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Acta Cryst. (1971). **B27**, 326

The Crystal Structure of Sulphathiazole II

BY G. J. KRUGER AND G. GAFNER

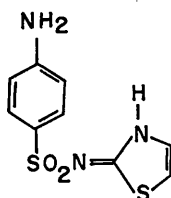
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(Received 13 March 1970)

Crystallographic data for the three known polymorphs of sulphathiazole, $\text{NH}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{-N=C}_3\text{SNH}_3$, are reported. A three-dimensional structure analysis of polymorph II has been carried out using diffractometer data and Mo $K\alpha$ radiation. The crystals are monoclinic, space group $P2_1/c$, with $a=8.235\ 0.004$, $b=8.550\pm 0.004$, $c=15.558\pm 0.008\ \text{\AA}$, $\beta=93.67\pm 0.01^\circ$ and $Z=4$. The structure was solved by Patterson methods and hydrogen atom positions were found from a three-dimensional difference synthesis. Refinement by least-squares methods resulted in a final R value of 0.038 excluding unobserved reflexions. The molecule exists in the imide tautomeric form. Molecules are linked together by $\text{NH}\cdots\text{N}$ and $\text{NH}\cdots\text{OS}$ hydrogen bonds.

Introduction

In spite of the increased use of antibiotics, the sulphonamides remain of importance in the treatment of certain infections. The relationship between their chemical structures and pharmacological activities has been under investigation since their introduction into chemo-therapy but has still not been completely elucidated (Seydel, 1968).



Sulphathiazole (N' -2-thiazolylsulphanilamide) is one of the most potent sulphonamides and is a typical example of this family of bacteriostatic drugs. It occurs in more than one crystalline modification and three polymorphs have been reported (Grove & Keenan, 1941; Miyazaki, 1947; Mesley & Houghton, 1967). These polymorphs have been named according to a number of different and confusing systems. The nomenclature used here is based on the melting beha-

viour of the different modifications and forms I, II and III correspond to forms B , A and C of Mesley & Houghton (1967). The crystal and molecular structure of polymorph II is reported here.

Experimental

Single crystals of polymorphs I and II were obtained by crystallization from a saturated n -propanol solution at 80°C and room temperature respectively. Polymorph III was crystallized by slow evaporation of a dilute ammonium hydroxide solution at room temperature. Melting of form III at $174\text{--}175^\circ$ was not always observed as a transition sometimes occurred at $173\text{--}175^\circ$, followed by melting at $200\text{--}202^\circ\text{C}$. Form II shows a similar transition and melting point. The powder diffraction pattern of form III crystals which behave in this way is the same as that reported by Higuchi, Bernado & Mehta (1967) for this form and it is clear that reversion to form II can take place during slow heating. Crystal densities were measured by the flotation method. The lattice parameters of the different crystals and the intensity data from form II were measured with a Hilger & Watts four-circle automatic diffractometer. Crystal data for the polymorphs of sulphathiazole are given in Table 1. The crystals

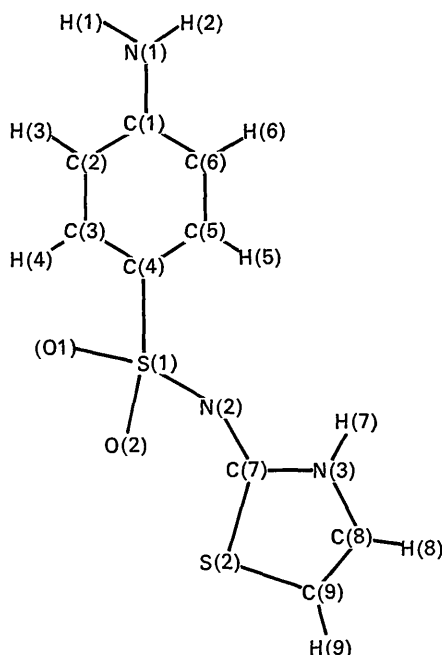


Fig. 1. The numbering of atoms in the sulphathiazole molecule.

of all three polymorphs belong to the monoclinic system and space group $P2_1/c$ is indicated in all three cases by the systematic absence of $h0l$ for l odd; $0k0$ for k odd.

