7)	2136 (4)	1052 (3)	62 (6)
O(13)	4306 (6)	4078 (4)	1320 (3)	53 (5)
O(21)	-472 (6)	2745 (5)	2361 (3)	70 (6)
C(30)	4398 (8)	6853 (5)	679 (3)	39 (6)
C(31)	5734 (9)	6773 (6)	1191 (4)	46 (6)
C(32)	7088 (9)	7558 (6)	1164 (4)	50 (7)
C(33)	7038 (9)	8423 (6)	623 (4)	49 (7)
C(34)	5680 (11)	8488 (6)	118 (4)	55 (7)
C(35)	4308 (10)	7717 (6)	133 (4)	49 (7)
N(40)	2982 (7)	6005 (4)	714 (3)	42 (5)
C(41)	2366 (12)	5553 (8)	-20 (5)	61 (9)
C(42)	1567 (13)	6468 (8)	1160 (7)	82 (12)
C(43)	8521 (14)	9258 (9)	563 (7)	79 (11)

tion in the sum of their intensities 5%. An empirical absorption correction was applied (North, Phillips & Mathews, 1968); the minimum and maximum correction factors used were 0.672 and 0.995 (minimum transmission 45.2%; maximum transmission 99.1%), 2471 reflections observed [$I > 2.0\sigma(I)$]. Structure determined by direct methods with *MITHRIL* (Gilmore, 1984). H atoms located in difference Fourier map. Full-matrix least-squares refinement [function minimized: $\sum w(F_o - F_c)^2$] with isotropic thermal parameters for H atoms, anisotropic parameters for other atoms, using *SHELX76* (Sheldrick, 1976). Final $R = 0.074$ and $wR = 0.08$ with $w = 1/[\sigma^2(F) + 0.019F^2]$ for 2384 unique observed reflections. Maximum Δ/σ in the final cycle refinement 0.2; maximum variations in the final difference Fourier map within $\pm 0.3 e \text{ \AA}^{-3}$. Atomic scattering factors were those incorporated in *SHELX*.

Discussion. The final atomic parameters are given in Table 1* and the bond lengths and angles in Table 2. The most significant feature of the structure (Fig. 1) is a transfer of an H ion from the *o*-sulfobenzamide N(2) atom to the N(40) atom of DMPT. The complex contains *o*-sulfobenzamide anions and *N,N*-dimethyl-*p*-toluidinium cations.

Saccharin (*o*-sulfobenzamide). The essential structural differences found in the complex when com-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52801 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Saccharin			
S(1)—N(2)	1.610 (3)	C(4)—C(5)	1.405 (5)
S(1)—C(8)	1.765 (3)	C(4)—C(9)	1.387 (4)
S(1)—O(11)	1.442 (3)	C(5)—C(6)	1.394 (6)
S(1)—O(21)	1.443 (3)	C(6)—C(7)	1.389 (5)
N(2)—C(3)	1.332 (4)	C(7)—C(8)	1.394 (4)
C(3)—C(9)	1.506 (4)	C(8)—C(9)	1.368 (4)
C(3)—O(13)	1.252 (4)	C(30)—C(31)	1.366 (4)
N(2)—S(1)—C(8)	97.0 (1)	C(5)—C(4)—C(9)	117.0 (3)
N(2)—S(1)—O(11)	111.2 (2)	C(4)—C(5)—C(6)	120.6 (3)
N(2)—S(1)—O(21)	110.9 (2)	C(5)—C(6)—C(7)	122.2 (3)
C(8)—S(1)—O(11)	110.6 (2)	C(6)—C(7)—C(8)	115.9 (3)
C(8)—S(1)—O(21)	110.9 (1)	S(1)—C(8)—C(7)	130.2 (3)
O(11)—S(1)—O(21)	114.8 (2)	S(1)—C(8)—C(9)	107.1 (2)
S(1)—N(2)—C(3)	111.3 (2)	C(7)—C(8)—C(9)	122.7 (3)
N(2)—C(3)—C(9)	113.9 (2)	C(3)—C(9)—C(4)	127.7 (3)
N(2)—C(3)—O(13)	124.4 (3)	C(3)—C(9)—C(8)	110.6 (3)
C(9)—C(3)—O(13)	121.6 (3)	C(4)—C(9)—C(8)	121.6 (3)
<i>N,N</i> -Dimethyl- <i>p</i> -toluidine			
C(30)—C(35)	1.391 (4)	C(33)—C(43)	1.508 (5)
C(30)—N(40)	1.482 (3)	C(34)—C(35)	1.380 (5)
C(31)—C(32)	1.395 (5)	N(40)—C(41)	1.473 (3)
C(32)—C(33)	1.388 (5)	N(40)—C(42)	1.481 (4)
C(33)—C(34)	1.388 (5)		
C(31)—C(30)—C(35)	121.5 (3)	C(34)—C(33)—C(43)	119.8 (3)
C(31)—C(30)—N(40)	118.4 (2)	C(33)—C(34)—C(35)	121.3 (3)
C(35)—C(30)—N(40)	120.1 (3)	C(34)—C(35)—C(30)	118.6 (3)
C(30)—C(31)—C(32)	119.2 (3)	C(30)—N(40)—C(41)	114.2 (2)
C(31)—C(32)—C(33)	120.6 (3)	C(30)—N(40)—C(42)	111.5 (3)
C(32)—C(33)—C(34)	118.8 (3)	C(41)—N(40)—C(42)	111.9 (3)
C(32)—C(33)—C(43)	122.4 (4)		

