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The Crystal Structure of Parabanic Acid*

By David R. Davies† and J. J. Blum‡

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

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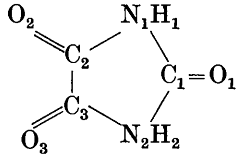
Parabanic acid, $(CO)_3(NH)_2$, crystallizes in the space group $P2_1/n$. The unit-cell dimensions are $a = 10{\cdot}685$, $b = 8{\cdot}194$, $c = 5{\cdot}054$ Å, $\beta = 92° 44'$, and $Z = 4$. A precise determination of the atomic coordinates has been carried out by the method of least squares. Separate anisotropic temperature factors have been assigned to each atom, and the thermal vibration parameters have been refined by least-squares treatment.

Introduction

The crystal structures of two substances containing *cis* amide groups have hitherto been investigated. They are diketopiperazine (Corey, 1938) and cyanuric acid (Wiebenga & Moerman, 1938; Wiebenga, 1952). In each of these substances the hydrogen bonds form an eight-membered ring system with opposite atoms in the ring connected by a symmetry centre. Cyanuric acid also forms a second kind of hydrogen bond, with the line connecting the N and O atoms parallel to the C–O bond, and the results of infra-red examination have shown that there is a large splitting of the N–H valence vibrations, indicating that these two types of hydrogen bond are considerably different (Newman & Badger, 1952), although the NH · · · O bond lengths are equal. The investigation of the crystal structure of parabanic acid was undertaken to discover the nature of its hydrogen bond system so that a comparison might be made between its infra-red spectrum and those of diketopiperazine and cyanuric acid, in the light of the known crystal structure. It is also of interest to compare the dimensions of the ring with those obtained in previous structure determinations of related compounds.

Experimental

Parabanic acid



prepared by the method of Menshutkin (1874) was kindly given to us by Dr D. Pullin of this laboratory. Crystals were easily grown by slowly cooling a hot concentrated water solution. They were well formed and varied from prismatic to tabular, with (100) and (010) well developed.

The crystals belong to the monoclinic system with the space group $P2_1/n$. The cell constants were determined from [010] and [001] rotation photographs taken in a powder camera of approximately 5 cm. radius, with the film in the Straumanis position. The crystals used were small, with a cross-sectional diameter of about 0·2 mm. A number of measurements were made with a measuring instrument designed and constructed in this laboratory on those high-order spectra which were clearly resolved into α_1 and α_2. The number of such spectra was increased by the fact that the X-ray tube yielded radiation characteristic of iron in addition to the original copper $K\alpha$ radiation, and these iron lines were also used in the determination of the cell constants. A least-squares analysis of these spectra yielded the following cell constants:

$$a = 10{\cdot}685 \pm 0{\cdot}001,\ b = 8{\cdot}194 \pm 0{\cdot}001,$$
$$c = 5{\cdot}054 \pm 0{\cdot}001 \text{ Å},\ \beta = 92° 44' \pm 2'.$$

The uncertainties quoted are the standard deviations obtained from the least-squares analysis. The wavelengths used in this determination were those tabulated in *Acta Cryst.* (1948), **1**, 46. The ratios

$$a/b : b/b : c/b = 1{\cdot}304 : 1 : 0{\cdot}6156\ ,$$

compare well with the values quoted in Groth (1910):

$$1{\cdot}3013 : 1 : 0{\cdot}6168\ .$$

The density was found by flotation to be 1·721 g.cm.$^{-3}$. There are four molecules in the unit cell. The crystals cleave well in the plane perpendicular to [010]. Optical measurements showed no evidence of any marked birefringence.

Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. The crystals used to obtain the data were cut from larger crystals and were square in cross-section, with thickness between 0·25 and 0·20 mm. Attempts to obtain crystals of cylindrical shape by grinding or dissolving the edges were un-

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* Contribution No. 1931 from the Gates and Crellin Laboratories of Chemistry.

† Present address: Research Department, Albright and Wilson Ltd, Oldbury, Birmingham, England.

‡ Merck Fellow, 1952–1953. Present address: Naval Medical Research Institute, Bethesda, Md., U.S.A.

successful, and always resulted in splitting the crystals. Data were obtained for the 0, 1, ..., 4th layers of the c axis, the 0, 1, ..., 5th layers of the b axis and the equatorial layer of the a axis. The multiple-film technique was used in collecting the data and the intensities were measured by visual comparison with an intensity scale. The intensities were measured independently by each of the authors.

After the intensities were put on a single scale by correlating the various layers, they were then placed on an absolute scale by the method of Wilson (1942). A temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$, with $B = 2{\cdot}5$ Å^2, was also obtained from this calculation. Atomic-form-factor curves of James & Brindley (*Internationale Tabellen*, 1935) were used for the trial structure determination, and in the early stages of refinement.*

Determination of the trial structure

The presence of the cleavage plane suggested a layer structure with hydrogen bonds parallel to (010). The observed lack of negative birefringence, however, implied that the molecules themselves could not lie wholly in this plane, but must be inclined to it.