Intensity data were collected using a crystal cut to a cubical shape with sides of length 0.2 mm. Zr-filtered Mo radiation was used and intensities were measured with the ω -scan method. Intensities of all reflexions with $2\theta \leq 60^\circ$ were measured. This corresponds to the limit of the Cu sphere. Background radiation was subtracted according to the background count at each scan limit and the dependence of background count on θ measured in this way agreed well with that obtained from measurements which were made at positions corresponding to systematic absences. Intensities were assumed to be unobservably weak if they were less than $2\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation in intensity as determined from counter statistics. These unobserved intensities

were given a value of $0.7\sigma(I)$. Of the 3203 independent reflexions measured, 1754 were observed according to this criterion. No absorption corrections were applied as $\mu R = 0.05$ and the corrections were thus trivial. All calculations were done on an IBM 360/65 computer.

Determination of the structure

The structure was determined by the heavy-atom method. The positions of the two sulphur atoms were deduced from a sharpened three-dimensional Patterson synthesis. The positions of the remaining fourteen non-hydrogen atoms were derived from a three-dimensional, sulphur-phased, Fourier synthesis.

The trial structure was refined by full-matrix least-squares procedures using the program *ORFLS* of Busing, Martin & Levy (1962). The quantity minimized is $w(|F_o| - k|F_c|)^2$. According to the suggestion by Dunning & Vand (1969), only the observed reflexions were used in the refinement of the structure.

After refinement of the positional and anisotropic thermal parameters a difference map was computed and this gave all the hydrogen atom positions. In subsequent refinement the hydrogen atoms were given the same thermal parameters as the atoms to which they were covalently bonded and these parameters were kept constant.

The weighting scheme proposed by Cruickshank (1965) was used [$w = (12 + |F_o| + 0.01|F_o|^2)^{-1}$] and refinement was terminated when none of the parameter shifts exceeded one tenth of the corresponding estimated standard deviations. The final R index was 0.038. A structure factor calculation of all the reflexions (unobserved included) showed no serious discrepancies. The observed and calculated structure factors of the observed reflexions are listed in Table 2.

The final atomic parameters are listed in Table 3(a) and (b) with the thermal parameters according to the expression

$$T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

The estimated standard deviations are given in brackets and refer to the least significant figures in the parameter values. The atoms are numbered according to Fig. 1.

Table 1. Crystal data for the polymorphs of sulphathiazole

Polymorph	I	II	III
Melting point ($^\circ\text{C}$)	200–202	200–202	173–175
Transition point ($^\circ\text{C}$)	–	173–175	–
Habit	elongated rods	hexagonal prisms	hexagonal plates
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (\AA)	10.554 (5)	8.235 (4)	17.570 (9)
b (\AA)	13.220 (7)	8.550 (4)	8.574 (4)
c (\AA)	17.050 (8)	15.558 (8)	15.583 (8)
β ($^\circ$)	108.06 (1)	93.67 (1)	112.93 (1)
Z	8	4	8
D_m (g.cm^{-3})	1.50	1.55	1.57
D_c (g.cm^{-3})	1.499	1.550	1.567

Table 3 (cont.)

