The present crystal structure determination thus suggests that the lack of the photoreaction in the solid state, despite the molecules *A*, *B* and (II) all being in the *cisoid* conformation, must be attributed to the overall unfavourable geometrical parameters.

The question at this point is whether the reactivity difference of benzoin alkyl ethers is primarily due to an entirely different conformation of the molecules in the solid benzoin alkyl ethers and in their cyclodextrin complexes. In the absence of detailed X-ray structure analyses of the complex under investigation, the best one could do at this stage is to make some reasonable hypotheses. In the crystals, the molecular motions are very restricted and reactions in the solid state tend to occur with a minimum of atomic and molecular movements (Schmidt, 1971). When molecules of (I) and (II) are complexed with cyclodextrin, the conformation of the molecules may be expected to be in the *cisoid* conformation. It seems reasonable to expect that in the complex the molecular traffic control is not as restrictive as in the crystals of the parent molecule.

The packing diagrams of the molecules (I) and (II) are illustrated in Figs. 4 and 5 respectively. The crystal structures of these molecules are mainly stabilized by van der Waals interactions.

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Structure of 2-Benzimidazolesulfonic Acid Monohydrate

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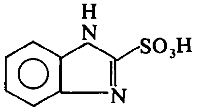
Abstract. $C_7H_6N_2O_3S.H_2O$, $M_r = 216$, monoclinic, $P2_1/n$, $a = 7{\cdot}064\,(2)$, $b = 15{\cdot}507\,(11)$, $c = 9{\cdot}084\,(4)$ Å, $\beta = 110{\cdot}22\,(3)°$, $V = 933{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}54$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}83$ mm^{-1}, $F(000) = 448$, $T = 296$ K, final $R = 0{\cdot}049$ for 1336 unique observed diffractometer data. The mean S—O distance of 1·439 (4) Å is close to the expected value for sulfonic acid structures. Equal bond distances are observed for the three S—O bonds and two C—N bonds indicating complete delocalization of charge over the molecule.

Introduction. 2-Benzimidazolethiol (I) is an important antioxidant used as a corrosion inhibitor, for example with copper (Chadwick & Hoshemi, 1979). Its oxidation products can vary depending on the conditions. The title compound (II) is obtained by using strong oxidants.



(II)

Experimental. Preparation: To 1·5 g (10 mmol) of (I) dissolved in 50 ml methanol, 0·8 g of sodium hydroxide dissolved in 5 ml water was added. To this 25 ml of

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *of non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\sum_{i=1}^{3} U_{ii}.$$

	x	y	z	$U_{\rm eq}$
S	0·0325 (1)	0·1489 (1)	0·0607 (1)	0·040 (1)
C(1)	0·1237 (5)	0·0924 (2)	0·2433 (4)	0·034 (2)
C(2)	0·2353 (5)	−0·0116 (2)	0·4175 (4)	0·037 (2)
C(3)	0·2128 (5)	0·0628 (2)	0·4948 (4)	0·037 (2)
C(4)	0·2560 (6)	0·0660 (3)	0·6578 (4)	0·049 (2)
C(5)	0·3261 (6)	−0·0124 (3)	0·7369 (5)	0·059 (2)
C(6)	0·3480 (6)	−0·0878 (3)	0·6581 (5)	0·054 (2)
C(7)	0·3042 (6)	−0·0891 (2)	0·4964 (5)	0·046 (2)
N(1)	0·1788 (4)	0·0100 (2)	0·2600 (3)	0·036 (1)
N(2)	0·1415 (4)	0·1265 (2)	0·3822 (4)	0·038 (1)
O(1)	−0·1585 (4)	0·1065 (2)	−0·0223 (3)	0·043 (1)
O(2)	0·1821 (5)	0·1315 (2)	−0·0098 (4)	0·068 (2)
O(3)	0·0124 (5)	0·2357 (2)	0·1047 (4)	0·064 (2)
O(4)	0·0269 (5)	0·2754 (2)	0·4840 (5)	0·067 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with their e.s.d.'s in parentheses*