A preliminary examination of the possible packing and hydrogen bonding in the crystal resulted in a trial structure which satisfied the above conditions. In this trial structure the molecules were arranged on the glide plane approximately as shown in Fig. 4(a), which gives the final arrangement of the molecules. The molecules were tilted so that the axis of the molecule made an angle of 30° with (010), and the pairs of chemically equivalent atoms had the same y coordinates. There was then an excellent arrangement of hydrogen bonds between molecules related by the operation of the glide plane, provided that the glide plane cut roughly through the centre of the molecule.

In this trial structure the orientation of the molecule is known and, by making use of the directional property of the hydrogen bonds, approximate y coordinates may be obtained. The x and z coordinates, however, are not known, since in order to determine these coordinates it is necessary to know the location of the twofold screw axes which relate the molecules on one glide plane with those on the glide planes $b/2$ above and below. To obtain this information, a three-dimensional Patterson function was computed.

Examination of the peaks around the origin of the Patterson function confirmed the orientation of the molecule in the unit cell, and showed that the angle of tilt to (010) should be increased to 33°.

In this trial arrangement of the molecules, the pairs of atoms O_2, O_3; N_1, N_2; C_2, C_3 have the same y coordinates: it follows that there will be a line of double weight (non-Harker) peaks on the Harker section at $(u, \frac{1}{2}, w)$. These peaks arise from vectors between pairs of atoms such as that between the atom O_2 at (x_2, y_2, z_2) and the atom O_3' at $(\frac{1}{2}-x_3, \frac{1}{2}+y_3, \frac{1}{2}-z_3)$, which would bisect the line between the Harker peaks corresponding to O_2 and O_3. They are discussed at length by Donohue & Trueblood (1952). Since the axis of the molecule, when projected on to (010), is parallel to c, it follows that this line of three peaks on the Harker section will be parallel to w.

Examination of the Harker section showed that there was only one such line of peaks, and when a double-scale projection of the molecule on to (010) was placed on the Harker section, there was only one position which fitted the observed peaks. The Harker section is shown in Fig. 1 and the positions of the vectors corresponding to the final coordinates of the molecule are superimposed.

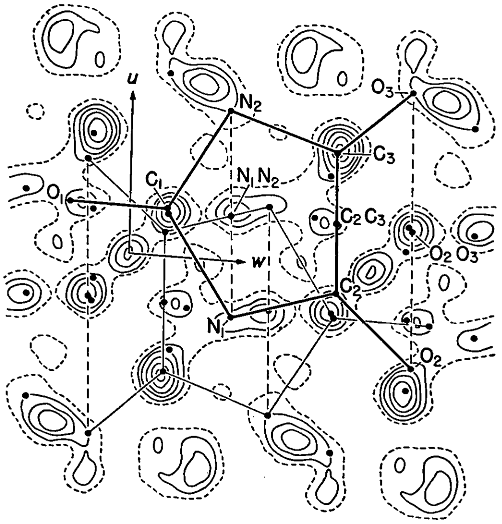

Fig. 1. The Harker section $P(u, \frac{1}{2}, w)$. Harker interactions and those non-Harker interactions between the pairs of atoms N_1, N_2; C_2, C_3; O_2, O_3, are marked.

Improved y coordinates were obtained from an examination of the general Patterson peaks, and the (x, y, z) coordinates for the trial structure were then used to calculate $h0l$, $hk0$ and $0kl$ structure factors. Electron-density projections down the three crystal axes were prepared, and resulted in small adjustments to the original coordinates. Structure factors were recalculated with the new coordinates, and showed a fair measure of agreement with the observed amplitudes, with the residual $R = 0{\cdot}24$.

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* A table containing F_o and F_c values for about 900 reflections has been withdrawn and is deposited as Document No. 4418 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$3·75 for photoprints, or \$2·00 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. A copy may also be obtained from the authors.

Refinement of the positional parameters

Four electron-density projections were now calculated: Two $h0l$ syntheses, one with the observed structure factors, F_o, and the other with the calculated structure factors, F_c; and two $hk0$ syntheses, F_o and F_c. The back-shift corrections obtained from the F_c syntheses were applied to the coordinates obtained from the F_o syntheses (Booth, 1946). These coordinates were then used to calculate a half-cell projection down the b axis. This shows all the atoms of the molecule resolved, and with these new x and z coordinates and the old y coordinates, a least-squares refinement (Hughes, 1941) was carried out on the y parameters alone, with the three-dimensional data.

For this refinement all the off-diagonal terms of the type $\sum_{hkl} (\partial F/\partial y_i)(\partial F/\partial y_j)$ were calculated, but the difference produced in the shifts by inclusion of these terms was small, being one-seventh of the total shift. It was therefore decided to neglect the off-diagonal terms in future refinements.

