

The Crystal Structure of *Cyclopropanecarbohydrazide**

BY D. B. CHESNUT† AND R. E. MARSH

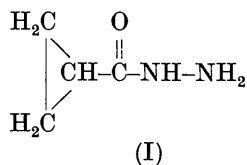
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, U.S.A.

(Received 1 August 1957)

The crystal structure of *cyclopropanecarbohydrazide* has been determined and refined, using three-dimensional Fourier and least-squares methods. The crystals are monoclinic with $a_0 = 9.813 \pm 0.005$, $b_0 = 4.847 \pm 0.005$, $c_0 = 11.660 \pm 0.005$ Å, and $\beta = 97^\circ 43' \pm 5'$; the space group is $P2_1/c$, and there are four molecules in the unit cell. The molecules are held together by chains of $\text{NH} \cdots \text{O}$ hydrogen bonds running parallel to the b axis and by a network of weak $\text{NH} \cdots \text{N}$ bonds running along the twofold screw axes which relate the terminal nitrogen atoms. The value 1.48 ± 0.02 Å for the C-C distance between the *cyclopropane* and carbonyl groups suggests the presence of a fairly strong conjugative effect.

Introduction

Cyclopropanecarbohydrazide (I) contains three structurally interesting groups.



First, the *cyclopropane* ring is of special note because in many reactions it tends to behave like an olefinic double bond and to interact with attached conjugated systems. *Cyclopropanecarbohydrazide* affords a good opportunity for observation of this conjugative power in a system already known to display marked resonance effects. Secondly, one welcomes the chance to observe the amide group—which has been the object of much investigation in these laboratories—in such an unusual environment. The presence of the relatively unstudied hydrazide group represents the third major point of interest.

Experimental

The synthesis of *cyclopropanecarbohydrazide* has been reported in the literature (Roberts, 1951). The crystals used in this investigation were furnished by Prof. J. D. Roberts; they were in the form of nearly square needles, the needle axis being parallel to b . Needles approximately 1 mm. in length and 0.2×0.2 mm. in cross-section were used for Weissenberg photographs about the b axis; for photographs about the a axis, the crystals were cut to form cubes approximately 0.2 mm. on an edge. Since the samples exhibited a tendency to sublime at room temperatures, it was

necessary to mount them in thin-walled glass tubes during exposures of any length.

Zero- and first-layer-line Weissenberg photographs around the a and b axes yielded the conditions for non-extinction; the absence of $h0l$ reflections with l odd and $0k0$ reflections with k odd indicated the space group $P2_1/c-C_{2h}^5$. These Weissenberg photographs, together with a rotation photograph around the b axis, gave initial values for the cell constants. Accurate values for a_0 , c_0 , and β were subsequently obtained from a least-squares treatment of several high-angle reflections recorded on a Straumanis-type rotation photograph about the b axis, using Cr $K\alpha$ radiation; b_0 was determined from an $0kl$ Weissenberg photograph calibrated on the basis of the previously determined values of c_0 and β . The values found were:

$$a_0 = 9.813, \quad b_0 = 4.847, \quad c_0 = 11.660 \text{ \AA}, \quad \beta = 97^\circ 43', \\
 (\lambda(\text{Cr } K\alpha) = 2.2909 \text{ \AA}).$$

The estimated probable errors are approximately ± 0.003 Å in the axial lengths and approximately $\pm 3'$ in the angle β . On the basis of four molecules in the unit cell, the calculated density is 1.21 g.cm.^{-3} ; the observed density—determined by flotation in mixed solvents—is approximately 1.23 g.cm.^{-3} .

Photographs were taken around the a and b axes (layer lines 0-3 and 0-4, respectively) using the multiple-film Weissenberg technique with nickel-filtered copper radiation; intensities were estimated visually with the aid of a calibrated intensity strip. The maximum Bragg angle observed corresponds to $\sin \theta_{\text{Cu}} \approx 0.97$; owing to the rapid fall off of intensity with $\sin \theta$, corresponding to a high temperature factor, only 711 of some 1300 possible reflections were actually recorded.

