

Eine ähnliche Umgebung des Wassers wurde in der Salzsäuredihydratstruktur gefunden (Lundgren & Olovsson, 1967). Der kürzeste Abstand zweier Wassermoleküle beträgt hier 2,41 Å, während die Chlor-Wasser-Abstände zwischen 3,04 Å und 3,10 Å liegen. Aufgrund der Kenntnis der Wasserstoffpositionen konnte die Substanz als $[H_5O_2]^+Cl^-$ formuliert werden.

Dem Direktor des Mineralogisch-Kristallographischen Instituts, Herrn Professor Dr B. Brehler, danke ich für sein förderndes Interesse.

Die Deutsche Forschungsgemeinschaft hat die Arbeit durch Leihgaben und Sachbeihilfen gefördert.

Die Berechnungen wurden im Deutschen Rechenzentrum in Darmstadt auf der IBM 7094 und im Rechen-

zentrum der Technischen Universität Clausthal auf der Zuse Z 23 durchgeführt.

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Acta Cryst. (1970). **B26**, 1547

The Crystal Structure of Urea Parabanic Acid

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(Received 24 October 1969)

The crystal structure of urea parabanic acid has been determined from its three-dimensional Patterson function. The structure, refined by least-squares with anisotropic thermal parameters for all but the hydrogen atoms, exhibits short intermolecular carbon-oxygen contacts of the type found in parabanic acid and four other organic solids. The contact angle $C=O \cdots C'$ is 131.6° and, as such, is outside the range of data reviewed by Bolton (*Nature, Lond.* (1964) **201**, 987)

Introduction

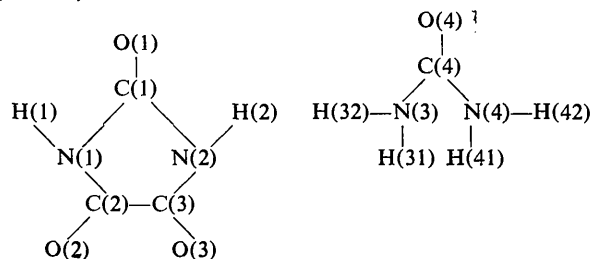
The existence of short intermolecular carbon-oxygen contacts in parabanic acid (Davies & Blum, 1955), chloranil (Chu, Jeffrey & Sakurai, 1962), barbituric acid (Bolton, 1963), alloxan (Bolton, 1964*a*) and triketointhane (Bolton, 1965) has been reviewed by Bolton (1964*b*). In order to investigate the importance of the second of two criteria for the formation of the contact, *viz.* that there be a deficiency of protons for complete hydrogen bonding of all electronegative atoms attached to the ring, the structure of a complex of urea, $CO(NH_2)_2$, and parabanic acid, $(CO)_3(NH)_2$, has been investigated.

In the 1:1 complex there is a surplus of protons for hydrogen bonding to the four carbonyl groups in the structure and since the coexistence of a hydrogen bond and a contact on a given carbonyl oxygen atom has never been observed, the absence of contacts in this structure might be inferred. On the other hand the crystal structure of parabanic acid is stabilized by this contact mechanism and, in addition, the alloxan struc-

ture provides an example of unused hydrogen bonding facilities.

Experimental

Crystals of the 1:1 complex of urea and parabanic acid (UPBA)



were grown by saturating a warm solution of parabanic acid with urea. The crystal habit is tabular prismatic, elongated in the **b** direction with the (101) face well developed. The melting point is $183^\circ C$ and at approximately $220^\circ C$ the clear melt decomposes.

Systematic extinction along reciprocal lattice rows defined by $(h, 0, 2n+1)$ and $(0, 2n+1, 0)$ gives the space group unequivocally as $P2_1/c$. The dimensions of the unit cell as determined by calibrating *a* and *b*-axis Weis-

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senberg photographs with sodium chloride lines and by goniometric measurements of the angles between external faces are:

$$a = 9.137 \pm 0.014, b = 5.623 \pm 0.003, c = 15.013 \pm 0.045 \text{ \AA};$$

$$\beta = 109^\circ 08' \pm 02'.$$

The density was found by flotation to be 1.61 g.cm^{-3} and the calculated density of a cell with four asymmetric units, each of molecular weight 174, is 1.585 g.cm^{-3} . Measurements of optical anisotropy revealed that $2V$ was near 90° .