(b) Thermal parameters with e.s.d.'s of the non-hydrogen atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.0086 (1)	0.0084 (1)	0.0030 (1)	0.0012 (1)	0.0013 (1)	-0.0001 (1)
S(2)	0.0263 (2)	0.0144 (1)	0.0034 (1)	-0.0041 (2)	0.0043 (1)	-0.0010 (1)
O(1)	0.0109 (3)	0.0109 (2)	0.0049 (1)	0.0007 (3)	0.0029 (2)	0.0012 (2)
O(2)	0.0129 (4)	0.0141 (4)	0.0037 (1)	0.0014 (3)	0.0007 (2)	0.0022 (2)
N(1)	0.0104 (4)	0.0106 (4)	0.0039 (1)	-0.0001 (3)	0.0009 (2)	-0.0008 (2)
N(2)	0.0121 (4)	0.0101 (4)	0.0031 (1)	0.0028 (3)	0.0015 (2)	0.0005 (2)
N(3)	0.0132 (4)	0.0100 (4)	0.0030 (1)	-0.0011 (3)	0.0001 (2)	-0.0006 (2)
C(1)	0.0104 (4)	0.0075 (3)	0.0030 (1)	0.0001 (3)	0.0011 (2)	0.0005 (2)
C(2)	0.0094 (4)	0.0091 (4)	0.0031 (1)	0.0010 (3)	0.0017 (2)	-0.0004 (2)
C(3)	0.0107 (4)	0.0094 (4)	0.0026 (1)	0.0011 (3)	0.0017 (2)	0.0000 (2)
C(4)	0.0094 (4)	0.0079 (4)	0.0025 (1)	0.0009 (3)	0.0015 (2)	0.0006 (2)
C(5)	0.0100 (4)	0.0107 (4)	0.0030 (1)	0.0017 (3)	0.0021 (2)	-0.0009 (2)
C(6)	0.0114 (5)	0.0103 (4)	0.0031 (1)	0.0010 (4)	0.0014 (2)	-0.0011 (2)
C(7)	0.0101 (4)	0.0105 (4)	0.0026 (1)	0.0012 (3)	0.0000 (2)	-0.0001 (2)
C(8)	0.0171 (6)	0.0129 (5)	0.0043 (2)	0.0005 (5)	0.0007 (3)	0.0024 (3)
C(9)	0.0277 (10)	0.0166 (7)	0.0048 (2)	0.0024 (7)	0.0047 (4)	0.0034 (3)

Table 4. Bond lengths and angles

The e.s.d.'s of bond lengths and angles involving hydrogen are 0.05 Å and 3° respectively.

N(1)-C(1)	1.401 (4) Å	N(1)-C(1)-C(2)	122.1 (3)°
C(1)-C(2)	1.396 (4)	N(1)-C(1)-C(6)	119.3 (3)
C(2)-C(3)	1.379 (4)	C(1)-C(2)-C(3)	120.5 (3)
C(3)-C(4)	1.391 (4)	C(2)-C(3)-C(4)	120.0 (3)
C(4)-C(5)	1.387 (4)	C(3)-C(4)-C(5)	119.8 (3)
C(5)-C(6)	1.368 (5)	C(4)-C(5)-C(6)	120.2 (3)
C(6)-C(1)	1.396 (4)	C(5)-C(6)-C(1)	121.0 (3)
C(4)-S(1)	1.759 (3)	C(6)-C(1)-C(2)	118.6 (3)
S(1)-O(1)	1.444 (2)	C(3)-C(4)-S(1)	121.0 (2)
S(1)-O(2)	1.435 (2)	C(5)-C(4)-S(1)	119.2 (2)
S(1)-N(2)	1.589 (3)	C(4)-S(1)-O(1)	107.4 (1)
N(2)-C(7)	1.312 (4)	C(4)-S(1)-O(2)	107.9 (1)
S(2)-C(7)	1.742 (3)	O(1)-S(1)-O(2)	116.6 (2)
C(7)-N(3)	1.332 (4)	N(2)-S(1)-O(1)	105.4 (1)
N(3)-C(8)	1.375 (4)	N(2)-S(1)-O(2)	114.1 (1)
C(8)-C(9)	1.315 (6)	N(2)-S(1)-C(4)	104.7 (1)
C(9)-S(2)	1.720 (5)	S(1)-N(2)-C(7)	119.8 (2)
N(1)-H(1)	0.88	N(2)-C(7)-S(2)	130.7 (2)
N(1)-H(2)	0.86	N(2)-C(7)-N(3)	120.5 (3)
C(2)-H(3)	0.93	C(7)-N(3)-C(8)	115.4 (3)
C(3)-H(4)	0.97	N(3)-C(8)-C(9)	113.6 (4)
C(5)-H(5)	0.93	C(8)-C(9)-S(2)	111.2 (3)
C(6)-H(6)	0.92	C(9)-S(2)-C(7)	91.1 (2)
N(3)-H(7)	0.87	S(2)-C(7)-N(3)	108.7 (2)
C(8)-H(8)	0.90		
C(9)-H(9)	0.88	H(1)-N(1)-C(1)	115
		H(2)-N(1)-C(1)	117
		H(3)-C(2)-C(1)	120
		H(4)-C(3)-C(4)	117
		H(5)-C(5)-C(4)	119
		H(6)-C(6)-C(1)	122
		H(7)-N(3)-C(7)	118
		H(8)-C(8)-N(3)	121
		H(9)-C(9)-C(8)	132

