

Fig. 1. The labelling scheme of the title compound.

repulsions involving the *ortho* H atoms. C(10)–C(11) [1.485 (4)] and C(20)–C(21) [1.472 (4) Å] are consistent with single bonds between  $sp^2$ -hybridized C atoms, indicating little electron delocalization in the five-membered P–O–C–C–C– rings, but the shortness of C(10)–O(11) and C(20)–O(21) suggests that significant multiple-bond character should be assigned to them.

*Acta Cryst.* (1978). B34, 1393–1395

## Hydrogen-Bond Motifs of Carboxylic Acids: The $\alpha$ Form of Cyanoacetic Acid at $-150^\circ\text{C}$

BY J. A. KANTERS, G. ROELOFSEN AND L. H. STRAVER

*Structural Chemistry Group, Rijksuniversiteit Utrecht, Padualaan 8, Utrecht, The Netherlands*

(Received 5 December 1977; accepted 30 December 1977)

**Abstract.**  $\text{C}_3\text{H}_3\text{NO}_2$ , monoclinic,  $P2_1/c$ ,  $a = 11.629$  (6),  $b = 7.761$  (3),  $c = 13.758$  (3) Å,  $\beta = 108.92$  (3)°,  $Z = 12$ ,  $D_c = 1.460$  g cm $^{-3}$  at  $-150^\circ\text{C}$ . The structure contains two types of hydrogen-bond motifs. The asymmetric unit consists of three independent molecules. One molecule forms cyclic dimers by carboxyl-group coupling across centres of symmetry, the other two form separate infinite O–H...N-linked polymers.

**Introduction.**  $\text{C}_3\text{H}_3\text{NO}_2$  exists in two distinct crystalline varieties (Schaum, Schaeling & Klausung, 1916). Sublimation *in vacuo* at a temperature of  $70^\circ\text{C}$  yielded the monoclinic modification, which was also obtained by recrystallization from ether. Since Sinha & Katon (1972), from changes upon cooling of IR and Raman spectra of cyanoacetic acid, inferred an order–disorder

We thank Dr I. Granoth and Dr Y. Segall for providing the crystals, the Universidad de Los Andes for a Fellowship to AVR, and the Science Research Council for a contribution towards the cost of the diffractometer. Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by GMS.

### References

- CADOGAN, J. I. G., GOULD, R. O., GOULD, S. E. B., SADLER, P. A., SWIRE, S. J. & TAIT, B. S. (1975). *J. Chem. Soc. Perkin Trans. 1*, pp. 2392–2395.
- CARRELL, H. L., BERMAN, H. M., RICCI, J. S., HAMILTON, W. C., RAMIREZ, F., MARECEK, J. F., KRAMER, L. & UGI, I. (1975). *J. Am. Chem. Soc.* **97**, 38–46.
- DAHLÉN, B. (1974). *Acta Cryst.* **B30**, 647–651.
- HOWARD, J. A., RUSSELL, D. R. & TRIPPE, S. (1973). *J. Chem. Soc. Chem. Commun.* pp. 856–857.
- KÁLMÁN, A., SASVÁRI, K. & KAPOVITS, I. (1973). *Acta Cryst.* **B29**, 355–357.
- SEGALL, Y. & GRANOTH, I. (1977). Abstr., 44th Ann. Meet. Israel Chem. Soc., OR-10.
- SEGALL, Y., GRANOTH, I., KALIR, A. & BERGMANN, E. D. (1975). *J. Chem. Soc. Chem. Commun.* p. 399.
- WUNDERLICH, H., MOOTZ, D., SCHMUTZLER, R. & WIEBER, M. (1974). *Z. Naturforsch. Teil B*, **29**, 32–34.

transition relating to the hydrogen-bond system, the structure has been determined at room and liquid-nitrogen temperatures. As the results of both structure determinations, which were performed to elucidate the hydrogen-bond motif, only differ within experimental error, the low-temperature structure is reported.