Of the reflexions within the limiting sphere for Cu $K\alpha$ radiation, 956 were estimated visually from the b axis setting and 879 of these were assigned non-zero intensity. The crystal used had a diameter of 0.2 mm and absorption effects were therefore negligible ($\mu = 13.0 \text{ cm}^{-1}$). The morphology made it difficult to obtain a crystal suitable for the collection of intensity data about some other axis and a modified double-slit Weissenberg technique (Colman, 1969) was used to determine the scaling constants for the four layers of b axis data. The intensities were put on an absolute scale by Wilson's (1942) method.

Structure determination

The structure was solved from the three-dimensional Patterson function by searching for characteristic molecular images. An image of the oxygen network of parabanic acid was found in the origin of the Patterson function and the orientation of this image implied that the (211) plane was a molecular plane. The intersection of this plane with the Harker section $v = \frac{1}{2}$ resulted in gross overlap along these lines and further information was not available from this section of the Patterson function.

At this stage an investigation of the structure of thiourea parabanic acid (TUPBA) (Colman & Medlin, 1970) revealed that the unique carbonyl group in parabanic acid, C(1)–O(1), which is not involved in hydrogen bonding in that crystal structure, does accept a hydrogen bond under certain conditions. Although the two structures UPBA and TUPBA are not isomorphous, information on the hydrogen bonding between thiourea and parabanic acid was of assistance in determining the UPBA structure. In particular TUPBA is planar and an extensive search of the UPBA Patterson function revealed an image of the oxygen and nitrogen atoms of the urea molecule. This image was in the Patterson plane $2x + y + z = 1/2$, and it now seemed likely that the complex would be planar. Further, there was a high density of interatomic vectors in only one of the planes $2x + y + z = d$, viz. for $d = 0$, and from this it was concluded that the molecular planes passed through the origin. This result was further supported by the high unitary values of both the 211 and 422 reflexions. These values of 0.3 and 0.45 respectively are most likely when there is only one (211) molecular plane per unit

cell and this requires that these planes pass through the origin.

The use of superposition methods subsequently revealed two sets of peaks on the Harker plane which could have arisen from the interaction of screw-related parabanic acid molecules (only the oxygen–oxygen peaks were resolved) and the corresponding real space coordinates for one of these sets provided for hydrogen bonding between parabanic acid molecules related by the centre of symmetry. Sufficient phases were deter-