Smith, 1958). The C(2)-C(3) and C(5)-C(6) bonds are shortened to a mean value of 1.374 Å and the other bond correspondingly lengthened. Similar distortion of benzene rings in *p*-substituted anilines has been found in *p*-aminobenzoic acid (Lai & Marsh, 1967), β -sulphanilamide (O'Connell & Maslen, 1967) and *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). It can thus be accepted that this bond shortening in

sulphathiazole is real and that resonance forms of the quinoid type contribute significantly to the structure.

The equation of the least-squares plane through the six-membered ring was calculated with reference to the orthogonal coordinate system a , b , c^* as $0.152 X + 0.849 Y - 0.506 Z + 0.158 = 0$. The deviations of the atoms in the ring and those bonded to it from this plane are listed in Table 5(a). The deviations of the ring-atoms are very slight but the nitrogen and sulphur atoms are displaced quite markedly. Since the hydrogen atoms could not be located accurately, their deviations have little significance.

Table 5. Deviations of atoms from the best planes

(a) Deviations from the best plane through the six-membered ring

C(1)	0.008 Å	N(1)	-0.015 Å
C(2)	-0.004	S(1)	-0.019
C(3)	-0.001	H(3)	0.00
C(4)	0.001	H(4)	0.01
C(5)	0.003	H(5)	0.02
C(6)	-0.008	H(6)	-0.04

(b) Deviations from the best plane through atoms C(7), N(3), C(8) and C(9)

C(7)	0.001 Å	N(2)	-0.016 Å
N(3)	-0.001	H(7)	0.03
C(8)	0.001	H(8)	-0.05
C(9)	-0.001	H(9)	0.30
S(2)	-0.022		

The hydrogen atoms bonded to N(1) are not coplanar with the benzene ring, but conform to the distorted tetrahedral arrangement expected for the quasi- sp^3 -hybridized nitrogen atom. The N(1)-C(1) bond length of 1.401 Å is considerably shorter than the 1.472 ± 0.005 Å determined for 3-covalent nitrogen in paraffinic compounds (Sutton, 1965), but insignificantly longer than the 1.385 ± 0.026 Å found by O'Connell & Maslen (1967).

The atoms around the sulphamide sulphur atom S(1) are arranged in a slightly distorted tetrahedral configuration. The bonding distances to the sulphur atom are compared with equivalent bonds found in β -sulphanilamide (O'Connell & Maslen, 1967) and methanesulphonanilide (Klug, 1968) in Table 6. The lengthening of the S(1)–O(1) bond can be attributed to hydrogen bonding effects.

Table 6. Some bonding distances between carbon and tetrahedral sulphur

	β -Sulpha- nilamide	Methane- sulphonanilide	Sulpha- thiazole II
S(1)–O(1)	1.448 (2) Å	1.425 (2) Å	1.444 (2) Å
S(1)–O(2)	1.454 (2)	1.443 (2)	1.435 (2)
S(1)–N(2)	1.620 (2)	1.633 (2)	1.588 (3)
S(1)–C(4)	1.750 (2)	1.746 (2)	1.761 (3)

The five-membered ring is not planar as the sulphur atom S(2) is displaced significantly from the best plane through the other four atoms. The least-squares plane through atoms C(7), N(3), C(8) and C(9) was calculated in the orthogonal system a, b, c^* and has the equation $0.882 X + 0.126 Y + 0.455 Z + 2.167 = 0$. The displacements from this plane are listed in Table 5(b).