The usual Lorentz and polarization corrections were made, and the corrected intensities were normalized to an arbitrary scale by applying the appropriate film factors determined by cross-correlation between the various sets of films. Final values for reflections ap-

* Contribution No. 2231 from the Gates and Crellin Laboratories.

† Present address: Department of Physics, Duke University, Durham, North Carolina, U.S.A.

pearing more than once were obtained by subjectively weighting the separate observations according to their estimated reliabilities. Absorption and extinction corrections were neglected, although it appears that a number of the larger observed intensities have been reduced by the latter effect.

The majority of the calculations were carried out by punched-card methods on standard IBM equipment; two final structure-factor and least-squares calculations were made on the Institute's Datatron digital computer, using a program developed here by Pasternak (1956) for space group $P2_1$ and subsequently modified to accommodate space groups of the class $2/m$.

Determination of the structure

A molecular configuration was postulated for which the terminal nitrogen atom was coplanar with the amide group and in the *cis* position with respect to the C-N bond; the plane of the cyclopropane ring was taken to be normal to the plane of the amide group. It was then observed that placing the proposed molecule in the unit cell such that the C-O bond was parallel to the *b* axis (thus allowing a system of $\text{NH}\cdots\text{O}$ hydrogen bonds to be formed along the *b* axis) would account very well for the *b*-axis identity distance.

(i) Projection studies

A Patterson projection on to (010) showed a significant elongation of the peak at the origin along the direction [101]. The length and direction of this peak elongation, along with the very large value of the 202 reflection, were consistent with a trial structure in which the C-O bond was parallel to b_0 and the principal molecular axis was along the [101] direction. Trial parameters were calculated and adjusted until rough agreement was obtained for the strongest $h0l$ terms; the signs of several other terms were determined with the aid of Harker-Kasper inequalities (Harker & Kasper, 1948). When it was felt that the signs of the larger terms were probably correct, an $h0l$ Fourier map was made, using fourteen of the stronger reflections. The resulting projection was very well resolved considering the fact that so few terms had been used and especially in view of the fact that an incorrect model had been assumed; that is, the molecule had been rotated 180° from its correct orientation, the terminal nitrogen atom being placed where the cyclopropane ring turned out to be and vice versa. All the atoms were easily located on the Fourier projection; the assumption that the C-O bond was approximately parallel to the *b* axis was borne out by the appearance of a region of high electron density at the assumed C_1 , O position. The surprisingly good resolution presented strong evidence of the validity of the structure.* The (010) projection was refined by

* At this stage of the investigation, further supporting evidence for our trial structure was found in a preliminary

Fourier and difference maps until the parameter changes led to only very small changes in the overall agreement between observed and calculated structure factors. The final Fourier projection on to (010) is shown in Fig. 1.

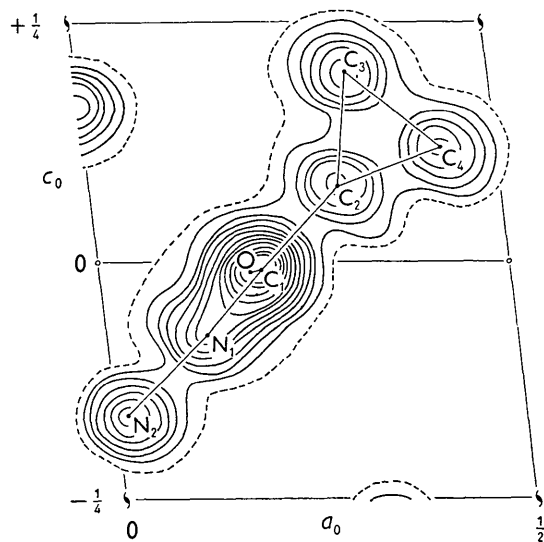


Fig. 1. Final $h0l$ Fourier map. Contours are at approximately $1 \text{ e.}\text{\AA}^{-2}$ intervals, beginning with the zero contour (dashed).