A second refinement of the y parameters with only the diagonal terms was calculated. Comparison of the observed and calculated structure factors used in this refinement showed that better agreement could be obtained if the calculated structure factors were multiplied by a factor $\exp(-B'k^2b^{*2})$. New structure factors were calculated, using McWeeny atomic form factors (McWeeny, 1951). Comparison of these structure factors with the observed values showed that good agreement could be obtained with a temperature factor of the form

$$\exp(-B \sin^2 \theta/\lambda^2) \exp(-B'k^2b^{*2}),$$

where $B = 1{\cdot}85$ Å^2, and $B' = 0{\cdot}134$ Å^2. The scale factor was also adjusted and this set of structure factors then showed the same agreement with F_o, whether they were arranged in groups according to $\sin\theta$, h, k, or l.

A three-dimensional least-squares refinement of the 24 positional parameters was carried out. A new set of structure factors calculated with these parameters showed good agreement with F_o, the value of R being 0·16. A second three-dimensional least-squares refinement gave average shifts of 0·004 Å, the maximum shift being 0·016 Å in x_3, as can be seen from Table 1.

Table 1. *The atomic coordinates obtained from the first and second three-dimensional least squares analysis for the positional parameters*

	x/a		y/b		z/c	
Atom	1	2	1	2	1	2
C_1	0·2984	0·2985	0·3702	0·3697	0·3294	0·3299
C_2	0·2241	0·2245	0·2307	0·2303	0·6764	0·6761
C_3	0·3681	0·3666	0·2073	0·2081	0·6697	0·6716
N_1	0·1934	0·1936	0·3272	0·3267	0·4656	0·4645
N_2	0·4016	0·4014	0·2952	0·2949	0·4571	0·4565
O_1	0·2998	0·3002	0·4513	0·4509	0·1313	0·1303
O_2	0·1565	0·1569	0·1736	0·1731	0·8389	0·8398
O_3	0·4326	0·4323	0·1299	0·1294	0·8262	0·8264

A three-dimensional $(F_o - F_c)$ synthesis was next computed. Examination of this synthesis showed that there were peaks of maximum height about 0·7 e.Å^{-3}, and of irregular shape and indeterminate centres, in approximately the positions where the hydrogen atoms would be expected, that is, about 1·0 Å from the nitrogen atoms and along the bisector of the CNC angle. An unexpected feature of this synthesis was the evidence of marked anisotropy of the three oxygen atoms. It was apparent that a correction of this anisotropy would considerably improve the agreement between the observed and calculated structure factors, particularly for the high-order spectra. Although the resulting shifts in atomic coordinates would probably be small, this correction would clearly reduce the standard deviations of the coordinates. It was therefore decided to correct for this anisotropy, and to treat it as anisotropy in the thermal vibration parameters of the atoms, although it is well known that the oxygen atoms possess inherent anisotropy in their electron densities.

Cochran (1951) has demonstrated how anisotropy in the thermal vibration of atoms may be corrected by examination of $(F_o - F_c)$ syntheses. However, in this case, it was considered more convenient to calculate the thermal vibration parameters by the method of least squares.

Refinement of the thermal vibration parameters

The modified atomic form factors of each atom,

$$f_i \exp(-B \sin^2 \theta/\lambda^2) \exp(-B'k^2b^{*2}),$$

were regarded as being further modified by the factor

$$\exp -(\alpha_i h^2a^{*2} + \beta_i k^2b^{*2} + \gamma_i l^2c^{*2} + \delta_i hka^*b^* + \varepsilon_i klb^*c^* + \eta_i hla^*c^*) \quad (1)$$

and the coefficients α_i, β_i, γ_i, δ_i, ε_i, and η_i could then be determined by the method of least squares.

A set of structure factors was calculated with the coordinates obtained from the second three-dimensional least-squares adjustment. Hydrogen atoms were included in these structure factors with coordinates (Table 2) obtained by placing the atoms H_1 and H_2 1·0 Å from N_1 and N_2 respectively, and on the bisector of the angles $C_1N_1C_2$ and $C_2N_2C_3$. The hydrogen scattering factors were modified by a temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$, where $B = 1$ Å^2, and their contributions were added to the structure factors for the other atoms up to $\sin\theta = 0{\cdot}5$.

Table 2. *Hydrogen atom coordinates*

Atom	x/a	y/b	z/c
H_1	0·108	0·361	0·415
H_2	0·492	0·303	0·397

An initial refinement was then undertaken in which one axis of the ellipsoid of vibration was assumed to be parallel to the twofold symmetry axis of the crystal, that is, the coefficients δ_i and ε_i were taken to be zero. This refinement led to a slight improvement in the structure-factor agreement, and reduced the value of R from 0·147 to 0·137.