The non-aromaticity of the thiazole ring is demonstrated by the non-planarity of the ring and the localization of the C(8)–C(9) double bond. This bond has a length of 1.315 ± 0.006 Å which is fractionally, but not significantly, shorter than a normal C=C bond (1.335 ± 0.004 Å, Sutton, 1965).

The S–C bond lengths in the five-membered ring are of the same order as the lengths of similar bonds in other heterocyclic compounds, e.g. 1.728 and 1.762 ± 0.003 Å found by Smith (1969) in 5-anilino-3-

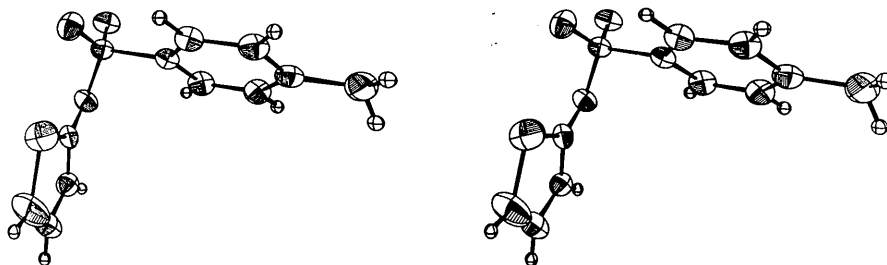


Fig. 2. A stereopair showing the molecular configuration of the sulphathiazole molecule and the thermal motion of the non-hydrogen atoms.

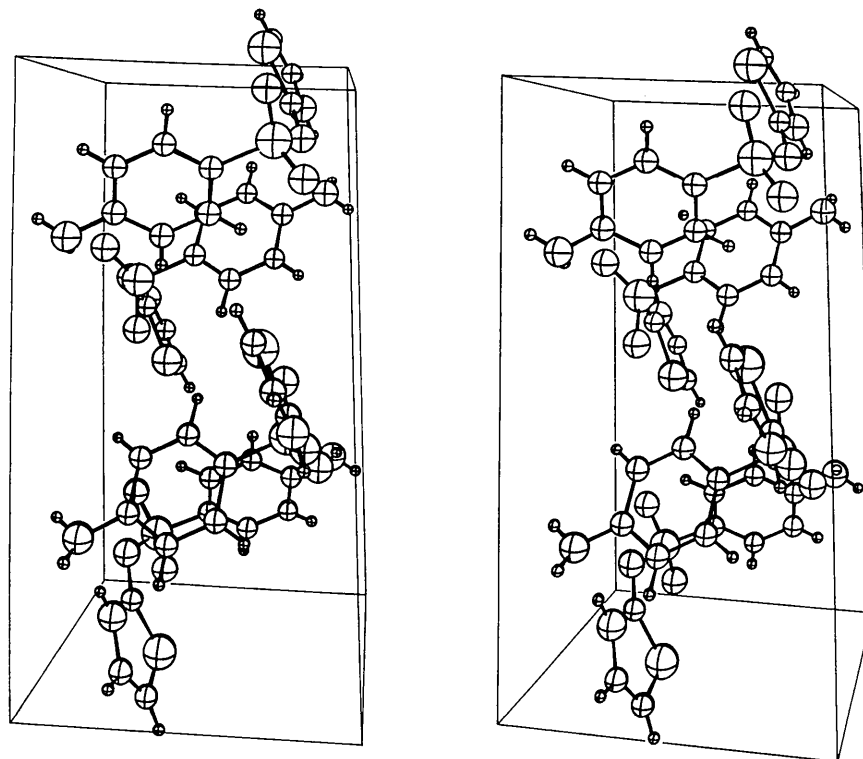


Fig. 3. A stereopair of the unit cell and its contents.

oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo [3,4-*d*] thiazole, and 1.759 ± 0.003 Å found by Allmann (1967) in 1,4-bis-(*N*-ethyl-1,2-dihydrobenzthiazol-2-ylidene)tetrazen.