At this point, attention was turned to the (100) zone. A Patterson projection and several electron density projections were computed until resolution and structure-factor agreement was obtained. The difficult problem in this zone became apparent as the projection refined; as can be seen in Fig. 2, the projected

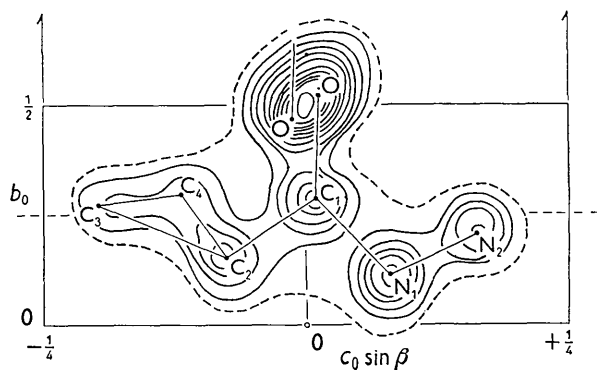


Fig. 2. Final $0kl$ Fourier map. Solid contours are in approximately $1 \text{ e.}\text{\AA}^{-2}$ intervals, beginning with $3 \text{ e.}\text{\AA}^{-2}$. The zero contour is dashed.

molecule has a pseudo plane of symmetry due to the similarity of the projected hydrazide and *cyclo-*

investigation by Jensen & Lingafelter (1953) of some *n*-aliphatic acid hydrazides. The Fourier projections of these compounds and of cyclopropane carbohydrazide were quite similar and the *b* identity distances were essentially identical, indicating a similarity in packing.

propane groups. Thus, the agreement of the structure factors with $k+l$ odd—which were generally weaker than the terms with $k+l$ even—was very sensitive to small changes in atomic parameters. The refinement was stopped with an $0kl$ R -factor of 0.32.

During these projection studies, Hoerni & Ibers (1954) form factors and a single isotropic temperature factor were used. McWeeny (1951) f -curves were used for the subsequent three-dimensional work, with the exception of the final calculations on the Datatron digital computer, for which Berghuis *et al.* (1955) form factors were used.

(ii) The three-dimensional study

The three-dimensional treatment consisted of about twelve structure-factor least-squares cycles, four difference maps and two line Fourier syntheses. The least-squares treatment (in which only the diagonal terms of the normal equations were calculated) progressed very slowly; although the agreement between calculated and observed structure factors continued to improve, the parameters did not converge rapidly. The slow rate of refinement was, we believe, primarily due to large errors in the y parameters. Thus, the y parameter for atom C_4 derived from the (100) projection—0.683—differed by about 0.57 Å from the final value. It is apparent that when parameters are in error by a large amount the shifts indicated by any refinement method in which only the assumed position is inspected will be far too small. In the present case the refinement was speeded by the calculation of a three-dimensional difference map; by this means, not only the slope at the assumed position but also the appearance of neighboring regions was inspected.

In the early stages of refinement an isotropic or a single anisotropic temperature factor was used to compensate for the thermal motions of the atoms. When it was felt that the errors in the calculated structure factors due to temperature anisotropies were comparable with those due to incorrect positional parameters, individual anisotropic temperature factors were introduced. These temperature factors were of the form

$$T_i = \exp(-B \sin^2 \theta / \lambda^2) \exp(-\alpha h^2 - \beta k^2 - \gamma l^2 - \delta hl).$$

The form of this expression leads to some simplification in the calculations; it implies that, for each atom, one axis of the temperature-factor ellipsoid is parallel to the b axis. This simplifying assumption was made only after study of a three-dimensional difference map indicated it to be approximately valid. The temperature-factor parameters were originally calculated using a least-squares method (Davies & Blum, 1955) and compared favorably with values computed from the difference map (Cochran, 1951); they were subsequently refined by a second least-squares treatment. Final values for the coefficients of the temperature factors are listed in Table 1.

