Crystal Structure of α-Cyanoacetohydrazide

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Crystals of the title compound are monoclinic with $a = 7{\cdot}459(6)$, $b = 8{\cdot}694(7)$, $c = 7{\cdot}915(6)$ Å, $\beta = 116{\cdot}6(5)°$, space group $P2_1/c$ and $Z = 4$. The structure was determined from diffractometer data by symbolic addition procedures, and refined by least-squares methods to R 0·058 for 609 independent reflections. Hydrogen atom positions were also refined. Bond distances are N≡C 1·122(5), C(sp)–C(sp^3) 1·453(5), C(sp^3)–C(sp^2) 1·524(5), C(sp^2)–N 1·330(5), N–N 1·411(5), and C=O 1·224(4) Å. The molecules are held together by hydrogen bonds.

IN the structure of α-cyanoacetamide,[1] a weak hydrogen bond of N–H · · · N≡C– type with a distance of **3·14** Å was observed. α-Cyanoacetohydrazide is closely related to α-cyanoacetamide and although a preliminary *X*-ray study had been reported,[2] no detailed structural information was available. In an e.s.r. spectral study,[3] the *X*-ray-irradiated (40 kV Mo-radiation) sample acquired a dark purple colour in contrast to a slight yellow colour observed for α-cyanoacetamide. The e.s.r. spectra were compatible with the presence of radicals of the type: $N{\equiv}C{-}CH_2{-}CO{-}\dot{N}H{-}\dot{N}H$ with the unpaired electron being in a π MO. It is conceivable that the following resonance structure may also be present: $N{\equiv}C{-}CH_2{-}CO{-}\underset{+}{N}\dot{H}{-}\underset{-}{\ddot{N}}H$.

The crystal structure analysis was undertaken to determine the orientation and correlations of the molecules in the solid state.

EXPERIMENTAL

Crystals of α-cyanoacetohydrazide from water are prisms with no preferred direction of elongation. Cell constants were obtained from rotation, Weissenberg, and precession photographs.

Crystal Data.—$C_3H_5N_3O$, $M = 99{\cdot}1$. Monoclinic, $a =$

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[1] P. C. Chieh and J. Trotter, *J. Chem. Soc.* (*A*), **1970**, 184.

[2] J. L. Armoros and J. J. Coves, *Acta. Cryst.*, **1954**, **7**, 647.

[3] W. C. Lin and J. N. Nickel, *J. Chem. Phys.*, **1972**, **57**, 3581, and subsequent personal communication (with W. C. L.)

7·459(6), $b = 8{\cdot}694(7)$, $c = 7{\cdot}915(6)$ Å, $\beta = 116{\cdot}6(5)°$, $U = 458{\cdot}9$ Å^3, $D_m = 1{\cdot}435$ (by flotation), $Z = 4$, $D_c = 1{\cdot}433$, $F(000) = 208$. Space group $P2_1/c$ (C^5_{2h}) from systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 1·22 cm^{-1}.

Intensities were measured on a General Electric XRD 6 automatic diffractometer with a scintillation counter, Mo-K_α radiation, (zirconium filter and pulse-height analyser), and a θ—2θ scan. The scan range in 2θ was (1·80 + 0·6 tan θ)°, and backgrounds were measured at the beginning and end of each scan. Four strong reflections were remeasured every 100 reflections in order that corrections (<10%) could be applied for fluctuation over the course of measurement. No appreciable reduction of intensity was observed. Standard deviations of intensities were calculated from counting statistics and 609 reflections having $I > 3\sigma(I)$ were considered observed, from 1305 independent reflections (2θ < 60°) measured. The crystal used had dimensions 0·20 × 0·18 × 0·16 mm along a^*, b, and c directions and was mounted with a^* parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied to derive the structure amplitudes. A Wilson plot[4] with all the reflections was carried out to evaluate the scale and temperature factors from which the normalized structure factors, E, were computed. The statistical averages and distribution of the E values correspond to those for a centrosymmetric crystal in agreement with the space group $P2_1/c$.