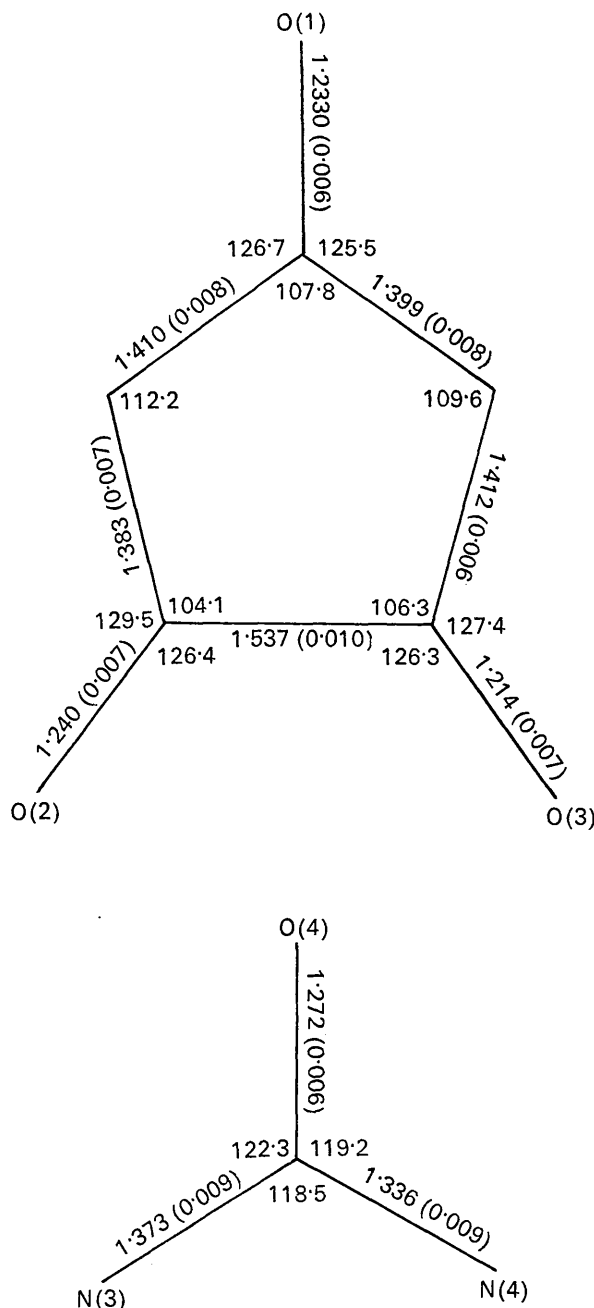


Fig. 1. Dimensions of urea and parabanic acid molecules in UPBA.

Table 1. Observed and calculated structure factors

Table with multiple columns containing numerical data for observed and calculated structure factors, including indices h, k, l and values F_o and F_c.

mined from this molecule alone to generate a region of high density in the electron density map. The urea coordinates were assigned from packing considerations and the residual for the model was 0.59. A second

Fourier synthesis implied shifts of up to 0.1 Å and when these were applied R was 0.47. Further convergence to $R=0.37$ resulted from one cycle of least-squares refinement.

Table 2. UPBA structure parameters

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)
O(1)	3921 (4)	-2240 (9)	-5325 (2)	129 (5)	271 (29)	28 (2)	-54 (8)	33 (2)	-4 (4)
O(2)	2114 (4)	-1155 (9)	-2782 (3)	129 (5)	303 (29)	42 (2)	-24 (9)	47 (3)	22 (5)
O(3)	4007 (4)	-5603 (10)	-2501 (3)	129 (5)	313 (31)	43 (2)	-48 (8)	40 (3)	-56 (5)
N(1)	2786 (4)	-1126 (11)	-4181 (3)	95 (5)	133 (33)	31 (2)	-50 (8)	24 (3)	-2 (5)
N(2)	4262 (4)	-4463 (10)	-3953 (3)	85 (4)	146 (29)	30 (2)	-31 (8)	24 (2)	-4 (5)
C(1)	3675 (5)	-2575 (12)	-4575 (3)	74 (5)	145 (38)	30 (2)	-13 (9)	17 (3)	10 (6)
C(2)	2762 (5)	-1981 (13)	-3322 (3)	73 (5)	217 (37)	32 (2)	14 (9)	23 (3)	17 (7)
C(3)	3752 (5)	-4250 (13)	-3165 (3)	75 (5)	241 (37)	31 (2)	9 (9)	27 (3)	5 (6)
O(4)	1091 (5)	2508 (10)	-5110 (3)	162 (5)	289 (33)	47 (2)	127 (9)	58 (3)	51 (6)
N(3)	1953 (6)	2238 (14)	-6396 (4)	154 (7)	201 (37)	54 (3)	45 (11)	61 (4)	17 (7)
N(4)	461 (5)	5421 (12)	-6197 (3)	140 (6)	255 (36)	34 (2)	54 (11)	37 (3)	19 (7)
C(4)	1179 (5)	3372 (13)	-5874 (3)	78 (5)	178 (38)	32 (2)	11 (10)	28 (3)	1 (7)
H(1)	2340 (87)	186 (164)	-4439 (50)	as for N(1)					
H(2)	4956 (81)	-5649 (150)	-4099 (44)	as for N(2)					
H(31)	2016 (93)	3165 (182)	-6855 (54)	as for N(3)					
H(32)	2357 (101)	699 (207)	-6179 (59)	as for N(3)					
H(41)	598 (88)	5912 (175)	-6673 (51)	as for N(4)					
H(42)	-46 (88)	6249 (174)	-5773 (46)	as for N(4)					