A second refinement was therefore carried out in which the general case (1) was considered. It was pointed out by Dr J. Rollett (private communication) that if there is an atom at (x, y, z) with temperature factor (1), then the temperature factor of the atom at $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, related to this by the twofold screw axis, is

$$\exp\,(-\alpha_i h^2a^{*2}-\beta_i k^2b^{*2}-\gamma_i l^2c^{*2} \\ +\delta_i hka^*b^*+\varepsilon_i klb^*c^*-\eta_i hla^*c^*)\,.$$

The expression for the structure factor for this space group then becomes

$$F(hkl) = \sum_i 2f'_i \exp\,(-a_i) \\ \times\{[\exp\,(-b_i)+\exp\,(+b_i)] \cos 2\pi(hx_i+lz_i) \cos 2\pi ky_i \\ +[\exp\,(+b_i)-\exp\,(-b_i)] \sin 2\pi(hx_i+lz_i) \sin 2\pi ky_i\} \quad (2)$$

for $h+k+l$ even, with a corresponding expression for $h+k+l$ odd, where

$$f'_i(hkl) = f_i(hkl) \exp\,(-B \sin^2 \theta/\lambda^2) \exp\,(-B'k^2b^{*2}),$$
$$a_i = (\alpha_i h^2+\beta_i k^2+\gamma_i l^2+\eta_i hl), \text{ and}$$
$$b_i = (\delta_i hk+\varepsilon_i kl).$$

The structure-factor expressions for centrosymmetric monoclinic space groups, with anisotropic thermal vibrations are derived and listed by Rollett & Davies (1955). This least-squares refinement, which was carried out with the diagonal terms only, led to a marked improvement in the agreement between F_o and F_c, giving $R = 0{\cdot}11$. The scale factor was then adjusted by least squares, and a final simultaneous refinement of the thermal-vibration parameters and the positional parameters was carried out. The shifts in the positional parameters which resulted were small, with an average value of 0·003 Å, and a maximum value of 0·009 Å. The final values of the positional parameters for one molecule are shown in Table 3. Structure factors calculated with these final parameters gave $R = 0{\cdot}09$. The unobserved spectra were included in this calculation with zero amplitude for F_o.

Table 3. *The final coordinates*

	x/a	y/b	z/c
C_1	0·2989	0·3690	0·3293
C_2	0·2242	0·2304	0·6755
C_3	0·3673	0·2085	0·6710
N_1	0·1940	0·3278	0·4642
N_2	0·4011	0·2948	0·4560
O_1	0·3005	0·4509	0·1298
O_2	0·1570	0·1730	0·8392
O_3	0·4322	0·1293	0·8256

The effect of the off-diagonal coefficients on the least-squares refinement of the thermal vibration parameters

The normal equations of the least squares refinement may be written

$$\sum_{hkl} \omega_{hkl}(F_o(hkl)-F_c(hkl))\left(\frac{\partial F_c(hkl)}{\partial \xi_i}\right) \\ = \sum_{hkl}\left\{\sum_j \omega_{hkl}\left(\frac{\partial F_c(hkl)}{\partial \xi_i}\right)\left(\frac{\partial F_c(hkl)}{\partial \xi_j}\right) \Delta\xi_j\right\},$$

where ω_{hkl} is a weight factor, and the $\Delta\xi_j$ are the corrections to be solved for and added to the values of ξ_j used to calculate the quantities $F_c(hkl)$. It has been demonstrated by Shoemaker *et al.* (1950) that, for refinement of the positional parameters alone, with three-dimensional data in an orthogonal unit cell, the errors resulting from neglect of the off-diagonal coefficients are small. These off-diagonal coefficients were therefore omitted from the normal equations in this refinement. In the refinement of the thermal vibration parameters, however, analysis shows and observation confirms that certain of the off-diagonal coefficients are significantly large and cannot be neglected.

If $F_i(hkl)$ is the contribution of the ith atom to the structure factor $F_c(hkl)$, then, from (2),

$$\partial F_c(hkl)/\partial\alpha_i = -h^2a^{*2}F_i(hkl)\,,$$
$$\partial F_c(hkl)/\partial\beta_i = -k^2b^{*2}F_i(hkl)\,,$$
$$\partial F_c(hkl)/\partial\gamma_i = -l^2c^{*2}F_i(hkl)\,,$$

and the diagonal coefficients are then

$$\sum_{hkl} \omega_{hkl}\left(\frac{\partial F_c(hkl)}{\partial \alpha_i}\right)^2 = \sum_{hkl} \omega_{hkl}h^4a^{*4}F_i^2(hkl)\,.$$

The off-diagonal coefficients for interactions of the type $\alpha_i\beta_i$ are

$$\sum_{hkl} \omega_{hkl}\left(\frac{\partial F_c(hkl)}{\partial \alpha_i}\right)\left(\frac{\partial F_c(hkl)}{\partial \beta_i}\right) = \sum_{hkl} \omega_{hkl}h^2k^2a^{*2}b^{*2}F_i^2(hkl)\,.$$

For a three-dimensional analysis the magnitude of these coefficients will be approximately one-third that of the diagonal coefficients (Schomaker, V., private communication). Calculation of off-diagonal coefficients of this type confirmed this, and to a first approximation their magnitudes may be assumed to be one-third that of the diagonal coefficients for all future calculations.