Structure Analysis.—Signs were derived from the normalized structure factor magnitudes by means of the symbolic addition procedure for centrosymmetric crystals.[5,6] The E-map calculated from the solution with the highest consistency index (a measure of the consistency of the sign-determining relations) of 0·87 revealed the positions of all non-hydrogen atoms. The structure was then refined by full-matrix least-squares methods with anisotropic temperature factors for each atom to R 0·10. A difference-Fourier map then calculated had five peaks with electron density of 0·5—0·7 eÅ^{-3}, corresponding to the positions of the five hydrogen atoms. Further refinements including the hydrogen atoms and minimizing $\Sigma w \Delta F^2$ with $w = (5{\cdot}0 + F_o + 0{\cdot}04F_o{}^2)^{-1}$ reduced R to 0·058.* The results of the weighting analyses are given in Table 1. Atomic scattering factors from ref. 7 were used for carbon, nitrogen, and oxygen and from ref. 8 for hydrogen atoms. Unobserved reflections were given zero weight in the refinements. Final co-ordinates and temperature parameters are given in Table 2.

TABLE 1

Weighting analyses based on ranges of $|F_o|$ and (sin θ/λ)

Range of $\lvert F_o\rvert$	Error *	n	Range of (sin θ/λ)	Error *	n
0·0—3·6	0·18	81	0·0—0·378	0·16	175
3·6—4·1	0·20	74	0·378—0·476	0·15	143
4·1—4·9	0·20	81	0·476—0·545	0·15	117
4·9—5·8	0·15	75	0·545—0·600	0·15	69
5·8—7·2	0·13	73	0·600—0·646	0·21	59
7·2—9·8	0·14	80	0·646—0·687	0·21	59
9·8—14·2	0·14	75	0·687—0·723	0·28	8
14·2—up	0·17	70			

* Error = $\left[\dfrac{\Sigma(|F_o| - |F_c|)^2 \times n_t}{(n_t - n_v)\,n}\right]^{\frac{1}{2}}$ where n_t is total no. of reflections (609), n_v no. of variables (85), and n no. of reflections in the range.

TABLE 2

Final positional (fractional ×10^4 for C, N, and O; ×10^3 for H) and thermal parameters with standard deviations in parentheses

Atom	x	y	z	B/Å^2
N(1)	6888(7)	−3069(4)	4825(5)	
C(2)	6862(6)	−1857(4)	4330(5)	
C(3)	6818(7)	−0308(4)	3622(5)	
C(4)	7630(5)	0873(4)	5212(4)	
N(5)	8196(5)	2181(4)	4720(4)	
N(6)	8755(6)	3437(4)	5982(5)	
O(7)	7702(4)	0633(3)	6763(3)	
H(31)	543(6)	005(5)	270(6)	3·8(9)
H(32)	754(7)	− 026(6)	281(7)	4·6(10)
H(51)	812(7)	232(6)	353(7)	4·5(11)
H(61)	1011(8)	361(6)	646(6)	4·1(11)
H(62)	829(7)	429(6)	532(7)	4·2(10)

Anistropic thermal parameters (Å^2) in the form:

$$\exp -10^{-4} \times (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	356(13)	75(5)	175(9)	−14(7)	92(8)	3(5)
C(2)	170(9)	62(5)	108(6)	−9(6)	49(6)	−23(5)
C(3)	219(10)	62(5)	95(6)	−29(6)	64(7)	−13(4)
C(4)	111(8)	61(5)	88(6)	21(5)	43(6)	2(4)
N(5)	198(9)	69(5)	80(6)	−17(5)	72(6)	−6(4)
N(6)	210(10)	57(4)	119(6)	−15(5)	86(6)	15(4)
O(7)	264(7)	85(4)	111(5)	3(4)	107(5)	12(3)

RESULTS AND DISCUSSION

Bond lengths and angles (Table 3) are all comparable with those observed for α-cyanoacetamide.[1] The skeleton of the molecule is rather flat (Figures 1 and 2). Equations of various planes in the molecule are given in

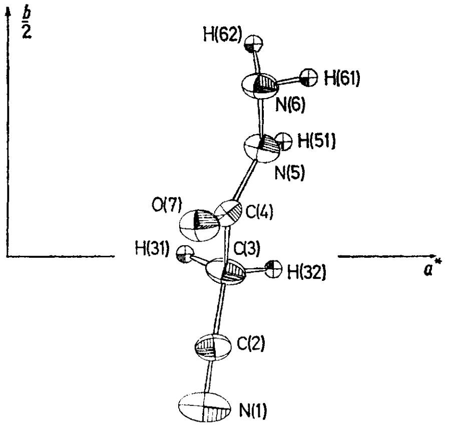

FIGURE 1 A view of the molecule projected along c axis showing the atom numbering system

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* Tables of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20800 (2 pp., 1 microfiche). For details of Supplementary Publications see *J.C.S. Dalton*, 1972, Index issue.