The C(8)–N(3) bond length of 1.375 ± 0.004 Å agrees with the 1.371 ± 0.004 Å found by Allmann (1967) for heterocyclic C–N single bonds but the C(7)–N(3) bond distance of 1.332 ± 0.004 Å is much shorter. The C(7)–N(2) bond length of 1.312 ± 0.004 Å is longer than the values of 1.27 ± 0.02 Å found in dimethylglyoxime (Sutton, 1965), and 1.302 ± 0.004 Å in 1,4-bis-(*N*-ethyl-1,2-dihydrobenzthiazol-2-ylidene)tetrazen (Allmann, 1967). This lengthening is not statistically significant but when viewed in conjunction with the shortening of the single bond, suggests involvement of the lone pair of electrons on N(3) in a resonance system. This argument is given more weight by the shortening of the N(2)–S(1) bond whose length is 1.589 Å as compared with the 1.620 ± 0.016 Å in β -sulphanilamide (O'Connell & Maslen, 1967) and the 1.633 ± 0.002 Å in methane-sulfonanilide (Klug, 1968) suggesting the involvement of the $3d$ orbitals of S(1).

The molecular packing in crystals of sulphathiazole II is illustrated by the stereopair of the unit cell and its contents in Fig. 3 (Johnson, 1965). The view is along the *b* axis with the *a* axis across the page and the origin in the lower left hand corner of the unit cell nearest to the viewer.

Separate molecules are linked by means of hydrogen bonds to form infinite sheets of molecules parallel to the (001) plane. The hydrogen bonds which form are of the N–H...N and N–H...O types and are indicated in Fig. 4. The nitrogen atom N(1) is bonded to the O(1) oxygen atoms of two neighbouring molecules through the hydrogen atoms H(1) and H(2) attached to it, and to the nitrogen atom N(3) through H(7) which is attached to N(3). The oxygen atom O(1) is thus bonded to two different N(1) nitrogen atoms. Atoms N(2) and O(2) do not take part in any hydrogen bonding. The lengths of the N(1)–H(1)...O(1) and N(1)–H(2)...O(1) bonds are 2.999 and 3.027 Å respectively, while the length of the N(1)–H(7)–N(3) bond is 2.870 Å. These are normal values indicating fairly strong hydrogen bonding.

Except for the hydrogen bonds, all contacts between molecules are of the van der Waals type and fall within the expected range. Hydrogen bond distances and angles and other close intermolecular approaches are listed in Table 7(a) and (b) respectively.

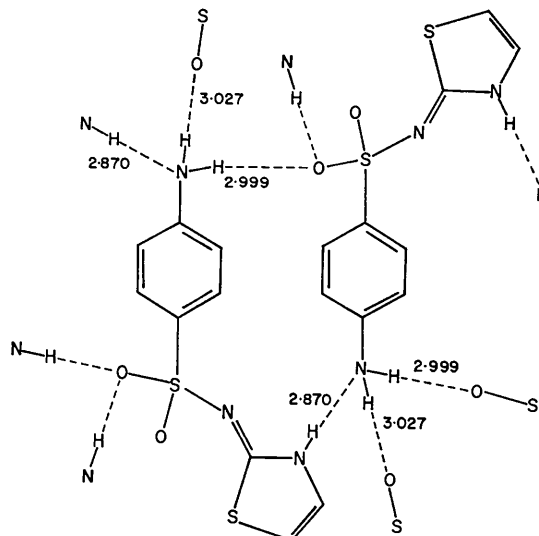


Fig. 4. The hydrogen bonding in sulphathiazole II.

Table 7 (cont.)