It can be demonstrated that the magnitudes of all the off-diagonal coefficients representing the interactions between the thermal vibration parameters, except those between α_i, β_i and γ_i, will be small compared to the magnitudes of the diagonal coefficients. This conclusion was confirmed by calculation of a number of these coefficients. All the coefficients involving interactions between the thermal-vibration parameters and the scale factor were computed; their inclusion resulted in very small changes in the thermal-vibration parameters and a change of 3% in the scale factor.

The final values of the total thermal-vibration parameters, including the parameters for isotropic vibration, are given in Table 4. They were obtained from the values of B, B', α_i, . . . , η_i, as follows:

$$\alpha_i = \alpha_i+\tfrac{1}{4}B, \qquad \beta_i' = \beta_i+\tfrac{1}{4}B+B',$$
$$\gamma_i' = \gamma_i+\tfrac{1}{4}B, \qquad \eta_i' = \eta_i+\tfrac{1}{2}B\cos\beta^*,$$
$$\delta_i' = \delta_i, \qquad \varepsilon_i' = \varepsilon_i\,.$$

Table 4. *The temperature factor coefficients*

Values in Å²

Atom	α'	β'	γ'	δ'	ε'	η'
C_1	0·559	0·443	0·495	0·084	0·085	0·070
C_2	0·265	0·501	0·421	−0·004	−0·094	0·029
C_3	0·280	0·568	0·476	0·002	0·253	0·033
N_1	0·377	0·502	0·502	0·144	0·106	−0·111
N_2	0·362	0·698	0·580	0·015	0·332	0·220
O_1	0·943	0·600	0·584	−0·083	0·347	0·070
O_2	0·276	0·742	0·594	−0·082	0·036	0·334
O_3	0·338	0·878	0·871	−0·061	0·775	−0·252

The final thermal-vibration parameters

In order to examine the anisotropy of the atoms more closely, a transformation to the principal axes of the ellipsoids of vibration was made for the three oxygen atoms. These parameters are then expressed in the form

$$\sum_{i=1}^{3} q_i(g_{i1}ha^*+g_{i2}kb^*+g_{i3}lc^*)^2.$$

The q_i are thermal-vibration parameters for the three principal axes of the ellipsoid, and g_{i1}, g_{i2}, and g_{i3} are the direction cosines of these principal axes with respect to a^*, b^* and c^*, respectively. A description of this transformation is given by Rollett & Davies (1955). The values of q_i, g_{i1}, g_{i2}, and g_{i3} are given in Table 5 for the three oxygen atoms the coordinates of which are listed in Table 3. There is good qualitative agreement between the thermal-vibration parameters for the three oxygen atoms and the anisotropies indicated on the (F_o-F_c) synthesis.

Table 5. *Principal axis parameters for the three oxygen atoms*

Atom	i	q_i	g_{i1}	g_{i2}	g_{i3}
O_1	1	0·9515	0·981	−0·166	−0·101
	2	0·411	0·040	−0·694	0·719
	3	0·764	0·199	0·701	0·684
O_2	1	0·746	−0·066	0·996	−0·064
	2	0·208	−0·9195	−0·085	−0·383
	3	0·644	−0·388	0·026	0·921
O_3	1	1·278	−0·086	−0·691	−0·717
	2	0·267	−0·880	−0·285	0·380
	3	0·5565	−0·471	0·661	−0·584

The accuracy of the structure

The standard deviations, $\sigma(x_i)$, for the atomic coordinates were calculated from the diagonal coefficients alone of the least-squares equations (Shoemaker *et al.* 1950). They are very low, with an average value of 0·003 Å. It may safely be assumed that the effect of neglecting the off-diagonal coefficients for interactions between positional parameters will not produce a significant error in these standard deviations, and therefore these low values are entirely due to the small value of $\sum_{hkl}(F_o-F_c)^2$. If there are no systematic errors in the data which have been corrected by the use of anisotropic thermal vibration parameters, these values will give a fair estimate of the standard deviations of the coordinates. However, since there may be some systematic errors due to the variation in spot shapes in the higher layers of equi-inclination Weissenberg photographs, and possible errors in the correlation of the different layers, it is more probable that the true standard deviations are intermediate in magnitude between these values and the original values obtained before refinement of the thermal-vibration parameters. The average value of these original standard deviations was 0·006 Å, so that standard deviations of the order of 1·5 times those quoted in Table 8 would probably be more indicative of the accuracy of the parameters.

The bond lengths before and after refinement of the thermal vibration parameters are listed in Tables 6 and 7 respectively. The only large changes are in the bonds C_2–C_3 (0·011 Å) and C_1–N_1 (0·008 Å).