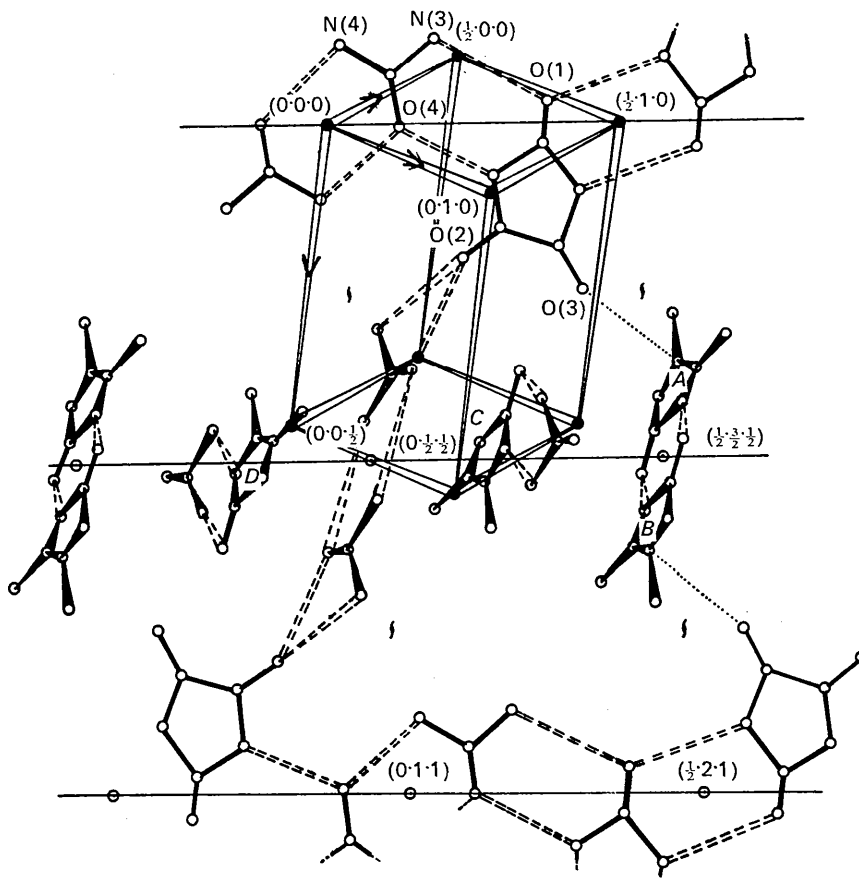


Fig. 2. Three-dimensional packing of UPBA as seen down the normal to the $(2\bar{1}1)$ plane.

Premature convergence of the least-squares refinement near $R=0.20$ was overcome by the application of a correction for secondary extinction of the form $I_{\text{corr}} = I_0 / (1 - 2g I_0)$ (where $2g = 6.3 \times 10^{-5}$) to all intensities greater than 500. This was justified in that the seven largest values of $\Delta (= |F_o| - |F_c|)$ were all negative, and in addition the $|F_o|$ values were large.

The hydrogen atoms were introduced into the refinement at $R=0.106$. The residual improved to 0.098 when the coordinates of these atoms, as determined from a difference Fourier synthesis, were supplied and

the refinement ultimately converged at $R=0.089$. For observed reflexions only $R=0.086$.

Anisotropic thermal parameters ($\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$) were refined in latter cycles ($R < 0.15$) and the atomic scattering factors used are those given in *International Tables for X-ray Crystallography* (1962). The structure factors and the final structural parameters are given in Tables 1 and 2. The F_o values listed are those obtained after application of the extinction correction.