[4] F. R. Ahmed, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 55; also programs made available to us from Dr. Ahmed.

[5] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[6] R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[8] R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

TABLE 3

Bond distances (Å) and angles (deg.), with standard deviations in parentheses

(*a*) Distances

N(1)–C(2)	1·122(5)	C(3)–H(31)	1·01(5)
C(2)–C(3)	1·453(5)	C(3)–H(32)	1·01(6)
C(3)–C(4)	1·524(5)	N(5)–H(51)	0·92(5)
C(4)–N(5)	1·330(5)	N(6)–H(61)	0·92(6)
N(5)–N(6)	1·411(5)	N(6)–H(62)	0·88(5)
C(4)–O(7)	1·224(4)		

(*b*) Angles

N(1)–C(2)–C(3)	177·9(2)	C(4)–C(3)–H(31)	107(3)
C(2)–C(3)–C(4)	112·0(2)	C(4)–C(3)–H(32)	112(3)
C(3)–C(4)–N(5)	113·3(2)	H(31)–C(3)–H(32)	101(4)
C(4)–N(5)–N(6)	119·1(2)	C(4)–N(5)–H(51)	122(3)
C(3)–C(4)–O(7)	122·1(2)	N(6)–N(5)–H(51)	119(3)
N(5)–C(4)–O(7)	124·7(1)	N(5)–N(6)–H(61)	109(3)
C(2)–C(3)–H(31)	114(3)	N(5)–N(6)–H(61)	108(3)
C(2)–C(3)–H(32)	111(3)	H(61)–N(6)–H(62)	100(5)

TABLE 4

Equations of mean planes in the form $lX + mY + nZ = p$ where X, Y, and Z are co-ordinates in Å referred to orthogonal axes a, b, and c^*

Plane	Atoms	l	m	n	p	Max. displacement/Å
(1)	N(1) C(2)—(4)	0·9889	−0·1268	0·0770	3·99	0·004
(2)	C(3), C(4), N(5), O(7)	0·8744	−0·3703	0·3131	4·23	0·007
(3)	C(4), N(5), N(6)	0·8510	−0·318	0·4177	4·57	0
(4)	C(4), N(5), N(6) O(7)	0·8774	−0·3068	0·3690	4·52	0·024

Interplanar angles (deg.)

(1)–(3)	20·6	(1)–(4)	20·8
(1)–(3)	23·9	(2)–(4)	4·8
(2)–(3)	6·8	(3)–(4)	3·2

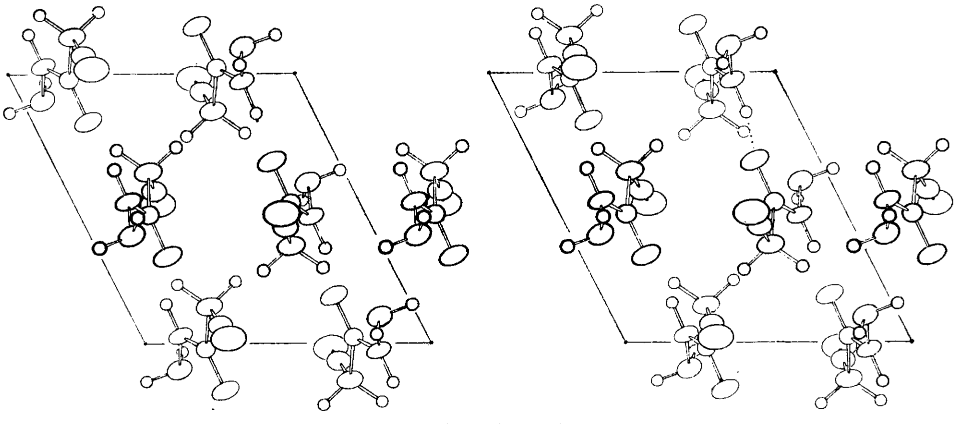

FIGURE 2 A packing diagram

Table 4. Planes (2) [C–C(=O)–N] and (3) [C–N–N] have a very small dihedral angle (6·8°) and this might be responsible for the delocalization of the unpaired electron in a π-molecular orbital[3] for the radicals, $\mathrm{N{\equiv}C{-}CH_2{-}CO{-}\ddot{N}H{-}\dot{N}H}$ result in resonance structures of $\mathrm{N{\equiv}C{-}CH_2{-}CO{-}\ddot{N}H{-}\dot{N}H} \longleftrightarrow \mathrm{N{\equiv}C{-}CH_2{-}CO{-}\underset{+}{\dot{N}}H{-}\underset{-}{\ddot{N}}H}$. After irradiation with *X*-rays the crystal became dark purple and the colour remained unchanged. It was suggested[3] that the enol form of the radical might contribute to the change of colour through the resonance structures:

$$\mathrm{N{\equiv}C{-}CH{=}C(OH){-}\ddot{N}H{-}\dot{N}H} \longleftrightarrow \mathrm{N{\equiv}C{-}CH{=}(OH){-}\underset{+}{\dot{N}}H\ \underset{-}{\ddot{N}}H}$$

$$\longleftrightarrow \mathrm{N{\equiv}C{-}\dot{C}H{-}C(OH){=}\underset{+}{N}H{-}\underset{-}{\ddot{N}}H} \longleftrightarrow \mathrm{\dot{N}{=}C{=}CH{-}C(OH){=}\underset{+}{N}H{-}\underset{-}{\ddot{N}}H}$$

The *X*-ray-irradiation might activate the formation of the enol form in the radicals.

The thermal vibration ellipsoids, numbering of the atoms and the position of the molecule in the unit cell are given in Figure 1, in which the hydrogen atoms are given a mean square displacement of 0·1 Å instead of the isotropic temperature factor given in Table 2. This change is necessary to make the hydrogen atoms appear smaller than other atoms on the diagram. Figures 1 and 2 were drawn by use of the ORTEP program. Figure 2, a packing diagram looking from the negative *b* direction, clearly shows the intermolecular relationship.

The most significant feature of the molecular packing of α-cyanoacetamide is that the plane of the molecule is coplanar with the arrangement of the packing layer. In agreement with the packing theory suggested by Kitaigorodskii[9] each packing unit, either a single molecule or a dimer linked by N–H ··· O hydrogen bonds, is surrounded by six other units in the same layer (see Figure 2 of ref. 1). In α-cyanoacetohydrazide, the packing could also be considered as being composed of close-packed layers (Figure 2) but the molecules are not as flat as those of α-cyanoacetamide. One of the intermolecular attraction is a hydrogen bond, O(7) ··· H(51)–N(5), with for O(7) ··· H(51) 2·21(5) and O(7) ··· N(5) 2·913(5) Å (Figure 3). The weak attraction between O(7) and H(62) is also shown in Figure 3. Though the distances of 2·65(5) [O(7) ··· H(62)] and 3·176(5) Å [O(7) ··· N(6)] suggest that the attraction is very strong, geometrical limitation prevents the formation of a strong hydrogen bond. The other hydrogen

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[9] A. I. Kitaigorodskii, 'Organic Chemical Crystallography,' authorized translation from Russian, Consultants Bureau, New York, 1961.

atom, H(61), of the amide group is attracted toward the cyano-nitrogen atom, N≡C–, and the distances are N(1) · · · H(61) 2·87(5) and N(1) · · · N(6) 3·596(4) Å. The corresponding values are 2·30 and 3·14 Å, in α-cyanoacetamide, in which the hydrogen bond is apparent. The configuration around N(6) is trigonal pyramidal and there should be repulsive interactions between the lone-pair electrons of N(6) and those of O(7) and N(1). Because of these intermolecular interactions, the orientation of the amide group is fixed, and this might have made possible the location of the hydrogen atoms by *X*-ray diffraction. An investigation of the packing in the two compounds would show that the molecules in α-cyanoacetamide are in a structure much more favourable for the formation of hydrogen bonds than that of α-cyanoacetohydrazide.

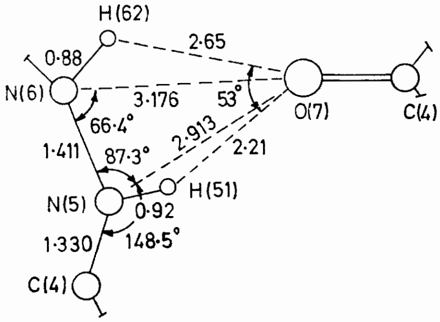

FIGURE 3 Important interatomic distances and angles in the hydrogen-bonding scheme around O(7)

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