S—C(1)	1·788 (4)	S—C(1)—N(1)	125·1 (2)
C(1)—N(1)	1·329 (5)	S—C(1)—N(2)	124·7 (3)
C(1)—N(2)	1·333 (5)	C(1)—N(1)—C(2)	104·5 (2)
N(1)—C(2)	1·387 (4)	C(1)—N(2)—C(3)	109·1 (3)
N(2)—C(3)	1·386 (5)	N(1)—C(2)—C(3)	106·2 (3)
C(2)—C(3)	1·388 (6)	N(2)—C(3)—C(2)	107·2 (3)
C(3)—C(4)	1·406 (6)	C(2)—C(3)—C(4)	122·8 (3)
C(4)—C(5)	1·412 (6)	C(3)—C(4)—C(5)	114·6 (3)
C(5)—C(6)	1·407 (7)	C(4)—C(5)—C(6)	122·5 (3)
C(6)—C(7)	1·393 (6)	C(5)—C(6)—C(7)	121·7 (3)
C(7)—C(2)	1·398 (5)	C(6)—C(7)—C(2)	116·1 (3)
S—O(1)	1·455 (3)	C(1)—S—O(1)	103·4 (2)
S—O(2)	1·438 (4)	C(1)—S—O(2)	103·7 (2)
S—O(3)	1·425 (4)	C(1)—S—O(3)	104·0 (2)
		O(1)—S—O(2)	112·1 (2)
		O(2)—S—O(3)	117·5 (2)
		O(3)—S—O(1)	114·1 (2)

200 m*M* H_2O_2 were added slowly with continuous stirring. As the reaction was highly exothermic, the reaction mixture was cooled over ice for 15 min and then evaporated to low volume. Acidification (HCl) gave a white precipitate, which was recrystallized from water. Analysis [found (calc.), %] C 38·79 (38·88), N 12·92 (12·96), S 14·89 (14·81), H 3·63 (3·70).

A crystal of size 0·55 × 0·20 × 0·15 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Lattice parameters were determined by least-squares refinement of θ values of 25 high-angle reflections between 15 and 19°. The intensity data were collected by ω–2θ-scan technique with scan interval $\Delta\omega = (0{\cdot}80 + 0{\cdot}35\tan\theta)°$ extended by 25% on both sides for background measurements. Two check reflections ($\bar{3}2\bar{4}$ and $\bar{4}53$) recorded at the end of every hour of data collection time showed no significant variation in intensity. 1861 reflections collected in the range $2 < \theta < 25°$ (h −8→8, k 0→18, l 0→10) yielded 1336 unique reflections with $I > 3\sigma(I)$ ($R_{\rm int}$ 0·01 after merging 102 reflections). No correction was made for absorption. The atomic scattering factors of non-H atoms (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965) and anomalous-scattering factors (Cromer & Liberman, 1970) were used in solving the structure. *SHELX76* direct-method procedure gave all 14 non-H atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the full-matrix least-squares refinement using *SHELX76* (Sheldrick, 1976). All non-H atoms refined anisotropically. All but the H atoms attached to the water O appeared in difference Fourier maps and were refined isotropically. Final difference Fourier map was featureless. One peak (1·3 e Å^{-3}) which appeared in the final Fourier map was rejected as it appeared inside the five-membered ring and was chemically meaningless. Maximum shift/e.s.d. observed in final refinement cycle is 0·399. Convergence was reached at $R = 0{\cdot}049$ and $wR = 0{\cdot}059$ {where the weighting scheme $w = 1/[\sigma^2(F_o) + 0{\cdot}0599|F_o|^2]$}. The final positions of non-H atoms are given in Table 1.* Bond lengths and bond angles are given in Table 2. Figs. 1 and 2 depict the molecule and the packing of the

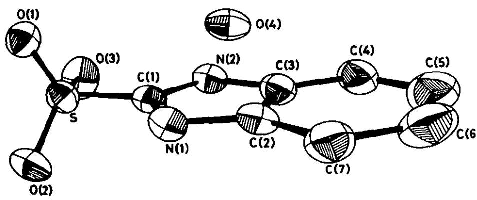

Fig. 1. Perspective view of the molecule.