A hexagonal rod-like crystal  $0.5 \times 0.2 \times 0.1$  mm was sealed in a capillary tube because of its very hygroscopic character. Cell dimensions and 1075 intensities ( $\sin \theta/\lambda < 0.48$  Å $^{-1}$ ) were measured with an  $\omega$ - $2\theta$  scan and Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) on a Nonius CAD-4 computer-controlled diffractometer. 195 reflexions with  $I < 2.5\sigma(I)$  were considered unobserved and given zero weight in the refinement. After Lorentz and polarization corrections the data were placed on an approximate absolute scale by means of a Wilson (1942) plot and a correction for

Table 1. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ )

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

	x	y	z
N(11)	4290 (3)	7618 (4)	-163 (2)
C(11)	4174 (3)	6546 (5)	2269 (2)
C(12)	4602 (3)	5699 (4)	1461 (2)
C(13)	4413 (3)	6789 (5)	556 (3)
O(11)	4654 (2)	5714 (3)	3161 (2)
O(12)	3489 (2)	7754 (3)	2125 (2)
H(11)	542 (2)	536 (4)	175 (2)
H(12)	411 (2)	473 (4)	122 (2)
H(13)	437 (2)	615 (4)	357 (2)
N(21)	2683 (3)	2378 (4)	6991 (3)
C(21)	2548 (3)	3225 (5)	4483 (2)
C(22)	2306 (3)	4237 (4)	5332 (2)
C(23)	2509 (3)	3190 (5)	6259 (3)
O(21)	2459 (2)	4278 (3)	3695 (2)
O(22)	2780 (2)	1701 (3)	4517 (2)
H(21)	152 (2)	465 (4)	514 (2)
H(22)	285 (2)	520 (4)	552 (2)
H(23)	263 (2)	376 (3)	329 (2)
N(31)	349 (3)	9643 (4)	1450 (2)
C(31)	702 (3)	9084 (5)	4021 (3)
C(32)	1271 (4)	8344 (5)	3277 (3)
C(33)	759 (3)	9070 (4)	2251 (3)
O(31)	1185 (2)	8416 (3)	4942 (2)
O(32)	-105 (2)	10162 (3)	3788 (2)
H(31)	114 (3)	707 (5)	326 (2)
H(32)	201 (3)	853 (4)	350 (2)
H(33)	85 (3)	874 (5)	529 (3)

absorption (Coppens, 1970) was applied [ $\mu(\text{Mo } K\alpha) = 1.36 \text{ cm}^{-1}$ ].

The structure was solved with the *MULTAN* program of the XRAY system (1972) from 217 reflexions with  $|E| > 1.4$ . 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 0.38 to 0.50 e  $\text{\AA}^{-3}$ ), which were assigned constant isotropic thermal parameters equal to those of the carrier atoms. Further anisotropic full-matrix refinement, with an isotropic correction for secondary extinction (Coppens, 1970), yielded a final *R* of 0.033 ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ).  $R_w$  was 0.034 ( $w = \sigma^{-2}(F_o)$ ) and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  and the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ . The goodness of fit,  $[\sum w(|F_o| - |F_c|)^2 / (m - s)]^{1/2}$ , where *m* is the number of observations and *s* the number of parameters refined, was 0.91. The scattering factors of Cromer & Mann (1968) were used for N, O and C and of Stewart, Davidson & Simpson (1965) for H. The final positional parameters are listed in Table 1.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33272 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

**Discussion.** The bond distances and angles of the three independent molecules (Table 2) compare well with values reported for the analogous bromoacetic (Leiserowitz & von der Brück, 1975) and chloroacetic acids (Kanters, Roelofsen & Feenstra, 1976; Kanters & Roelofsen, 1976). Corresponding bond distances and angles involving nonhydrogen atoms of independent molecules 1 and 2 do not differ significantly, while the differences between C—O lengths of molecules 1 and 2 and C—O lengths of molecule 3 might reflect the different type of hydrogen bonding of respective molecules. All molecules adopt the synplanar conformation commonly observed in substituted carboxylic acids (Leiserowitz, 1976). The dihedral angles  $C(i2)-C(i1)-O(i1)-O(i2)/C(i1)-C(i2)-C(i3)-N(i1)$  ( $i = 1, 2, 3$ ) are 17.7, 6.0 and 0.6° respectively.