Table 1. *Temperature parameters*

(a) Anisotropic temperature factors in the expression

$$T_i = \exp\{-\alpha_i h^2 - \beta_i k^2 - \gamma_i l^2 - \delta_i hl\}$$

(All values have been multiplied by 10^3)

	C_1	C_2	C_3	C_4	O	N_1	N_2
α	13.8	12.2	17.5	8.7	21.5	15.8	15.8
β	18.5	33.0	83.2	58.3	17.0	27.9	39.7
γ	9.5	8.9	7.1	10.4	14.0	8.2	6.4
δ	0.1	-4.5	-2.1	-3.2	-6.0	-1.1	-6.3

(b) Values of $\bar{\mu}^2$ (Å²) for the major axes of the temperature factor ellipsoids

ε_1 represents the larger of the two axes $\varepsilon_1, \varepsilon_2$, which lie in the ac plane; ε_b is the axis parallel to b_0 . $\angle(\varepsilon_2, a)$ is the angle the axis ε_2 makes with the lattice vector a_0

	C_1	C_2	C_3	C_4	O	N_1	N_2
ε_1	0.075	0.083	0.091	0.080	0.134	0.083	0.094
ε_2	0.058	0.041	0.044	0.036	0.072	0.051	0.032
ε_b	0.022	0.039	0.099	0.069	0.020	0.033	0.047
$\angle(\varepsilon_2, a)$	52°	48°	73°	29°	53°	69°	65°

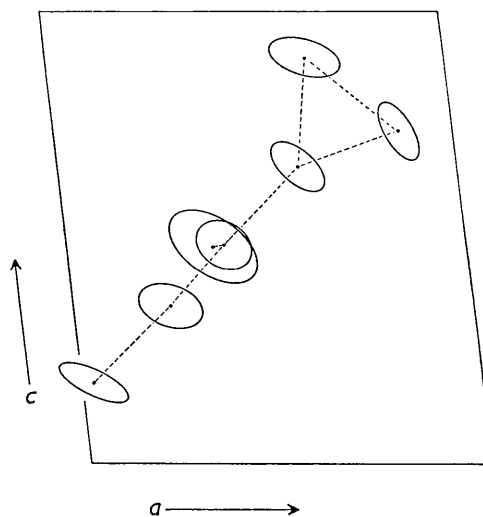


Fig. 3. A schematic representation of the relative magnitudes of thermal anisotropy in the cyclopropanecarbohydrazide molecule viewed down [010].

Table 2. *Final positions parameters*

(Values in parameter units)

	x	y	z
C_1	0.1973	0.7845	0.4908
C_2	0.3007	0.6492	0.5764
C_3	0.3263	0.7698	0.6977
C_4	0.4306	0.8001	0.6181
O	0.1840	0.0332	0.4867
N_1	0.1227	0.6084	0.4210
N_2	0.0124	0.7016	0.3374
$H_1(C_2)$	0.301	0.435	0.568
$H_2(C_3)$	0.334	0.647	0.772
$H_3(C_3)$	0.265	0.940	0.721
$H_4(C_4)$	0.521	0.691	0.636
$H_5(C_4)$	0.453	0.984	0.585
$H_6(N_1)$	0.133	0.409	0.438
$H_7(N_2)$	-0.067	0.815	0.367
$H_8(N_2)$	0.021	0.877	0.286

Table 3. Observed and calculated structure factors

The three columns in each group contain the values, reading from left to right, of *l*, 10*F*_o, and 10*F*_c.

Table of observed and calculated structure factors for cyclopropanecarbohydrazide, organized into columns labeled 00#, 80#, 41#, 12#, 52#, 23#, 11#, 64#, 10#, 90#, 51#, 22#, 82#, 03#, 33#, 13#, 63#, 44#, 24#, 70#, 30#, 02#, 10, 11#, 81#, 21#, 01#, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

