

## The Zwitterion 2-Amino-3-hydroxypent-4-ynoic Acid

BY JOHAN COETZER

National Physical Research Laboratory, CSIR, Box 395, Pretoria 0001, South Africa

AND RAYMOND BARTHO,\* MICHAEL LAING† AND CHARLES M. WEEKS‡‡

University of Natal, Durban 4001, South Africa

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**Abstract.**  $C_5O_3NH_7$ ,  $HC\equiv C.CH(OH).CH(NH_3)^+ . CO_2^-$ , monoclinic,  $P2_1$ ;  $a = 8.090(5)$ ,  $b = 5.820(5)$ ,  $c = 6.145(5)$  Å,  $\beta = 95.2(1)^\circ$ ,  $V = 288$  Å<sup>3</sup>,  $D_c = 1.49$ ,  $D_m = 1.50(3)$  g cm<sup>-3</sup>,  $Z = 2$ .  $R = 0.0535$  for 300 observed and unobserved data, all atoms isotropic and H atoms included. The *relative* configurations are: *S* at C(2) and *R* at C(3). The  $CO_2^-$  is joined by a strong intramolecular hydrogen bond to the  $NH_3^+$ , while the molecules are linked together by a complex three-dimensional network of intermolecular hydrogen bonds.

**Introduction.** Crystals of this physiologically active amino acid were isolated from the fungus *Sclerotium rolfsii* by Dr N. Vermeulen and Mr H. Potgieter (Biochemistry Department, University of Pretoria). Their work did not lead to an unequivocal structure so a crystallographic study was undertaken at their request. Data were collected on a Philips four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å) for  $\theta$  between 3 and 20°. The  $\omega$ - $2\theta$  scan technique was used: scan width 1.2°, scan time 30 s and background counted for 30 s for each peak. Three reflexions were used as standards and their intensities were remeasured after every 60 reflexions; no decomposition was detectable. Of the 303 reflexions measured, 30 were classed as unobserved [ $I < 2.0\sigma(I)$ ] and 3 (010, 030, 050) were space-group extinctions. Lorentz and polarization corrections were applied; absorption corrections were considered to be unnecessary. A temperature-sharpened Patterson map gave the approximate orientation of the long axis of the molecule in the unit cell and this information was then used as a criterion for choosing the origin definers and ambiguities (Laing, 1976) for use in the *MULTAN* 74 system (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The truncation of the data at  $\theta = 20^\circ$ , together with the small number of reflexions and severely non-linear Wilson plot, caused the program

*NORMAL* to generate the unrealistic value of 0.34 Å<sup>2</sup> for *B*. A value of 2.0 Å<sup>2</sup> was therefore arbitrarily used for the generation of the *E*'s, yielding  $\langle |E^2| \rangle = 0.97$ ,  $\langle |E^2 - 1| \rangle = 0.72$ ,  $\langle |E| \rangle = 0.87$ . Table 1 lists the origin definers and other reflexions in the starting set. The correct solution had the best CFOM; two others had comparable values (Table 1). The nine-atom

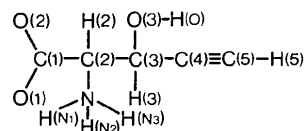


Fig. 1. Numbering system.

Table 1. *Starting set of reflexions*

The reflexion 201 was used as an origin definer because no other suitable  $h0l$  reflexion was available. The criterion was that the two  $h0l$  reflexions should be as close to orthogonal as possible: there was no reflexion with a negative  $l$  that had a large  $E$ .

(a) Origin-defining reflexions

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>
1	0	2	2.71
4	1	3	1.63
2	0	1	1.18

Reflexions whose phases were varied

1	5	1	2.20
5	0	0	2.01
1	1	-2	1.84
3	2	-4	1.72

(b) Results from *MULTAN*

	ABSFOM	PSIZERO ( $\times 10^{-4}$ )	RESID	CFOM
	1.23	0.232	25.7	2.29
	1.23	0.234	26.0	2.23
	1.23	0.238	25.5	2.20
Max.	1.33	0.264	39.9	
Min.	0.93	0.204	25.5	

\* Computer Centre.

† Chemistry Department.

‡ Visiting research fellow from The Medical Foundation of Buffalo, 73 High Street, Buffalo, NY, USA.

Table 2. Fractional atomic coordinates ( $\times 10^4$  for C, N and O;  $\times 10^3$  for H) and isotropic temperature factors

Estimated standard deviations in the last significant figure are given in parentheses; the  $y$  coordinate of O(3) was kept fixed; the parameters of the H atoms were not refined.