Discussion

The dimensions of the urea and parabanic acid molecules in UPBA are given in Fig. 1. The most significant difference between these parameters and those for parabanic acid and urea in their respective crystal structures is the severe lengthening of N(2)-C(3) and this has been related to the formation of the carbon-oxygen contact on C(3). A comparison of the ring bond lengths in parabanic acid with those in UPBA is drawn in the following table.

Percentage double-bond character
Parabanic acid UPBA

C(1)-N(1)	20	12
C(1)-N(2)	20	12
N(1)-C(2)	25	18
N(2)-C(3)	25	12
C(2)-C(3)	-	-

The implied double-bond character of the parabanic acid carbonyl groups in UPBA is consistent with the observed lengths of these bonds. It is interesting that in the parabanic acid structure, the length of C(1)-O(1) was overestimated by the use of Pauling's (1960) equation but in the present case no additional ionic character need be assigned any of the carbonyl groups in order to explain their length.

A similar treatment of the urea molecule in the complex revealed that the two C-N bond lengths are significantly different (2.9σ).

The asymmetrical crystal environment of each of the molecules in the complex has resulted in a degeneration of their point group symmetry from $mm2$ to m .

Least-squares analysis (Schomaker, Waser, Marsh & Bergman, 1959) was done on the following four sets of planes to determine any significant aplanarity.

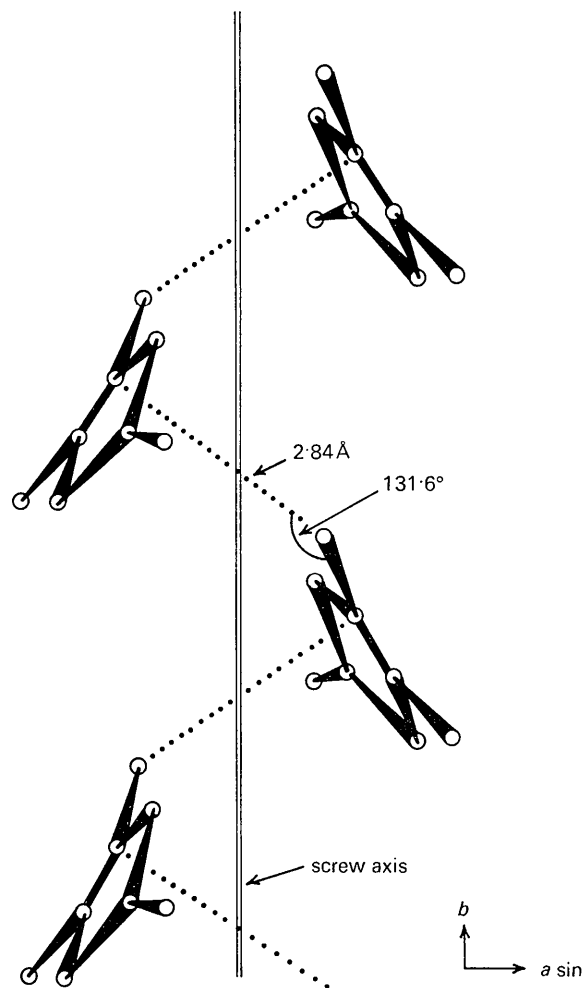


Fig. 3. Arrangement of parabanic acid molecules up the symmetry axis at $x = a/2$.

Table 3. *Hydrogen bonds in UPBA*

A-H---B							
A	H	B	A-B	$\sigma(A-B)$	H-B	$\sigma(H-B)$	$\angle AHB$
N(1)	H(1)	O(4)	2.665	0.008	1.808	0.011	168.1°
N(4)	H(42)	O(4) ^c	3.007	0.007	1.997	0.010	173.2
N(2)	H(2)	O(1) ^c	2.924	0.007	1.947	0.010	167.2
N(3)	H(32)	O(1)	3.204	0.009	2.284	0.012	161.4
N(3)	H(31)	O(2) ^d	3.067	0.002	2.203	0.011	152.2
N(4)	H(41)	O(2) ^d	3.236	0.007	2.494	0.010	166.5