In order to better picture the physical effects from which these parameters are derived, the indicated mean square displacements ($\bar{\mu}^2 = B/8\pi^2$) of each atom in the three principal directions were calculated (Waser, 1955). Values for these mean square displacements and their orientations relative to the *a* axis are given

in Table 1; a schematic representation of the implied atomic motions in the *ac* plane is shown in Fig. 3. As expected, the largest thermal motion is that of the oxygen atom in directions normal to the C-O bond. A final difference map was calculated in order to check on the positions of the hydrogen atoms. This

map showed very few spurious peaks and the positions of most of the hydrogen atoms were clearly indicated. These indicated positions checked closely with those calculated assuming tetrahedral or trigonal bond angles and the distances C-H, N-H = 1.0 Å. To inspect more clearly the hydrogen atoms on the terminal nitrogen atom, a section of the difference map normal to the N-N bond and at a distance of 0.5 Å from N₂ was plotted; this showed two positive peaks positioned in accordance with a pyramidal configuration and with the angle H₇-N₂-H₈ = 85°. The hydrogen-atom parameters are listed in Table 2. These are the calculated parameters for H₁-H₅ (the hydrogen atoms bonded to carbon atoms). H₆—the hydrogen bonded to N₁—showed up exceptionally well on the difference map, and at a distance of 0.96 rather than 1.0 Å from N₁; accordingly, the observed rather than the calculated parameters are listed. The observed parameters are also listed for H₇ and H₈, whose positions could not be adequately calculated.

The hydrogen atom contributions, including an isotropic temperature factor with $B = 3.6 \text{ \AA}^2$, were included in the next structure-factor calculation, with a resulting improvement in R of 1%. A least-squares refinement was then computed, and indicated that further shifts in the 'heavy' atoms were still needed. These shifts tended to move the atoms away from the hydrogens to which they were bonded. Since the anisotropic temperature factors had been introduced prior to including the hydrogen atom contributions in the structure factors, it seemed possible that they might have been affected by overlap of nearby hydrogen atoms. To check on this possible coupling, the second least-squares refinement of the temperature factors was undertaken. Subsequent least-squares on the positional parameters, however, gave negligible shifts.

The final positional parameters are given in Table 2, and in Table 3 are listed the observed and calculated

structure factors. The final R -factor was 0.13, excluding the unobserved reflections.

The bond distances and angles calculated on the basis of the parameters of Table 2 are listed in Table 4 and are shown in Fig. 4.*

Table 4. Bond distances and angles

Bond	d (Å)	Angle	(°)
C ₁ -C ₂	1.478	C ₂ -C ₃ -C ₄	59.7
C ₂ -C ₃	1.520	C ₃ -C ₄ -C ₂	61.5
C ₂ -C ₄	1.493	C ₄ -C ₂ -C ₃	58.8
C ₃ -C ₄	1.478	N ₂ -N ₁ -C ₁	121.3
C ₁ -O	1.213*	N ₁ -C ₁ -O	124.5
C ₁ -N ₁	1.329	O-C ₁ -C ₂	121.9
N ₁ -N ₂	1.429	N ₁ -C ₁ -C ₂	113.6
		C ₁ ¹ -C ₂ ¹ -C ₃	118.3
		C ₁ -C ₂ -C ₁	118.8
		C ₁ -C ₂ -N ₁	123.1

* See footnote.

Discussion

(i) Accuracy of the structure

The standard deviations of the atomic parameters were calculated using the weighted residuals from the least-squares treatment; the average value was 0.010 Å. This leads to an average standard deviation of about 0.015 Å in the bond distances and of about 2° in the bond angles.

(ii) Bond distances and angles

The dimensions of the amide group have not been appreciably affected by the presence of the terminal nitrogen or the conjugative effect of the cyclopropane ring; the angles and distances are essentially the same as those found in simple peptides (Pauling & Corey, 1953). The C₂C₁ON₁ group is planar with a maximum deviation of 0.002 Å; this plane is approximately normal to that of the cyclopropane ring. N₂ and M —the midpoint of the C₃-C₄ bond—are 0.08 Å from this plane.

The N₁-N₂ bond distance of 1.429 Å is shorter than that corresponding to the generally accepted single-bond covalent radius of 0.74 Å for nitrogen (Schoemaker & Stevenson, 1941). Although the difference in electronegativity between the two nitrogen atoms in cyclopropanecarbohydrazide might lead to a small shortening of the N-N bond, we feel that the value of 1.429 Å found in this compound presents evidence that a better value for the 'normal' nitrogen-nitrogen single-bond distance is in the range of 1.43-1.45 Å. Collin & Lipscomb (1951) found the N-N distance in crystalline hydrazine to be 1.46 Å.