	$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )
C(1)	2549 (7)	6952 (13)	3944 (10)	2.34 (14)
C(2)	2150 (7)	4799 (12)	5189 (10)	1.90 (13)
C(3)	2232 (8)	5314 (13)	7616 (11)	2.42 (14)
C(4)	1938 (9)	3217 (13)	8851 (11)	3.15 (16)
C(5)	1755 (9)	1434 (19)	9807 (12)	4.51 (19)
O(1)	3684 (5)	6806 (9)	2677 (6)	2.40 (9)
O(2)	1730 (5)	8691 (9)	4321 (7)	2.60 (10)
O(3)	3856 (6)	6230	8210 (7)	3.07 (10)
N	3319 (6)	2916 (10)	4754 (8)	2.38 (11)
H(2)	95	425	475	3.0
H(3)	125	675	775	3.0
H(5)	150	0	1065	5.0
H(O)	375	640	1025	4.0
H(N1)	365	325	315	3.0
H(N2)	265	175	435	3.0
H(N3)	440	310	550	3.0

Table 3. Molecular geometry

(a) Bond lengths ( $\pm 0.01$ ) ( $\text{\AA}$ )

C(1)—O(1)	1.26	C(3)—C(4)	1.47
C(1)—O(2)	1.24	C(4)—C(5)	1.21
C(1)—C(2)	1.52	C(2)—N	1.49
C(2)—C(3)	1.52	C(3)—O(3)	1.43

(b) Bond angles ( $\pm 1$ ) ( $^\circ$ )

O(1)—C(1)—O(2)	127	C(3)—C(4)—C(5)	177
O(2)—C(1)—C(2)	116	C(1)—C(2)—N	111
O(1)—C(1)—C(2)	117	C(2)—C(3)—O(3)	106
C(1)—C(2)—C(3)	110	C(3)—C(2)—N	110
C(2)—C(3)—C(4)	111	C(4)—C(3)—O(3)	112

(c) Torsion angles ( $^\circ$ )

O(3)—C(3)—C(2)—N	66
N—C(2)—C(1)—O(1)	4

(d) Separations between atoms involved in hydrogen bonds ( $\text{\AA}$ )

O(1) $\cdots$ N <sup>i</sup>	2.63
O(3) $\cdots$ O(1 <sup>i</sup> ) (001)	2.78
O(2) $\cdots$ N <sup>i</sup> (010)	2.78
O(1) $\cdots$ N <sup>ii</sup> (101)	2.84

Equivalent positions

- (i)  $x, y, z$       (ii)  $-x, \frac{1}{2} + y, -z$

structure was refined isotropically by block-diagonal least-squares calculations to  $R = 0.075$ . A difference map clearly showed the positions of all the H atoms which, when included in the structure factor calculations, reduced  $R$  to 0.060. The parameters of only the heavy atoms were further refined, and  $R$  converged to 0.0535 for all 300 data. Weighting was proportional to  $1/\sigma(F)$ ; scattering factors were for neutral atoms

(International Tables for X-ray Crystallography, 1962). Final positional and thermal parameters are given in Table 2, bond lengths and angles in Table 3. Fig. 1 gives the numbering system.\*

**Discussion.** Fig. 2 is a projection of the structure down  $a$ , showing the hydrogen bonding in one sheet of molecules. Fig. 3, a Newman projection down C(2)—C(3), shows the torsion angles. The amino group is on C(2), the hydroxyl group on C(3): the relative configurations are  $S$  at C(2) and  $R$  at C(3). All bond lengths are normal; the C—O lengths in the  $\text{CO}_2^-$  moiety show that the compound is a zwitterion and this is confirmed by the three H atoms which were found to be attached to the N atom. O(1) of the  $\text{CO}_2^-$  group is joined by a strong hydrogen bond to the  $\text{NH}_3^+$  group:

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32776 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

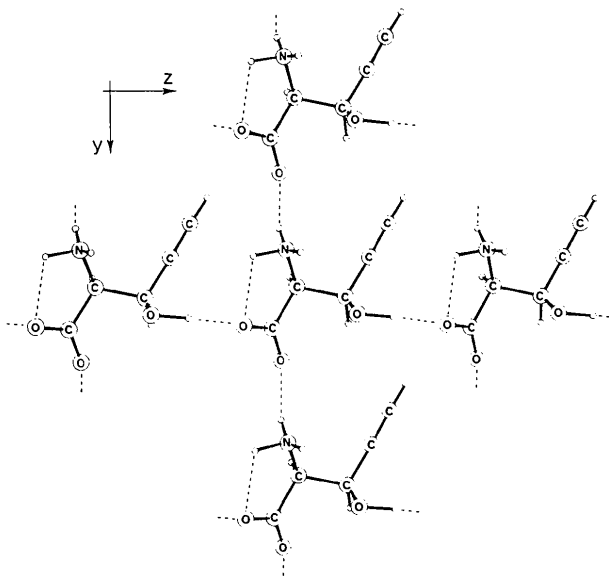


Fig. 2. A projection of the structure down  $a$ . Hydrogen bonds are shown by dotted lines. These layers of molecules are joined to those related by the  $2_1$  screw axis by hydrogen bonds from each  $\text{NH}_3^+$  to an adjacent  $\text{CO}_2^-$  group.