Table 6. *Bond lengths before refinement of the thermal vibration parameters*

Bond	Length (Å)
O_1–C_1	1·208
C_1–N_1	1·383
C_1–N_2	1·388
N_1–C_2	1·356
N_2–C_3	1·364
C_2–O_2	1·217
C_3–O_3	1·211
C_2–C_3	1·530

Table 7. *Bond lengths and angles after refinement of the thermal vibration parameters*

	Length (Å)		Angle
O_1–C_1	1·212	O_1–C_1–N_1	126° 10′
C_1–N_1	1·382	O_1–C_1–N_2	125° 58′
C_1–N_2	1·380	N_1–C_1–N_2	107° 49′
N_1–C_2	1·360	C_1–N_1–C_2	111° 20′
N_2–C_3	1·360	C_1–N_2–C_3	111° 25′
C_2–O_2	1·216	N_1–C_2–C_3	104° 47′
C_3–O_3	1·208	N_2–C_3–C_2	104° 40′
C_2–C_3	1·541	N_1–C_2–O_2	129° 30′
		N_2–C_3–O_3	129° 2′
		O_2–C_2–C_3	125° 44′
		O_3–C_3–C_2	126° 18′

Application of significance tests (Cruickshank, 1949) shows that the difference in the final lengths of the bonds C_2–O_2, C_3–O_3 is not significant ($\delta l/\sigma = 1{\cdot}40$). The mean of these bonds is identical with the length of C_1–O_1, 1·212 Å. Similarly, the pairs of chemically equivalent bonds C_1–N_1 and C_1–N_2, and C_2–N_1 and C_3–N_2 are not significantly different in length, and therefore their mean values may be used. The same is true of the chemically equivalent angles. However, the difference between the mean of the lengths of the

Table 8. *Averaged bond lengths and bond angles with their standard deviations*

Bond	Length (Å)	$\sigma(l)$ (Å)	Angle	θ (°)	$\sigma(\theta)$ (°)
C_1–O_1	1·212	$0{\cdot}004_0$	O_1–C_1–N_1	126·1	0·2
C_1–N_1	1·381	$0{\cdot}003_3$	N_1–C_1–N_2	107·8	0·3
N_1–C_2	1·360	$0{\cdot}003_3$	C_1–N_1–C_2	111·4	0·2
C_2–C_3	1·541	$0{\cdot}004_7$	N_1–C_2–C_3	104·7	0·2
C_2–O_2	1·212	$0{\cdot}003_0$	N_1–C_2–O_2	129·3	0·2
			O_2–C_2–C_3	126·0	0·2

bonds C_1–N_1 and C_1–N_2 and the mean of C_2–N_1 and C_3–N_2 is significant ($\delta l/\sigma = 4{\cdot}84$), and these bonds cannot therefore be regarded as being equivalent.

The mean values of the bond lengths and bond angles, together with their standard deviations, are listed in Table 8. A drawing of the molecule with these bond lengths and angles is reproduced in Fig. 2.

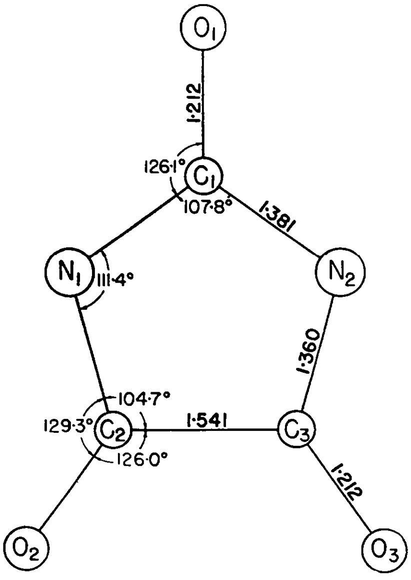

Fig. 2. The final mean bond lengths and bond angles.

The planarity of the molecule

The best plane through the eight heavy atoms of the molecule was obtained by least squares. The deviations, Δ, of the atoms from this plane are given in Table 9, column (*a*). To estimate the significance of the departure of these atoms from planarity, a χ^2 test was made (Wheatley, 1953). The values of Δ_i/σ_i were calculated, and from them

$$\chi^2 = \sum_{i=1}^{8} \left(\frac{\Delta_i}{\sigma_i}\right)^2$$

was evaluated.

Table 9. *Deviations of the atoms from a least-squares plane through* (*a*) *all 8 atoms*; (*b*) *the 5 ring atoms*

Atom	(*a*)	(*b*)
C_1	0·0135 Å	0·0037 Å
C_2	−0·0050	−0·0018
C_3	0·0038	0·0041
N_1	0·0021	0·0004
N_2	0·0015	−0·0056
O_1	−0·0124	−0·0272
O_2	0·0035	0·0132
O_3	−0·0042	−0·0005

The value of χ^2 was found to be 46·9; examination of the tables of χ^2 given by Weatherburn (1947) shows that for a system with five degrees of freedom, this value indicates a highly significant departure from planarity. However, this plane passes very closely through the six atoms N_1, N_2, C_2, C_3, O_2 and O_3, and for these atoms the value of χ^2 is 9·62. For a system with three degrees of freedom this represents a possibly significant departure from planarity. However, χ^2 for the best plane through these six atoms will certainly be still smaller; therefore, without independent confirmation, these atoms cannot be regarded as being significantly non-planar.

