Acta Cryst. (1978). B**34**, 1396–1397

Hydrogen-Bond Motifs of Carboxylic Acids: The β Form of Cyanoacetic Acid

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(*Received* 5 *December* 1977; *accepted* 30 *December* 1977)

Abstract. $C_3H_3NO_2$, triclinic, $P\bar{1}$, a = 5·536 (3), b = 7·793 (3), c = 9·936 (3) Å, α = 86·24 (4), β = 84·89 (3), γ = 69·77 (2)°, Z = 4, D_c = 1·411 g cm^{-3}. The asymmetric unit consists of two independent, O—H···N-linked molecules which form a centrosymmetric tetramer by carboxyl-group coupling.

Introduction. As part of a programme to study hydrogen-bond motifs in monosubstituted acetic acids the structure of the α form of cyanoacetic acid has been determined (Kanters, Roelofsen & Straver, 1978). Schaum, Schaeling & Klausing (1916) pointed out that cyanoacetic acid exhibits monotropic dimorphy. Sublimation *in vacuo* at a temperature of 40°C yielded a mixture of monoclinic and triclinic crystals. A block-shaped crystal 0·3 × 0·4 × 0·5 mm was sealed in a capillary tube because of its hygroscopic character. Cell dimensions and 1526 intensities ($\sin\theta/\lambda$ < 0·61 Å^{-1}) were measured with an ω–2θ scan and Cu $K\alpha$ radiation (λ = 1·5418 Å) on a Nonius CAD-4 diffractometer. 73 reflexions had $I < 2{\cdot}5\sigma(I)$ and were given zero weight in the refinement. After Lorentz and polarization corrections the data were placed on an approximately absolute scale by means of a Wilson (1942) plot. No correction was applied for absorption [μ(Cu $K\alpha$) = 10·6 cm^{-1}]. The structure was solved with the *MULTAN* program of the XRAY system (1972) from 238 reflexions with $|E| > 1{\cdot}4$. An E map revealed the positions of all non-hydrogen atoms. Isotropic block-diagonal least-squares refinement, followed by anisotropic refinement and a difference synthesis, revealed the positions of the H atoms (peak heights ranging from 0·27 to 0·65 e Å^{-3}), which were assigned isotropic thermal parameters equal to those of the carrier atoms. At this stage five strong low-order reflexions, apparently suffering from extinction, were excluded from the calculations. Further anisotropic full-matrix refinement gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0·062 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0·068 with $w = \sigma^{-2}(F_o)$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The goodness of fit $[\Sigma w(|F_o| - |F_c|)^2/(m - s)]^{1/2}$, where m is the number of observations and s the number of parameters refined, was 4·4; the average shift in the last cycle was 0·02σ. A final difference synthesis showed no peaks above 0·21 e Å^{-3}. Scattering factors of Cromer & Mann (1968) were used

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3)

The e.s.d.'s are in parentheses and refer to the last decimal position of respective values.

	x	y	z
N(11)	−3368 (5)	6385 (4)	7837 (3)
C(11)	1668 (5)	6609 (4)	5624 (3)
C(12)	−845 (6)	7943 (4)	6167 (3)
C(13)	−2254 (5)	7061 (4)	7111 (3)
O(11)	2848 (4)	7376 (3)	4710 (2)
O(12)	2480 (4)	5023 (3)	6012 (2)
H(11)	−51 (5)	904 (4)	644 (3)
H(12)	−186 (6)	838 (4)	532 (3)
H(13)	428 (6)	652 (4)	453 (3)
N(21)	−2924 (6)	9435 (4)	3095 (3)
C(21)	1278 (5)	7596 (4)	362 (3)
C(22)	−1299 (6)	7578 (4)	948 (3)
C(23)	−2229 (6)	8647 (4)	2153 (3)
O(21)	2039 (4)	6532 (3)	−694 (2)
O(22)	2462 (4)	8466 (3)	764 (2)
H(21)	−241 (6)	804 (4)	39 (3)
H(22)	−122 (5)	630 (4)	117 (3)
H(23)	334 (6)	648 (4)	−94 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

E.s.d.'s are given in parentheses.