From Fig. 1, a projection of the structure along *b*, it can be seen that the hydrogen-bond scheme is unique. Molecules 1 and 2 form two independent infinite, O—H...N-linked chains, whereas molecules 3 are arranged as cyclic centrosymmetric dimers by hydrogen bonding of the carboxyl groups.

The hydrogen-bond geometries of the two independent polymeric chains are very similar (Table 3). The donor angles (114.3°) are close to values found for the dimer motif (~113°), whereas the acceptor angles (~164°) are significantly greater than those in dimers (~123°). The geometry of the dimers (Table 3) formed by molecules 3 compares well with what is usually observed in this hydrogen-bond motif (Kanters, Roelofsen & Feenstra, 1976). The only intermolecular distance smaller than 3.2 Å between O atoms belong-

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

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

	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3
N(i1)—C(i3)	1.145 (5)	1.145 (5)	1.138 (4)
C(i3)—C(i2)	1.457 (5)	1.460 (5)	1.453 (5)
C(i2)—C(i1)	1.504 (5)	1.504 (5)	1.499 (6)
C(i1)—O(i1)	1.335 (4)	1.328 (4)	1.313 (4)
C(i1)—O(i2)	1.196 (4)	1.198 (5)	1.213 (4)
C(i2)—H(i1)	0.94 (3)	0.93 (3)	0.99 (4)
C(i2)—H(i2)	0.93 (3)	0.95 (3)	0.83 (3)
O(i1)—H(i3)	0.81 (3)	0.77 (3)	0.75 (4)
N(i1)—C(i3)—C(i2)	178.0 (4)	179.1 (3)	179.4 (4)
C(i3)—C(i2)—C(i1)	112.9 (3)	112.1 (3)	112.7 (3)
O(i1)—C(i1)—C(i2)	109.5 (3)	109.6 (3)	111.5 (3)
O(i2)—C(i1)—C(i2)	125.1 (3)	124.8 (3)	123.6 (3)
O(i1)—C(i1)—O(i2)	125.4 (3)	125.6 (3)	125.0 (4)
C(i3)—C(i2)—H(i1)	111 (2)	108 (2)	110 (2)
C(i3)—C(i2)—H(i2)	104 (2)	106 (2)	110 (2)
C(i1)—C(i2)—H(i1)	110 (2)	112 (2)	107 (2)
C(i1)—C(i2)—H(i2)	108 (2)	110 (2)	108 (2)
H(i1)—C(i2)—H(i2)	110 (2)	109 (2)	108 (3)
C(i1)—O(i1)—H(i3)	107 (2)	108 (2)	110 (2)

Table 3. *Hydrogen-bond geometry*

Dimer		Polymers			
O(31)···O(32''')	2.691 (4) Å	O(11)···N(11')	2.787 (4) Å	2.753 (4) Å	O(21)···N(21'')
H(33)···O(32''')	1.94 (4)	H(13)···N(11')	2.02 (3)	2.00 (3)	H(23)···N(21'')
O(31)–H(33)	0.75 (4)	O(11)–H(13)	0.81 (3)	0.77 (3)	O(21)–H(23)
O(31)–H(33)···O(32''')	173 (2)°	O(11)–H(13)···N(11')	160 (2)°	166 (2)°	O(21)–H(23)···N(21'')
C(31)–O(31)···O(32''')	108.5 (3)	C(11)–O(11)···N(11')	114.3 (3)	114.3 (3)	C(21)–O(21)···N(21'')
C(31)–O(32)···O(31''')	126.0 (3)	C(13')–N(11')···O(11)	163.6 (3)	164.0 (3)	C(23'')–N(21'')···O(21)

Symmetry-code superscripts: (')  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (')'  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (''')  $-x, 2 - y, 1 - z$ .