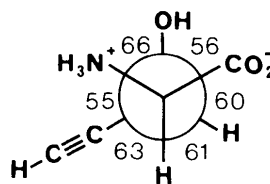


Fig. 3. A Newman projection down C(2)—C(3).

$N \cdots O(1) = 2.63 \text{ \AA}$ . The molecules are linked together by intermolecular hydrogen bonds parallel to  $y$  and  $z$  (Fig. 2), and these sheets are in turn linked by other hydrogen bonds parallel to  $x$  (Table 3). This three-dimensional network results in hard crystals (as shown by the relatively small values of  $B$  for the N and O atoms).

The C atom skeleton is similar to that of tricholomic acid and the unusual amino acid reported by Baldwin, Hoskins & Kruse (1976) and it is possible that these compounds are related biogenetically.

Details of the isolation and chemical properties will be published separately by Dr Vermeulen and Mr Potgieter.

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## Trimethylene Glycol Dibenzoate\*

BY SERGE PÉREZ AND FRANÇOIS BRISSE

*Département de Chimie, Université de Montréal, CP 6210, Succ. A, Montréal, PQ, Canada H3C 3V1*

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**Abstract.**  $C_{17}H_{16}O_4$ ,  $M_r = 284.3$ ,  $Pbcn$ ,  $Z = 4$ ,  $a = 11.224$  (4),  $b = 8.961$  (3),  $c = 14.692$  (4) Å,  $F(000) = 600$ ,  $d_c = 1.278$ ,  $d_o = 1.29 \text{ g cm}^{-3}$ . The structure was solved by direct methods. The anisotropic block-diagonal least-squares weighted refinement was concluded with the final values  $R = 0.064$  and  $R_w = 0.047$  for the 543 observed reflexions. The molecule lies on a twofold axis of rotation. The torsion angles within the 'trimethylene' part of the molecule correspond to a *gauche-gauche* conformation. The aromatic ring plane is tilted by  $6^\circ$  from the carboxylic plane.

**Introduction.** In our previous work on the crystal structures of small molecules related to the poly(oligomethylene terephthalates) it was found that the conformations of ethylene glycol dibenzoate and hexamethylene glycol dibenzoate were closely related to those of poly(ethylene terephthalate) and poly(hexamethylene terephthalate) respectively (Pérez & Brisse, 1976a, 1977). In order to arrive at a possible conformation for poly(trimethylene terephthalate), we determined the crystal structure of trimethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1976b). However,

since the comparison of the crystal structures of ethylene glycol dibenzoate and ethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1975) revealed that these molecules, differing only by Cl substitution on the terminal phenyl rings, adopted completely different conformations, we decided to undertake the crystal structure determination of trimethylene glycol dibenzoate.

Trimethylene glycol dibenzoate was synthesized according to the procedure described by Vogel (1962). The crystals, m.p.  $59^\circ\text{C}$ , were obtained by slow evaporation from a methanol solution. A preliminary photographic investigation indicated that the crystals were orthorhombic, space group  $Pbcn$  (systematic absences:  $hk0$ ,  $h + k \neq 2n$ ;  $h0l$ ,  $l \neq 2n$ ;  $0kl$ ,  $k \neq 2n$ ). The unit-cell dimensions were obtained by a least-squares fit to the settings of 12 reflexions centred on an automatic diffractometer.

Integrated intensities were collected on a Picker FACS-I diffractometer using  $\text{Mo } K\alpha$  ( $\lambda K\alpha_1 = 0.70926 \text{ \AA}$ ) graphite-monochromatized radiation for all the reflexions within one octant of the sphere limited by  $2\theta \leq 47.5^\circ$ . The  $\theta$ - $2\theta$  scan technique was used with a scan rate of  $1^\circ (2\theta) \text{ min}^{-1}$  and a minimum peak width of  $1.75^\circ (2\theta)$ . Background counts of 20 s were taken at each end of the scan range.

\* Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. VII.