	$i = 1$	$i = 2$
N(i1)—C(i3)	1·129 (4)	1·117 (4)
C(i3)—C(i2)	1·454 (5)	1·455 (4)
C(i2)—C(i1)	1·499 (4)	1·497 (4)
C(i1)—O(i1)	1·304 (4)	1·327 (4)
C(i1)—O(i2)	1·209 (3)	1·199 (4)
C(i2)—H(i1)	0·99 (4)	0·83 (3)
C(i2)—H(i2)	1·02 (3)	0·99 (3)
O(i1)—H(i3)	0·85 (3)	0·73 (4)
N(i1)—C(i3)—C(i2)	179·3 (3)	178·5 (3)
C(i3)—C(i2)—C(i1)	111·9 (2)	113·3 (3)
O(i1)—C(i1)—C(i2)	111·8 (2)	109·7 (3)
O(i2)—C(i1)—C(i2)	123·1 (3)	125·5 (3)
O(i1)—C(i1)—O(i2)	125·1 (2)	124·8 (3)
C(i3)—C(i2)—H(i1)	120 (2)	105 (2)
C(i3)—C(i2)—H(i2)	109 (2)	109 (2)
C(i1)—C(i2)—H(i1)	108 (2)	110 (2)
C(i1)—C(i2)—H(i2)	103 (1)	110 (1)
H(i1)—C(i2)—H(i2)	104 (2)	109 (3)
C(i1)—O(i1)—H(i3)	103 (2)	110 (3)

Table 3. *Hydrogen-bond geometry*

O(11)···O(12′)	2·683 (3) Å	O(21″)···N(11)	2·787 (4) Å
H(13)···O(12′)	1·84 (3)	H(23″)···N(11)	2·08 (3)
O(11)–H(13)	0·85 (3)	H(23″)–O(21″)	0·73 (3)
O(11)–H(13)···O(12′)	171 (2)°	O(21″)–H(23″)···N(11)	164 (2)°
C(11)–O(11)···O(12′)	109·5 (3)	C(21″)–O(21″)···N(11)	118·2 (3)
C(11)–O(12)···O(11′)	125·2 (3)	C(13)–N(11)···O(21″)	149·5 (3)

Symmetry-code superscripts: (′) $-x+1, -y+1, -z+1$; (″) $x-1, y, z+1$.

for N, O and C and of Stewart, Davidson & Simpson (1965) for H. The final positional parameters are listed in Table 1.*

Discussion. Chemically similar bond distances and angles of the two symmetry-unrelated molecules (Table 2) compare well with values of the α form of cyanoacetic acid (Kanters, Roelofsen & Straver, 1978), bearing in mind that this latter structure was determined at liquid-nitrogen temperature. The short C–C distances (1·499 and 1·497 Å) are also found in the α form as well as in other substituted acetic acids (Kanters & Roelofsen, 1976). The conformation of the molecules is synplanar and the dihedral angles C(i2)–C(i1)–O(i1)–O(i2)/C(i1)–C(i2)–C(i3)–N(i1) (i = 1, 2) are 5·0 and 4·1° respectively. Fig. 1 shows a projection of the structure along **a**. Two independent molecules are linked by an O–H···N hydrogen bond and the carboxyl groups of two such units are hydrogen-bonded across a centre of symmetry, thus constituting a tetramer.

The geometries of the dimer motifs in the α and β forms are very similar, while the O–H···N hydrogen bonds have different acceptor and donor angles [Table 3 and Kanters, Roelofsen & Straver (1978)].

The presence of two groups of comparable acceptor capacity (C=O and C≡N) enables cyanoacetic acid to form alternative hydrogen-bond motifs. Inspection of these motifs of the α and β forms reveals that in the α form the dimers do not use their C≡N acceptor groups and the polymers do not utilize the C=O acceptor groups. In the β form both acceptor groups of one of the independent molecules are involved, whereas the other molecule does not accept any hydrogen bond.

Some intermolecular contacts in the range 3·30–3·55 Å between atoms of different tetramers are indicative of van der Waals interactions.

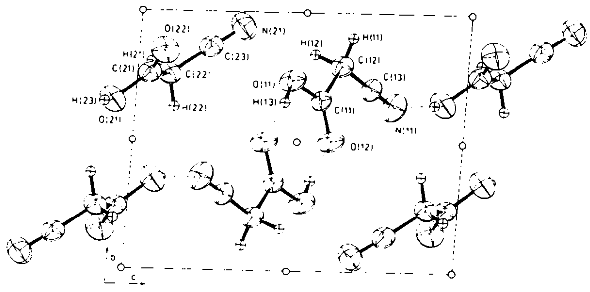

Fig. 1. Projection of the structure along **a**. Hydrogen bonds are denoted by dashed lines.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33273 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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