The best plane through the five ring atoms was also obtained, and in Table 9, column (*b*), the distances of the atoms from this plane are given. Application of the χ^2 test shows that these five atoms and the oxygen atom O_3 are not significantly displaced from this plane. However, the atoms O_1 and O_2 show significant deviations from this plane with $\Delta/\sigma = 10{\cdot}1$, and 5·3, respectively.

Thus there are two planes, each containing six atoms, which can be defined in the molecule, and the atom O_1 is displaced by a significantly large distance from each of these planes. This may be compared with the ethylenethiourea molecule (Wheatley, 1953), where the five ring atoms lie on a plane, but the sulphur atom is displaced from this plane by 0·03 Å, which is significantly large. Calculations carried out there showed that the energy involved in bending the C–S bond by such a small amount is very small compared with the lattice energy and a similar calculation shows that the same is true for the C–O bond. It is probable that these small deviations from planarity are the result of the unsymmetrical environment of the molecule.

Discussion of the structure

The arrangement of the molecules viewed down [010] and the shortest intermolecular distances are shown in Fig. 3.* The molecules are inclined by 36° to (010). Neighbouring molecules related by the *n* glide plane are linked in sheets by NH · · · O hydrogen bonds; a representation of this arrangement is shown in Fig. 4(*a*). The lengths of these bonds are $N_1 \cdots O_3' = 2{\cdot}873$; $N_2 \cdots O_2'' = 2{\cdot}837$ Å, and they may be compared with the values of 2·83 and 2·88 Å found in cyanuric acid (Wiebenga, 1952) and 2·84 Å in diketopiperazine (Corey, 1938). The oxygen atom O_1 is not

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Note added in proof, 5 *February* 1955.—Some of the intermolecular contacts showns in Fig. 3 were overlooked by us and were called to our attention by Mr E. H. Medlin. They included the distances of 2·77 Å between O_1 and C_2 which is rather surprisingly short.

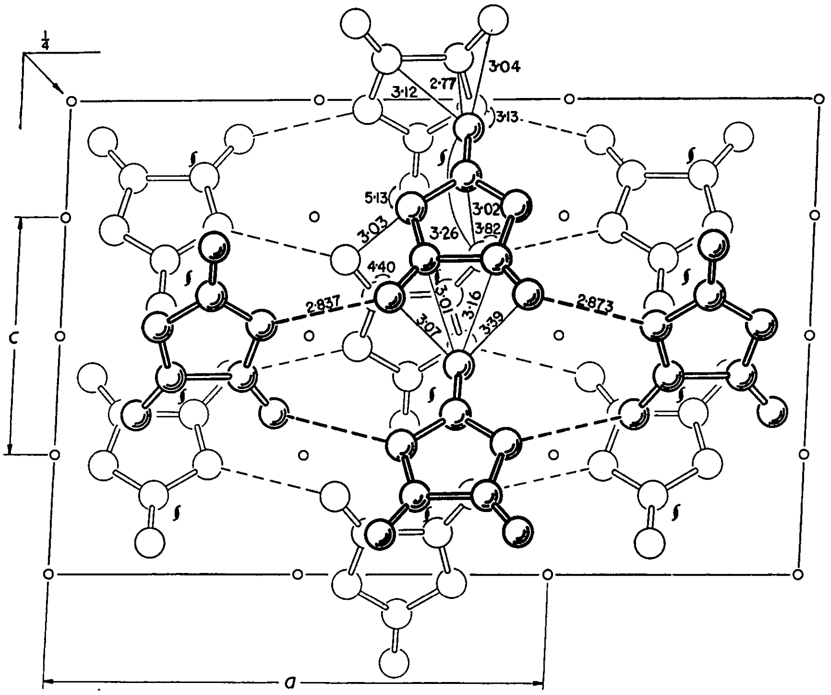


Fig. 3. The arrangement of molecules viewed down the *b* axis, showing the shortest intermolecular distances. Heavy lines denote molecules centred on one glide plane and light lines denote those on the glide plane $\frac{1}{2}b$ below this.

