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-dibromo-benzenesulfonic 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_3H structures the molecule is present as a zwitterion, which is reflected in the high melting point (≥ 653 K) of this compound. All the C—C bond distances and angles are normal.

The N and O atoms have short intra- and inter-molecular 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

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* A prime indicates a symmetry-related atom.

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

BY J. BERNSTEIN

Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

Abstract. $C_{11}H_{11}N_3O_2S$, $M_r = 249·3$, monoclinic, $P2_1/c$, $a = 13·56$ (4), $b = 6·48$ (1), $c = 14·12$ (3) Å, $\beta = 113·7$ (1)°, $V = 1136·4$ (44) Å^3, $Z = 4$, $D_x = 1·457$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·70926$ Å, $\mu = 2·29$ cm^{-1}, $F(000) = 520$, $T = 291$ K, final $R = 0·085$ 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

identifying six polymorphs of SP we were initially successful in obtaining only three forms (II, III and V) on which we reported earlier. Subsequent crystallization experiments yielded polymorph IV whose structure is described here.

Experimental. Single crystals were obtained by crystallization of a commercial sample of SP (Cyanamid) by slow evaporation from n-butanol, as described by Yang & Guillory (1972). Chunky colorless crystals, approximately 0·3 mm in all directions. Syntex $P\bar{1}$ diffractometer with graphite monochromator, cell dimensions refined by least-squares fit of 2θ values on 28 reflections ($5 < 2\theta < 20°$); intensities of 1643 unique reflections, $\omega/2\theta$ scans ($2\theta < 50°$); three reflections ($0\bar{1}1$, $\bar{1}02$ and $\bar{3}02$) monitored every 60 reflections during data collection indicated no crystal deterioration; intensities were corrected for Lorentz and polarization effects, but not for absorption; 1285 reflections considered as observed [$I > 3\sigma(I)$]. The structure was solved with $SHELX76$ (Sheldrick, 1976); least-squares refinement with anisotropic thermal parameters and scattering factors from Cromer & Waber (1974) for S, O, N, and C; minimization of $\sum w(|F_o| - |F_c|)$ with $w = 1$ converged at $R = 0·095$; at this stage all of the hydrogens were located on successive difference maps and included in the refinement with scattering factor from Cromer & Waber (1974), isotropic thermal parameters and a weighting scheme of $w = 0·721/[\sigma^2(F) + 0·0162F^2]$; 199 parameters, final $R = 0·085$, $wR = 0·093$; $(\Delta/\sigma)_{max} = 0·1$ for non-hydrogen atoms, 0·7 (one value) for hydrogen atoms; residual $\Delta\rho$ densities in difference map 0·7 and $-0·45$ e Å^{-3}.

Discussion. Atomic parameters are listed in Table 1.* The ORTEP diagram (Johnson, 1976) showing the atomic numbering is given in Fig. 1. Bond lengths and bond angles are presented in Table 2. These geometric features do not vary significantly from those reported earlier for three other polymorphs (Bar & Bernstein, 1985). The positive location of the H atom on the pyridine nitrogen N(3) and the geometric features in the vicinity of that atom indicate that this structure contains the imide form of the molecule as in the earlier structures, rather than the amide form.

imide

amide

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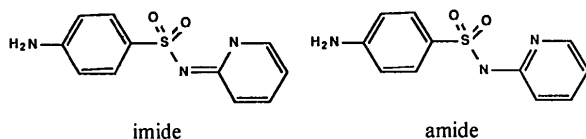
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44725 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and* U_{eq} ($\times 10^3$) *for form* IV *of SP*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
S	2415 (1)	3612 (2)	4286 (1)	42 (1)
O(1)	2100 (3)	1521 (7)	4045 (3)	51 (2)
O(2)	2150 (3)	5055 (7)	3458 (3)	53 (2)
N(1)	3718 (3)	3805 (8)	4870 (4)	46 (2)
N(2)	0706 (5)	6439 (14)	7327 (5)	58 (3)
N(3)	5425 (3)	2678 (8)	5835 (3)	44 (2)
C(1)	1857 (4)	4479 (9)	5149 (4)	42 (2)
C(2)	1952 (5)	6507 (10)	5445 (4)	50 (3)
C(3)	1574 (5)	7172 (11)	6162 (5)	50 (3)
C(4)	1088 (4)	5771 (10)	6617 (4)	39 (2)
C(5)	0971 (5)	3741 (10)	6285 (5)	54 (3)
C(6)	1347 (4)	3073 (9)	5560 (4)	47 (2)
C(7)	4357 (4)	2403 (8)	5570 (3)	37 (2)
C(8)	6153 (4)	1360 (10)	6490 (5)	50 (3)
C(9)	5868 (5)	−0276 (10)	6911 (4)	53 (3)
C(10)	4746 (5)	−0543 (10)	6680 (5)	53 (3)
C(11)	4011 (4)	0766 (10)	6008 (4)	46 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *for form* IV *of SP and hydrogen-bond geometry* (Å,°)

S—O(1)	1·412 (5)	C(4)—C(5)	1·383 (9)
S—C(1)	1·764 (7)	N(3)—C(8)	1·352 (7)
C(1)—C(2)	1·370 (9)	C(9)—C(10)	1·430 (9)
C(3)—C(4)	1·416 (10)	S—N(1)	1·628 (4)
N(3)—C(7)	1·354 (7)	N(2)—C(4)	1·371 (10)
C(8)—C(9)	1·354 (10)	C(2)—C(3)	1·374 (10)
S—O(2)	1·425 (5)	C(5)—C(6)	1·384 (11)
N(1)—C(7)	1·365 (6)	C(7)—C(11)	1·400 (9)
C(1)—C(6)	1·400 (9)	C(10)—C(11)	1·361 (8)