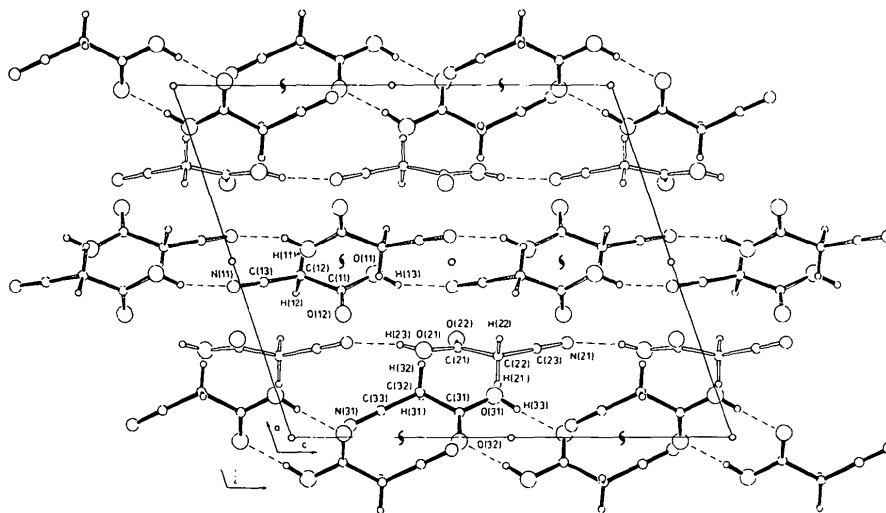


Fig. 1. Projection of the structure along **b**. Hydrogen bonds are denoted by dashed lines.

ing to the independent chains and dimers is that between O(11) and O(21) (3.08 Å). Though this contact suggests a weak hydrogen-bond interaction, the pertinent H atoms, H(13) and H(23), are at distances of 2.70 and 2.85 Å respectively, which are too far outside the normal range of H···O distances in hydrogen bonds to be classifiable even as a weak hydrogen-bond interaction.

The polymer hydrogen-bond motif, tentatively put forward by Sinha & Katon (1972), is for the greater part corroborated by our structure analysis, although one third of the structure displays the dimer motif. Another suggestion of these authors was an order-disorder transition involving the position of the H atoms forming the hydrogen bonds. The presence of this type of disorder will give rise to equal C–O distances and C–C–O angles in the carboxyl groups (Kanters, Roelofsen & Kroon, 1975). However, the clearly distinct values of these quantities in the  $\alpha$  form of cyanoacetic acid at liquid-nitrogen temperature (Table 2) and at room temperature (mean values: 1.196 Å for C=O, 1.318 Å for C–O, 124.2° for C–C=O and 110.6° for C–C–O) exclude such a transition within these temperature limits.

## References

- COPPENS, P. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 255–270. Copenhagen: Munksgaard.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–323.
- KANTERS, J. A. & ROELOFSEN, G. (1976). *Acta Cryst.* B32, 3328–3331.
- KANTERS, J. A., ROELOFSEN, G. & FEENSTRA, T. (1976). *Acta Cryst.* B32, 3331–3333.
- KANTERS, J. A., ROELOFSEN, G. & KROON, J. (1975). *Nature (London)*, 257, 625–626.
- LEISEROWITZ, L. (1976). *Acta Cryst.* B32, 775–802.
- LEISEROWITZ, L. & VOR DER BRÜCK, D. (1975). *Cryst. Struct. Commun.* 4, 647–651.
- SCHAUM, K., SCHÄLING, K. & KLAUSING, F. (1916). *Justus Liebig's Ann. Chem.* 411, 161–189.
- SINHA, D. & KATON, J. E. (1972). *Appl. Spectrosc.* 26, 599–605.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- WILSON, A. J. C. (1942). *Nature (London)*, 150, 151–152.
- XRAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland; implemented and extended by the Dutch X-ray System Group, 1973.