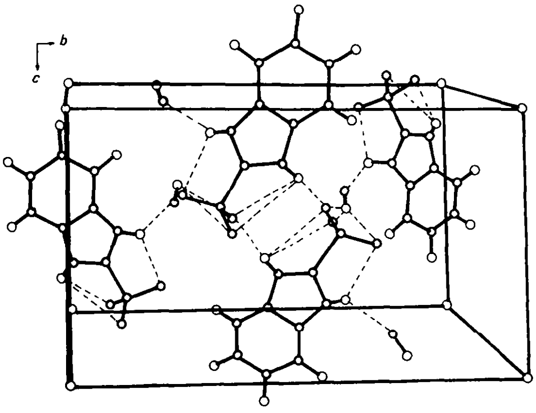

Fig. 2. Molecular packing in the unit cell of the molecule viewed down the *a* axis.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H, least-squares-planes' details and intramolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44692 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecule in the unit cell, respectively, and were drawn using *ORTEP* (Johnson, 1965).

Discussion. The mean S—O distance of 1·439 (4) Å observed in this structure is close to the average value of 1·45 Å in the structures of metanilic acid (3-aminobenzenesulfonic acid) (Hall & Maslen, 1965), sulfanilic acid (Rae & Maslen, 1962), 2,5-dibromobenzenesulfonic acid and 2,5-dichlorobenzenesulfonic acid (Lundgren & Lundin, 1972). Equal S—O bond distances indicate that the negative charge on the SO_3^- group is delocalized over all the O atoms. The N(1)—C(1) and N(2)—C(1) bond distances, 1·329 (5) and 1·333 (5) Å, indicate delocalization of the positive charge over both N atoms. Like many RSO$_3$H structures the molecule is present as a zwitterion, which is reflected in the high melting point ($\geq$653 K) of this compound. All the C—C bond distances and angles are normal.

The N and O atoms have short intra- and intermolecular contacts [O(4)···N(2) 2·71, O(1)···O(4′) 2·89, O(2)···O(4′) 2·85, O(3)···O(4′) 3·22, O(1)···N(1′) 2·78 Å]* possibly through hydrogen bonding, but the corresponding H atoms did not appear in the final difference Fourier maps. The water molecule plays an interesting role in this structure with the water O atom linked to one N of the RSO$_3$ moiety and the three O atoms of another RSO$_3$ moiety.

The X-ray photoelectron spectrum of the title compound was taken in the sulfur region. It showed a single $S(2p_{3/2})$ peak at 168·7 eV. This value is characteristic of sulfonic-type sulfur and is in keeping with the crystal-structure analysis. By way of comparison the $S(2p_{3/2})$ peak of (I) and its disulfide oxidation product were found at 163·0 and 164·7 eV respectively. These latter two values are in keeping with literature data (Yoshida, 1980; Chadwick & Hoshemi, 1979).

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* A prime indicates a symmetry-related atom.

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Polymorph IV of 4-Amino-*N*-2-pyridinylbenzenesulfonamide (Sulfapyridine)

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Abstract. $C_{11}H_{11}N_3O_2S$, $M_r = 249{\cdot}3$, monoclinic, $P2_1/c$, $a = 13{\cdot}56\ (4)$, $b = 6{\cdot}48\ (1)$, $c = 14{\cdot}12\ (3)$ Å, $\beta = 113{\cdot}7\ (1)°$, $V = 1136{\cdot}4\ (44)$ Å^3, $Z = 4$, $D_x = 1{\cdot}457$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 2{\cdot}29$ cm^{-1}, $F(000) = 520$, $T = 291$ K, final $R = 0{\cdot}085$ for 1287 independent observed reflections. Sulfapyridine is a sulfonamide drug with antibacterial, antithyroid and antidiabetic properties. The molecule exhibits the same conformation as in all except one of the polymorphs previously studied, despite a hydrogen-bonded packing mode which differs from that observed in the three earlier reported polymorphs. Form IV exhibits three hydrogen bonds of the type N···N = 2·91 (1) Å and N···O = 3·007 (7) and 3·076 (7) Å.

Introduction. Polymorphism is a widespread phenomenon among pharmaceutically important compounds (Kuhnert-Brandstatter, 1971; Haleblian & McCrone, 1969) and numerous examples of polymorphism have been reported for the sulfonamides (Yang & Guillory, 1972, and references therein). An important member of this class of drugs is sulfapyridine (SP) for which the structures of three polymorphs were recently reported (Basak, Mazumdar & Chaudhuri, 1984; Bar & Bernstein, 1985). This compound exhibits conformational polymorphism (Bernstein & Hagler, 1978), indicating that the crystal lattice plays a role in determining the molecular conformation observed in the crystal. While Yang & Guillory (1972) reported

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