O(1)—S—O(2)	118·5 (2)	O(1)—S—N(1)	110·8 (3)
O(1)—S—C(1)	107·3 (3)	O(2)—S—N(1)	103·4 (3)
O(2)—S—C(1)	108·7 (3)	N(1)—S—C(1)	107·6 (3)
S—N(1)—C(7)	124·1 (4)	S—C(1)—C(2)	120·1 (5)
S—C(1)—C(6)	119·9 (5)	C(2)—C(1)—C(6)	119·9 (6)
C(1)—C(2)—C(3)	120·5 (7)	C(2)—C(3)—C(4)	120·7 (6)
N(2)—C(4)—C(3)	120·6 (7)	N(2)—C(4)—C(5)	121·5 (7)
C(3)—C(4)—C(5)	117·8 (6)	C(4)—C(5)—C(6)	121·4 (6)
C(1)—C(6)—C(5)	119·5 (6)	C(7)—N(3)—C(8)	120·9 (5)
C(8)—C(9)—C(10)	117·5 (5)	C(9)—C(10)—C(11)	120·0 (6)
C(7)—C(11)—C(10)	119·8 (5)		

	N—H	H···N/O	N···N/O	N–H···N/O
N(3)—H(N3)···N(1^i)	1·26 (11)	1·97 (10)	2·91 (1)	127 (5)
N(2)—H(N2A)···O(2^{ii})	0·79 (9)	2·23 (9)	3·007 (7)	169 (8)
N(2)—H(N2B)···O(1^{iii})	0·74 (8)	2·51 (8)	3·076 (7)	143 (6)

Equivalent positions: (i) $1-x$, $1-y$, $1-z$; (ii) x, $\tfrac{1}{2}-y$, $\tfrac{1}{2}+z$; (iii) x, $\tfrac{1}{2}-y$, $\tfrac{1}{2}+z$.
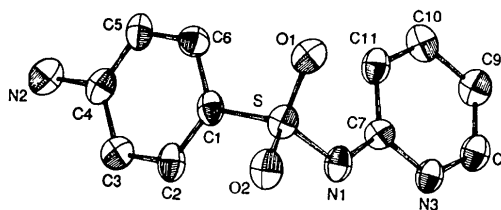

Fig. 1. ORTEP drawing (Johnson, 1976) of the molecule, showing atomic numbering.

The packing diagram is shown in Fig. 2. The distinguishing feature of the sulfapyridine system, and others which have multiple hydrogen-bond donors and acceptors, is the variety of ways these hydrogen bonds
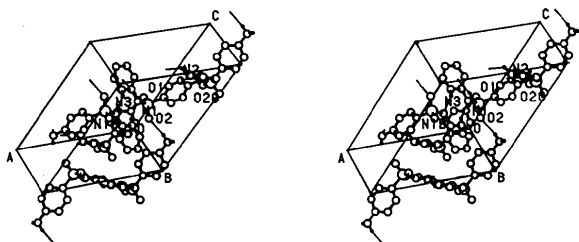
Fig. 2. Packing diagram of SP IV, showing the hydrogen bonds. For clarity only N and O are labeled, and only the hydrogens on N(1) and N(3) have been included.

may be formed, thus leading to the proliferation of polymorphic structures. The hydrogen-bonding motifs of polymorphs II, III and V have been discussed earlier in considerable detail. One of the features which distinguish the current structure is a pair of hydrogen bonds of the type N(3)—H(N3)···N(1) forming a cyclic system about a center of symmetry (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in Fig. 2). This type of hydrogen bonding was found previously only in form V, but in that case the cyclic system is based on the two crystallographically independent molecules in the asymmetric unit. In forms II and III there is an interaction involving parallel plane-to-plane contact of neighboring molecules. For form II the pyridine rings exhibit this mode, while in form III the aniline rings are in this arrangement. No such interaction exists in form IV reported here.

The hydrogen bonding of the anilino hydrogens also differs considerably among the four forms. In both forms II and V one of these H atoms is hydrogen bonded to O(2) of the sulfone, in both cases with symmetry-related molecules. In form III the anilino hydrogen interacts with N(1) rather than an oxygen. In the present structure one of the anilino hydrogens forms a hydrogen bond with O(2) of the sulfone, leading to the formation of chains along the c axis. These chains are in turn linked by the cyclic hydrogen-bonding pattern noted above. The second anilino H atom forms a hydrogen bond with O(1) of a second sulfone moiety (Table 2).

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Structure Cristalline de la L-Glycyl-L-leucyl-L-phenylalanine Hémihydraté

PAR JEAN DELETTRÉ, JEAN BERTHOU ET ALAIN LIFCHITZ

Laboratoire de Minéralogie et Cristallographie (LA CNRS n° 09), Université Pierre et Marie Curie, 75231 Paris CEDEX 05, France

ET PIERRE JOLLÈS

Laboratoire des Protéines (UA CNRS n° 1188), Université Paris V, 45 rue des Saints Pères, 75270 Paris CEDEX 06, France

Abstract. $C_{17}H_{25}N_3O_4.\frac{1}{2}H_2O$, $M_r = 344.4$, monoclinic, $B2$, $a = 18.299$ (6), $b = 18.781$ (6), $c = 5.917$ (3) Å, $\gamma = 110.65$ (3)°, $V = 1902.9$ (10) Å^3, $Z = 4$, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 0.73$ mm^{-1}, $F(000) = 740$, $D_x = 1.202$ Mg m^{-3}, room temperature, final $R = 0.048$ and $wR = 0.048$ for all (1470) reflections. The molecules are stacked in layers along the a axis. There are five intermolecular hydrogen bonds.