The C₁-C₂ bond is significantly shorter than the normal single-bond distance of 1.54 Å. It appears

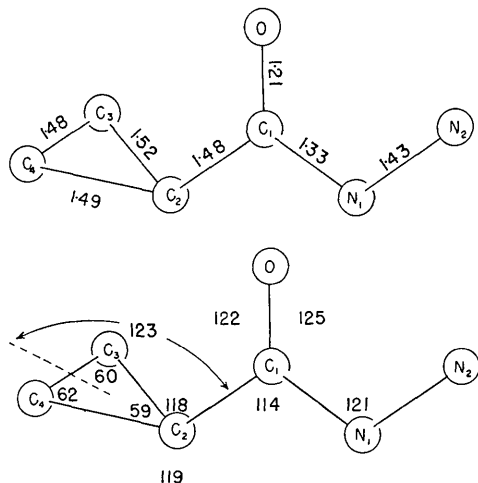


Fig. 4. Bond distances and angles in cyclopropanecarbohydrazide.

* A simple treatment of the temperature factors (Cruickshank, 1956) indicates a shortening of the C₁-O bond length by approximately 0.02 Å due to the differences in the magnitudes of the anisotropic motion of these two atoms. Thus the 'real' C₁-O distance is approximately 1.23 Å. It is felt that similar corrections to the other bond lengths are not justified.

probable that this shortening is brought about by the conjugating power of the cyclopropane ring. In many chemical reactions the cyclopropane group tends to behave like a double bond; in particular, when it is located near an unsaturated linkage such as a carbonyl group or an olefinic double bond, the resulting changes in dipole moments, shifts in absorption spectra, and reaction properties of the molecule can be interpreted on the basis of the conjugation between the cyclopropane ring and the unsaturated linkage.* In Table 5

Table 5. Bond lengths for carbon-carbon single bonds between conjugating systems

Standard deviations are quoted where available

Compound	d (Å)	σ (Å)	Reference
1,3-Butadiene	1.47	—	Bastiansen†
Diphenyl	1.48	—	Bastiansen (1949)
Benzoic acid	1.48	0.016	Sim <i>et al.</i> (1955)
Nicotinamide	1.524	0.017	Wright & King (1954)
1,3,5-Triphenylbenzene	1.51, 1.48, 1.50	0.03	Farag (1954)
Salicylic acid	1.458	0.009	Cochran (1953)
Oxamide	1.542	0.006	Ayerst & Duke (1954)
Oxalic acid dihydrate	1.529	0.020	Ahmed & Cruickshank (1953)

† Private communication quoted by Allen & Sutton (1950).

are listed some distances for carbon-carbon single bonds located between unsaturated or conjugating systems. While the analogy between most of these compounds and cyclopropanecarbohydrazide is far from complete, it is interesting to note that the magnitude of the shortening is about the same. Using Pauling's notation (Pauling, 1940), a C-C distance of 1.48 Å corresponds to about 10–15% double-bond character.

If the C₁-C₂ bond contains some double-bond character, one would expect that the C₃-C₂-C₄ angle in the cyclopropane ring would be slightly greater than 60°, and that the C₃-C₄ bond distance would be the largest in the ring. The opposite effect is, in fact, observed. However, it is felt that the uncertainties in the bond lengths are such that the differences in the ring distances and angles in cyclopropanecarbohydrazide are of doubtful significance.‡ The average distance of

* For a list of references on this topic, see Roberts (1951).

‡ It has been pointed out to us by Prof. Roberts that there is evidence from solvolysis rate studies indicating that a possible stabilization of the bonded amide-cyclopropane system might result from a configuration in which the planes of the amide group and the cyclopropane ring are not normal to one another (Roberts, Bennett & Armstrong, 1950). The nature of this stabilization might be expected to produce asymmetry in the ring bond lengths. Although the sense of the asymmetry observed in the cyclopropane ring in cyclopropanecarbohydrazide is in agreement with these predictions, the value observed for the dihedral angle—89° 22'—is so close to 90° as to make any such effect of doubtful significance. On the basis of Walsh's (1949) model of cyclopropane, one would predict the dihedral angle to be 90°.