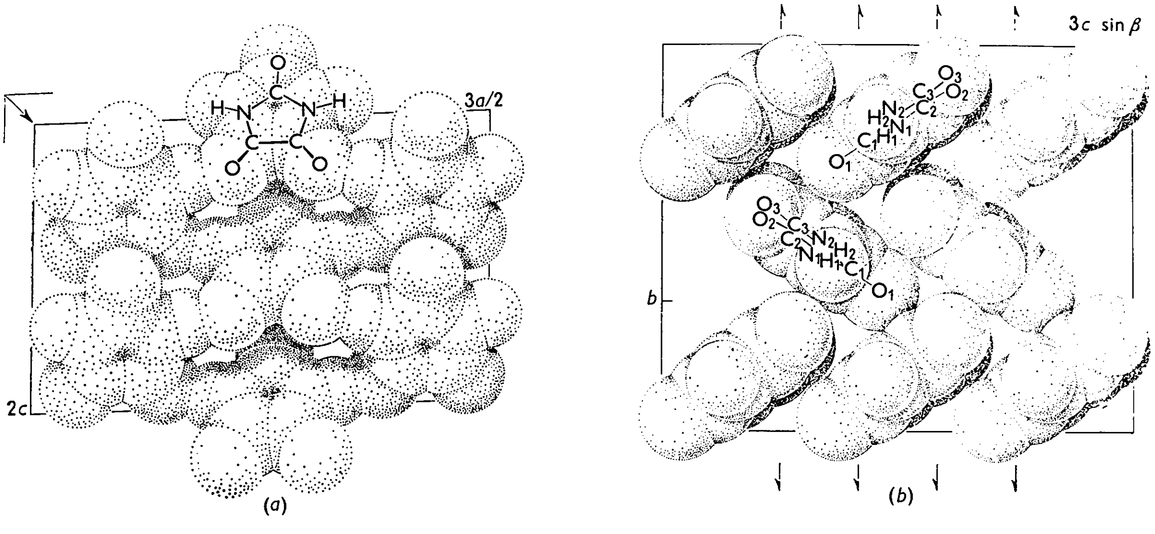


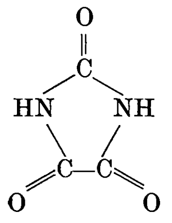
Fig. 4. (*a*) The packing and hydrogen-bond system between molecules related by the glide plane, viewed down the *b* axis as a slice of thickness $\frac{1}{2}b$.

(*b*) The arrangement of molecules related by the twofold screw axis, viewed down the *a* axis as a slice of thickness $\frac{1}{2}a$.

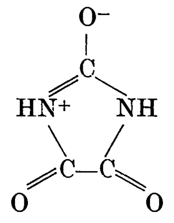
involved in hydrogen-bond formation. The arrangement of hydrogen bonds is, however, different from that found in cyanuric acid and diketopiperazine, where the bonds form an eight-membered ring system, with opposite atoms of the ring related by a centre of symmetry.

Molecules on one glide plane are related to those on the adjacent glide plane by the action of the twofold screw axis. A representation of the packing of the molecules related by this screw axis, viewed down [100] from $x = 0$ to $x = \frac{1}{2}$, is given in Fig. 4(*b*).

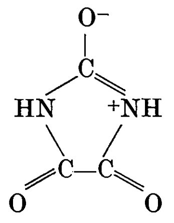
It is of interest to discuss the observed bond lengths in terms of resonance theory. Consider the eight valence-bond structures



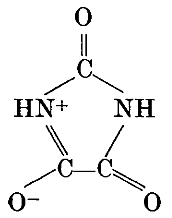
A



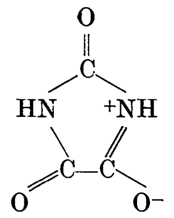
B



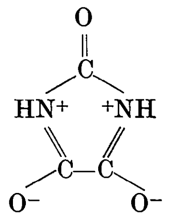
C



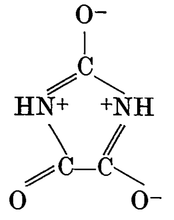
D



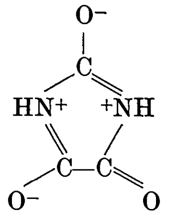
E



F



G



H

The observed length of the bond C_2–C_3, 1·541 Å, is consistent with the single-bond character of C_2–C_3 in all structures. The bond C_1–N_1 (1·381 Å) we believe to be significantly longer than C_2–N_1 (1·360 Å); the former is double bonded in two structures, *B* and *G*, while the latter is double bonded in three, *D*, *F* and *H*. The mean C–N bond length in cyanuric acid, 1·355± 0·012 Å, does not differ significantly from our values. In urea (Vaughan & Donohue, 1952) and in ethylenethiourea (Wheatley, 1953), however, the C–N bonds (1·335 and 1·322 Å, respectively) are shorter than in parabanic acid, in agreement with expectations based on comparison of the above structures with corresponding structures for urea.

Bond length is related to double-bond character by Pauling's (1940) equation. For standard single- and double-bond lengths we have adopted the values used by Vaughan & Donohue (1952) of 1·48 and 1·24 Å for C–N single- and double-bond lengths respectively, and 1·42 and 1·20 Å for C–O. From the observed C–N bond lengths in parabanic acid, the double-bond character of the C–N bonds was estimated, and was found to be 20% for C_1–N_1 and 25% for C_2–N_1. The double-bond character of the C–O bonds, and hence their expected lengths, was now found from the condition that the total double-bond character around any carbon atom be unity. The C–O bond lengths found in this way are 1·24 and 1·22 Å for C_1–O_1 and C_2–O_2, respectively. For C_1–O_1 the predicted length is significantly larger than the observed length of 1·212 Å. Similar short C–O bond lengths have also been reported in the accurate analyses of α-oxalic acid, 1·19 Å (Cox, Dougill & Jeffrey, 1952), DL-alanine, 1·21 Å (Donohue, 1950), N-acetylglycine, 1·19 Å (Carpenter & Donohue, 1950), and cyanuric acid, 1·21 Å (Wiebenga, 1952).

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