- I Imidazole ring
 $6.374x + 3.032y + 3.260z = 0.073$
 II Parabanic acid
 $6.443x + 2.991y + 3.180z = 0.137$
 III Urea
 $6.432x + 2.784y + 3.744z = 0.511$
 IV UPBA
 $6.391x + 3.121y + 2.944z = 0.152$

Hydrogen atoms were excluded from the analysis. O(1), O(2) and O(3) are all significantly displaced from plane I and O(3) is on the opposite side of this plane to O(1) and O(2). Significant displacements of O(1), O(3) and N(2) also occur from plane II. The urea molecule is planar whilst the complex is not, at least not at atomic dimensions. The dihedral angle between planes II and III is 2.7° . The most significant of these results are as follows.

Displacement in multiples of standard deviations

	Plane I	Plane II
O(1)	2.8	6.3
O(2)	4.3	
O(3)	-8.3	-6.8
N(2)		4.0

Only displacements greater than 2.5σ for planes I, II and III are shown in this table.

The value of χ^2 for plane II is 110.0 and it must be concluded that this set of 8 atoms is significantly non-planar.

The packing of the complex into the (211) and ($2\bar{1}1$) planes is shown in Fig. 2. In fact the screw axes indicated are not perpendicular to the diagram but are parallel to the **b** direction of the cell. The pairs of molecules along the line $z = \frac{1}{2}$ are in the planes

$$2x + y + z = -1, 0, 1, 2, 3$$

from left to right respectively. The parabanic acid molecules *A* and *C* are below the plane $2x - y + z = 0$ and *B* and *D* are above this plane. *B* and *C* are related by the **b** translation and *C* and *D* by the centre at $(0, \frac{1}{2}, \frac{1}{2})$. The outline of one quarter of the unit cell is also shown.

The crystal structure is a set of interlocking planar chains. The first four hydrogen bonds in Table 3 are in the plane of the complex and the last two are between symmetry related (211) and ($2\bar{1}1$) planes.

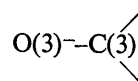
A further intermolecular bond is the carbon-oxygen contact which forms about the screw axis (Fig. 3). The dimensions of the contact are

$$\begin{aligned} C(3)^s \cdots O(3) &= 2.838 (0.008) \text{ \AA} \\ < C(3)-O(3) \cdots C(3)^s &= 131.6 (0.5)^\circ \end{aligned}$$

The superscripts *s*, *c* and *g* refer to molecules in the screw, centre and glide related positions as shown in Fig. 2.

Fuller (1959) has reviewed the hydrogen bond data and included in this review are eleven compounds which exhibit N-H...O=C bonds, where N and C are ring atoms. The observed N(2)...O(1)^c distance is within this range of data (2.62 to 2.93 Å). The H(42) bond length is comparable with the hydrogen bonds in urea (Vaughan & Donohue, 1952), *viz.* 2.99 and 3.04 Å, whilst the bond on H(41) is very weak. It is interesting that the three atoms in this bond form the least linear set of all atoms in hydrogen bonds in this structure and the bond is therefore predictably the weakest.

The anomaly in the hydrogen-bond network in this structure is the failure of O(3) to participate. However this result is consistent with other examples of the carbon-oxygen contact and it implies that affinity for hydrogen bonding and contact formation cannot be simultaneous properties of a given carbonyl oxygen atom. Wallwork (1962) has related the length of A-H...B bonds to the electronegativity of *A* and the van der Waals radius of *B*. The UPBA data implicate the electronegativity of *B* in the following way. The carbonyl group C(3)-O(3) has more double-bond character than any other carbonyl group in the structure. The contribution of resonance structures of the type



will therefore be small and since the neutral oxygen atom has less affinity for protons than the O⁻ ion, this group will compete less strongly for hydrogen bonds. In all the contact compounds so far investigated the carbonyl groups in the contact are the shortest such groups in the structure.