1.50 Å is not unreasonable; the generally accepted value for cyclopropane itself is 1.52 Å, while in spiro-pentane (Donohue, Humphrey & Schomaker, 1945) central distances of 1.48 Å are reported. Similar short distances are found in Feist's acid (Peterson, 1956). In ethylene oxide and ethylene sulfide (Cunningham *et al.*, 1951), and the analogous nitrogen compound (Turner, Fiora & Kendrick, 1955), one finds C-C distances of 1.47, 1.49, and 1.48 Å respectively.

(iii) Hydrogen bonds

The hydrogen bond distances and angles are listed in Table 6. Each oxygen atom has associated with it

Table 6. Hydrogen-bond data

Bond	d (Å)	HN...X (°)
N ₁ H ₆ ...O	2.94	6.7
N ₂ H ₃ ...N ₂ '	3.16	10.1
N ₂ H ₇ ...O	3.26	19.9

two hydrogen bonds—one 'strong' bond along the b axis from an α -nitrogen and a long, weak interaction (approximately in the (010) plane) with a terminal nitrogen atom. The main bond is shown as a broken line in Fig. 5; the long NH...O bond (and the

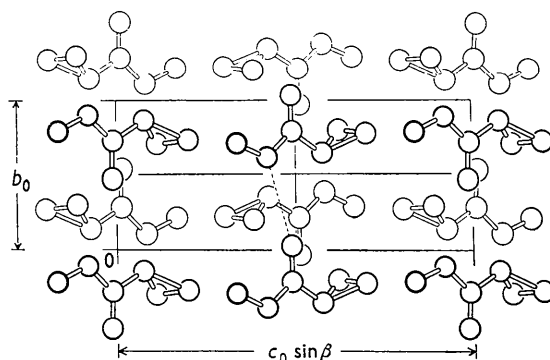


Fig. 5. A view of the structure along the a axis. The broken line shows the strong NH...O hydrogen bond.

NH...N bond) is shown as broken lines in Fig. 6. The long N₂H...O distance (3.26 Å) and the associated angle are such that the bond must be considered a very weak link.

The 3.16 Å distance for the NH...N bond in cyclopropanecarbohydrazide is a little larger than the average value of 3.11 Å found in a tabulation of NH...N distances by Robertson (1953). The NH...N bonds link terminal nitrogens across the twofold screw axis, forming a zigzag chain of hydrogen bonds up the b axis. It is interesting to note that crystalline hydrazine (Collin & Lipscomb, 1951) has non-bonded nitrogens related by a twofold screw axis just as in this case; in hydrazine the distance is 3.19 Å. Although no direct observation of the positions of the hydrogen atoms was made in Collin & Lipscomb's determination, the conclusions at which they arrived

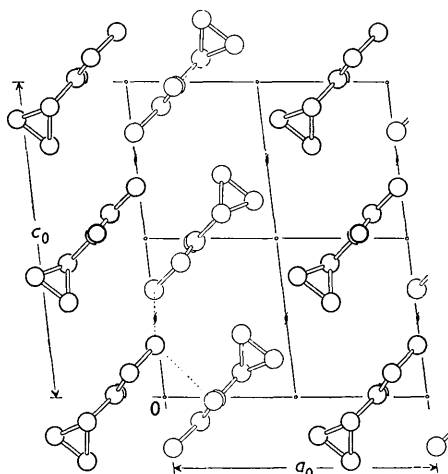


Fig. 6. A view of the structure along the b axis. The broken lines show the $\text{NH}\cdots\text{N}$ and the long $\text{NH}\cdots\text{O}$ hydrogen bonds.

lead to the same sort of $\text{N}\cdots\text{N}$ hydrogen bonding as was found in *cyclopropanecarbohydrazide*.