(b) Other close intermolecular approaches

O(1)···C(6)	3.381 Å
···C(1)	3.447
···C(2)	3.480
···H(3)	2.76
···H(6)	2.97
O(2)···H(8)	2.83
C(1)···N(3)	3.364
···O(1)	3.447
···H(7)	2.65
C(2)···O(1)	3.480
C(3)···H(4)	2.93
C(6)···O(1)	3.381
···N(3)	3.493
N(3)···C(1)	3.364
···C(6)	3.493

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Table 7. Intermolecular contact distances

(a) Hydrogen bond distances and angles

N(1)···N(3)	2.871 (4) Å	N(3)–H(7)···N(1)	168 (3)°
N(1)···H(7)	2.01 (5)	C(1)–N(1)···H(7)	100 (3)
O(1)···N(1)	2.999 (4)	N(1)–H(1)···O(1)	153 (3)
O(1)···H(1)	2.19 (5)	S(1)–O(1)···H(1)	128 (3)
O(1)···N(1)	3.027 (4)	N(1)–H(2)···O(1)	164 (3)
O(1)···H(2)	2.20 (5)	S(1)–O(1)···H(2)	122 (3)

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Acta Cryst. (1971). **B27**, 333

Glycolic Acid: Direct Neutron Diffraction Determination of Crystal Structure and Thermal Motion Analysis*

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(Received 23 February 1970)

Glycolic acid (hydroxyacetic acid) crystallizes in $P2_1/c$ with $a=8.9649$, $b=10.5634$, $c=7.8261$ Å, $\beta=115.083^\circ$, at $24 \pm 1^\circ\text{C}$, with $Z=8$. The structure was solved directly from single-crystal neutron diffraction data by the 'squared structure amplitude' method followed by symbolic addition and Fourier synthesis. The structure consists of a loose three-dimensional hydrogen-bonded network of two closely similar but crystallographically distinct types of molecules. Averaged interatomic distances corrected for thermal effects deduced from a rigid-body motion analysis are C-C=1.517, C-O(H) in -COOH=1.326, C=O=1.226, C-O(H) in -CH₂OH=1.420, C-H=1.116 Å. Averaged O-H distances, corrected with the 'riding model' formula, are 1.009 in the carboxyl and 0.993 Å in the α -hydroxyl groups. With the exception of the aliphatic and α -hydroxyl hydrogen atoms, each molecule is nearly planar. The structure explains the nearly orthorhombic symmetry of the electron spin resonance spectrum of irradiated glycolic acid.

Introduction

Glycolic acid (hydroxyacetic acid) is the simplest member of the α -hydroxycarboxylic acid series. Crystal structure studies have been carried out on relatively few members: the dicarboxylic acids tartronic (Van Eijck, Kanters & Kroon, 1965) (HOOC-CHOH-COOH), tartaric (Okaya, Stemple & Kay, 1966) (HOOC-CHOH-CHOH-COOH), and dihydroxyfumaric (Gupta & Gupta, 1968) (HOOC-COH=COH-COOH); the tricarboxylic acid citric (Johnson, 1966; Glusker, Minkin & Patterson, 1969) (HOOC-CH₂-COHCOOH-CH₂-COOH); and acid salts containing the bisglycolate ion (Golič & Speakman, 1965; Van der Helm, Glusker, Johnson, Minkin, Burow & Patterson, 1968) (HOOC-CH₂-CHCOO⁻-CHOH-COOH). Glycolic acid affords a favorable case for observation of the dimensions of

the >COHCOOH group, some of which seem rather variable from member to member: C-C from 1.502 to 1.544, C=O from 1.198 to 1.24, C-OH (carboxyl) from 1.28 to 1.319, C-OH (α -hydroxyl) from 1.39 to 1.426 Å.

A study (Atherton & Whiffen, 1960) of the electron spin resonance spectrum of γ -irradiated glycolic acid revealed an interesting pseudo-symmetry; the authors proposed an orientation in the crystal of the glycolyl radicals produced by irradiation, and by implication that of the parent molecules. The present study permits testing of the suggested orientation and provides an explanation of the pseudo-symmetry.

Some results of the present study have appeared in preliminary form (Levy & Ellison, 1967; Ellison & Levy, 1967, 1968).

Experimental

The space group of glycolic acid was determined to be $P2_1/c$ by Hughes & Small (see Atherton & Whiffen,

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.