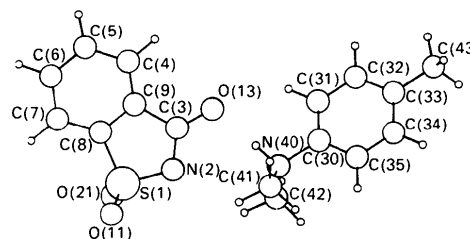


Fig. 1. Perspective view of the complex showing the atomic labelling scheme.

pared with the values observed in the free saccharin molecule (Okaya, 1969) are listed in Table 3. The saccharin part is anionic. The deprotonation of the imide N atom produces some minor changes in the dimensions of the *o*-sulfobenzamide group. We can point out a slight decrease in S(1)—N(2) ($\delta = 0.053 \text{ \AA}$), C(3)—N(2) ($\delta = 0.037 \text{ \AA}$) and a lengthening in C(3)—C(9) ($\delta = 0.032 \text{ \AA}$), C(3)—O(13) ($\delta = 0.038 \text{ \AA}$) with slight variations in the corresponding valence angles. The location of a negative charge N(2) induces a slight deformation in the five-membered ring.

***N,N*-Dimethyl-*p*-toluidine (DMPT).** The terminal amino group is protonated in the structure. The dimensions of the DMPT cation are normal and

Table 3. Structural differences between the complex and the individual molecule of saccharin

	Present structure	Free molecule
Bond distances (Å)		
S(1)—N(2)	1.610 (3)	1.663 (4)
N(2)—C(3)	1.332 (3)	1.369 (5)
C(3)—O(13)	1.252 (3)	1.214 (5)
C(3)—C(9)	1.506 (3)	1.474 (5)
Bond angles (°)		
C(8)—S(1)—N(2)	97.0 (3)	92.2 (6)
C(9)—C(3)—O(13)	121.6 (3)	126.5 (6)
S(1)—N(2)—C(3)	111.3 (3)	115.1 (6)
N(2)—C(3)—C(9)	113.9 (3)	109.6 (6)
Maximum displacement of saccharin ring (Å)	0.025 (4)	0.007 (5)

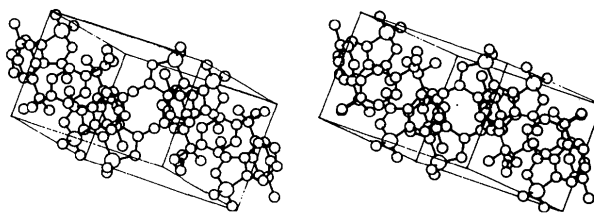


Fig. 2. Stereo packing diagram.

notes the crystal packing (Fig. 2). Molecules of the complex are linked together by weak van der Waals interactions.

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compare well with those found in *p*-toluidinium hydrochloride (Colapietro, Domenicano & Portalone, 1982) and in diisothiocyanatobis(*p*-toluidine)zinc (Caira & Nassimbeni, 1976). The dihedral angle between the two rings (saccharin and toluidine) is 41°.

Intermolecular bonding. The H atom on the toluidine amino group is directed toward the saccharin ketone oxygen, forming a strong hydrogen bond: O(13)⋯N(40) = 2.676 (3), O(13)⋯H(60) = 1.84 (6) Å and O(13)⋯H(60)—N(40) = 165 (6)°. This hydrogen bond between the anionic and cationic parts domi-

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Structure of Oxacycloheptane (Oxepane) at 105 K

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Abstract. C₆H₁₂O, *M_r* = 100.16, monoclinic, *C2/c*, *a* = 22.669 (8), *b* = 6.466 (4), *c* = 8.154 (6) Å, β = 92.11 (5)°, *V* = 1194.4 Å³, *Z* = 8, *D_x* = 1.114 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 0.79 cm⁻¹, *F*(000) = 448, *T* = 105 K, final *R*(*F*) = 0.085 for 1368 independent observed reflections. In the crystal the seven-membered ring adopts an approximate twist-chair conformation with the pseudo-twofold axis passing through C(2), so that a *C*-type twist-chair ring is present. The average C—O and C—C bond lengths are 1.429 (4) and 1.528 (4) Å. Application of the Cremer–Pople concept leads to the surprising result that the ring-puckering parameters of this conformation are intermediate between twist chair (TC) and twist boat (TB) in the pseudo-rotation circle.

Introduction. A series of crystal structure investigations on small unsubstituted cyclic ethers has so far resulted in the determination of the structures of ethylene oxide (Luger, Zaki, Buschmann & Rudert, 1986), oxetane (Luger & Buschmann, 1984), tetrahydrofuran (Luger & Buschmann, 1983) and dioxane (Buschmann, Müller & Luger, 1986) (ring sizes *n* = 3, 4, 5, 6). It was of interest to include the seven-membered ring oxacycloheptane, C₆H₁₂O, also called oxepane. In comparison with five- and six-membered rings the seven-membered ring should have a higher flexibility, so that one might expect any of a number of possible conformations to occur, including the chair (C), the boat (B), the twist chair (TC), the twist boat (TB) and intermediate forms (Bocian &