(iv) *Molecular packing*

Views of the structure along the a and b axes are shown in Figs. 5 and 6. As can be seen in Fig. 6, the molecules form a sheet-like structure, the sheets being oriented parallel to the $(10\bar{1})$ plane. In view of the $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds joining the terminal nitrogen atoms, these sheets are perhaps better described as a two-molecule-wide ribbon running along the b axis in the $(10\bar{1})$ plane. The atomic motions shown in Fig. 3 show a remarkable degree of agreement with the type of thermal vibrations one would expect in this structure; they can be described as a superposition of a molecular motion normal to the sheets and the atomic oscillations to be expected in the free molecule.

Nearly all the intermolecular distances are compatible with the values predicted by Pauling's (1940) van der Waals' radii. The distances between C_3 - and C_4 -type atoms related by a screw axis (see Fig. 6) represent the shorter non-bonding C-C distances in the structure; they are 3.92, 3.76, 3.99, and 4.23 Å, the last two values corresponding to the $\text{C}_3-\text{C}'_3$ and $\text{C}_4-\text{C}'_4$ intermolecular contacts. That these lengths are essentially equal to twice the van der Waals' radius for an unrestricted methyl group is indicative of a rather loose packing, an effect one might expect with the relatively large thermal motion found in the crystal.

The authors wish to thank Prof. J. D. Roberts for providing the crystals used in this investigation, and for helpful discussions.

References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
 ALLEN, P. W. & SUTTON, L. E. (1950). *Acta Cryst.* **3**, 46.
 AYERST, E. M. & DUKE, J. R. C. (1954). *Acta Cryst.* **7**, 588.
 BASTIANSSEN, O. (1949). *Acta Chem. Scand.* **3**, 408.
 BERGHUIS, J., HAANAPPEL, I. J. M., POTTERS, M., LOOPSTRA, B. O., VEENENDAAL, A. L. & MACGILLAVRY, C. H. (1955). *Acta Cryst.* **8**, 478.
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
 COCHRAN, W. (1953). *Acta Cryst.* **6**, 260.
 COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 10.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
 CUNNINGHAM, G. L., BOYD, A. W., MYERS, R. J. & GWINN, W. D. (1951). *J. Chem. Phys.* **19**, 676.
 DAVIES, D. R. & BLUM, J. J. (1955). *Acta Cryst.* **8**, 129.
 DONOHUE, J., HUMPHREY, G. L. & SCHOMAKER, V. (1945). *J. Amer. Chem. Soc.* **67**, 332.
 FARAG, M. S. (1954). *Acta Cryst.* **7**, 117.
 HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 JENSEN, L. H. & LINGAFELTER, E. C. (1953). *Acta Cryst.* **6**, 300.
 McWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 PASTERNAK, R. A. (1956). *Acta Cryst.* **9**, 341.
 PAULING, L. (1940, reprinted 1948). *The Nature of the Chemical Bond*, pp. 175, 189. Ithaca: Cornell University Press.
 PAULING, L. & COREY, R. B. (1953). *Proc. Royal Soc. B.* **141**, 10.
 PETERSON, D. R. (1956). *Chemistry and Industry*, 904-905.
 ROBERTS, J. D., BENNETT, W. & ARMSTRONG, R. (1950). *J. Amer. Chem. Soc.* **72**, 3329.
 ROBERTS, J. D. (1951). *J. Amer. Chem. Soc.* **73**, 2959.
 ROBERTS, J. D. & MAZUR, R. H. (1951). *J. Amer. Chem. Soc.* **73**, 2509.
 ROBERTSON, J. M. (1953). *Organic Crystals and Molecules*, pp. 243-5. Ithaca: Cornell University Press.
 SCHOMAKER, V. & STEVENSON, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157.
 TURNER, T. E., FIORA, V. C. & KENDRICK, W. M. (1955). *J. Chem. Phys.* **23**, 1966.
 WALSH, A. D. (1949). *Trans. Faraday Soc.* **45**, 179.
 WASER, J. (1955). *Acta Cryst.* **8**, 731.
 WRIGHT, W. B. & KING, G. S. D. (1954). *Acta Cryst.* **7**, 283.