The occurrence of the contact in UPBA has previously been reported (Colman & Medlin, 1969). The contact distance O(3)...C(3)^s is increased by the displacement of O(3) from the ring plane. A similar displacement of O(1) in the parabanic acid structure is also found in the Davies & Blum (1955) data.

A discussion of a contact mechanism which will account for the spread in contact angle now observed will be given elsewhere (Colman, 1970). It is necessary to conclude that the strong dipole fields normally associated with the carbonyl groups in these compounds are weakened by hybridization of the oxygen atom in the contact, the extent of this hybridization being largely determined by other intermolecular forces. A Coulombic force field places no restrictions on the geometry of C=O...C' atoms and is therefore recommended.

One of us (P.M.C.) acknowledges the assistance of a Commonwealth Post Graduate Award. This work was supported by the Australian Research Grants Committee.

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Acta Cryst. (1970). **B26**, 1553

The Crystal Structure of Thiourea Parabanic Acid

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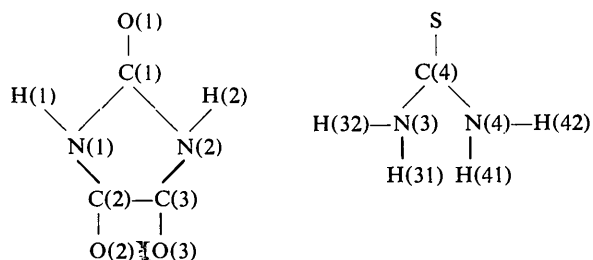
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(Received 24 October 1969)

The crystal structure of thiourea parabanic acid has been determined from its three-dimensional Patterson function. The structure has been refined by least-squares methods with anisotropic thermal parameters (for all but the hydrogen atoms) to $R=9.7\%$ for observed reflexions. The planar (010) complex crystallizes in the $P2_1$ system (b unique) and exhibits a new intermolecular contact between sulphur and carbon atoms on adjacent layers in the structure. In the absence of other intermolecular bonds in the b direction, this contact determines the position of the complex relative to the screw axis.

Introduction

In the course of determining the structure of urea parabanic acid (Colman & Medlin, 1970) the substitution of one of the light atoms for a heavier atom was considered. Crystals of the 1:1 complex of thiourea parabanic acid (TUPBA)



were grown and, although they are not isomorphous with urea parabanic acid, the structure was determined in order to investigate hydrogen bonding facilities on the three parabanic acid carbonyl groups.

Experimental

Faintly yellow coloured crystals of TUPBA were grown by adding excess thiourea to a concentrated

water solution of parabanic acid. The tabular prismatic crystals have a well defined zone axis [010] along which they are elongated. There is a well pronounced cleavage plane perpendicular to this unique axis and the possibility of hydrogen bonding in this direction seemed remote. Whilst no other cleavages, as such, were found it is possible to cut the crystal along two other planes, *viz.* ($\bar{1}01$) and (601), the former being the plane of the plate. The ($\bar{2}01$) face is also well developed. The crystals melt at 213°C.

The unit-cell dimensions were determined by calibrating a Weissenberg film with NaCl lines and from goniometric measurements of the angle between the faces. These latter measurements were made independently on two separate crystals. The dimensions are: $a=10.984 \pm 0.019$, $b=6.298 \pm 0.003$, $c=6.238 \pm 0.012$ Å; $\beta=115^\circ 34' \pm 02'$. The only systematic extinction condition is along $(0, 2n+1, 0)$ and the space group $P2_1$ is therefore defined unequivocally. The measured density of 1.59 g.cm^{-3} compares satisfactorily with the value calculated (1.63 g.cm^{-3}) for two asymmetric units of molecular weight 190 in a cell of the above dimensions.

Four layers of unintegrated data were collected about both the b and the [102] axes. In all, 639 of the 900 reflexions accessible to Cu $K\alpha$ radiation were recorded. Absorption corrections for both sets of data were considered negligible since the optimum thickness $2/\mu$ is 0.6 mm for TUPBA and is approximately 3

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