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The Structure of the Crystalline Complex of Purine and Urea (2:1)

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$C_5H_4N_4 \cdot \frac{1}{2}(CH_4N_2O)$, FW 150·14, is orthorhombic, space group $Fdd2$, $a = 20·921$ (4), $b = 35·274$ (5), $c = 3·622$ (1) Å, $V = 2672·9$ Å^3, $Z = 16$, $D_m = 1·490$, $D_x = 1·496$ g cm^{-3}. The purine molecules are stacked along the c axis and are held together by $N(9)-H \cdots N(1)$ and $N(urea)-H \cdots N(7)$ hydrogen bonds. The protonation site in the imidazole ring is $N(9)$ instead of the usual $N(7)$ in purine. The overlapping mode of the purine molecules differs from that in the crystal of purine. The urea molecules are also associated with each other through hydrogen bonding. Two half-weight urea molecules are arranged around the diad axis parallel to [001] with their O atoms on the diad and their molecular planes nearly parallel to (010). Because of the short axial length of c, the repeat distance of the urea molecules must be a multiple of c, thus indicating disorder along the c axis.

Introduction

We found that purine and urea form a stable 2:1 molecular complex in the solid state. The complex retains the same stoichiometric ratio through sublimation at 105 °C/23 mmHg as well as recrystallization from various organic solvents. The infrared spectrum (in KBr) of the complex shows a drastic change in the 1550 ~ 1700 cm^{-1} region compared with the mixture of the same composition. At present, there is no evidence of the analogous complex formation in solution. In order to clarify the state of association between purine and urea in this molecular complex, we have carried out the crystal structure analysis.

Experimental

Crystals of the complex were prepared by dissolving purine and urea in a 2:1 stoichiometric ratio in warm ethyl acetate and allowing the mixture to stand at room temperature. A crystal 0·3 × 0·1 × 0·45 mm was cut with a razor and used for the X-ray experiments. X-ray data were collected on a Philips PW 1100 automatic diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate. The systematic absences (Table 1) established the orthorhombic, face-centred space group $Fdd2$. The calculated density, assuming 16 structural units in a cell, accorded well with that measured in CCl_4–n-hexane by flotation. This indicates that the urea

Table 1. *Allowed reflexions in space group Fdd2*

hkl:	$h + k, k + l, l + h = 2n$	hk0:	$h,k = 2n$
0kl:	$k + l = 4n; k,l = 2n$	h00:	$h = 4n$
h0l:	$l + h = 4n; l,h = 2n$	0k0:	$k = 4n$
		00l:	$l = 4n$

molecules must be on a diad. The intensities of 756 non-zero, independent reflexions with $2\theta \leq 156°$ out of 812 possible reflexions were measured by the θ–2θ scanning technique. Three reference reflexions were measured periodically during the data collection, but they exhibited no significant decrease in intensity. Intensities were corrected for Lorentz and polarization factors but not for absorption or extinction.

Determination and refinement of the structure

The structure was solved by the direct method with *MULTAN* (Main, Woolfson & Germain, 1971) using 95 reflexions with $E \geq 1 \cdot 40$. From the E map the coordinates of the nine atoms of the purine ring were obtained along with some peaks of the urea molecule near the diad. A subsequent difference Fourier synthesis revealed two alternative positions for urea, each with an occupancy factor, m, of $0 \cdot 5$. Though it had been thought that the diad of the urea molecule might coincide with that of the crystal, the result of the difference Fourier synthesis could not be interpreted by such a model but showed a disordered arrangement of the molecule around the crystal diad. This structure was refined by several cycles of block-diagonal least-squares calculations assuming anisotropic thermal

motion. The R index was reduced to $0 \cdot 075$. The parameters of the O atom of urea could not be refined well since the two O atoms related by the diad were too close to each other owing to the disorder. The second difference Fourier map gave the four H atoms of purine, but no distinct peaks were found for those of urea. Subsequent least-squares calculations reduced R to $0 \cdot 052$, assuming isotropic thermal motion for the H atoms. The weighting scheme used was: $\sqrt{w} = 1 \cdot 0$ when $F_o \leq 10 \cdot 0$ and $\sqrt{w} = 10 \cdot 0/F_o$ when $F_o > 10 \cdot 0$. The scattering factors used for O, N and C were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). The final atomic positional parameters are given in Table 2.*

Results and discussion

The bond distances and valency angles are shown in Fig. 1. Comparison with those found in the crystal of purine (Watson, Sweet & Marsh, 1965) shows significant differences in molecular dimensions, especially in the valency angles. The C(8)—N(9) bond, $1 \cdot 363$ Å, is considerably longer than that in the latter crystal, $1 \cdot 311$ Å. While the angles C(5)—N(7)—C(8) and C(5)—C(4)—N(9) are smaller (respectively $103 \cdot 2$ and $105 \cdot 6°$ *vs.* $106 \cdot 5$ and $109 \cdot 6°$ in purine), C(4)—N(9)—C(8) and C(4)—C(5)—N(7) are larger ($106 \cdot 2$ and $110 \cdot 7°$ *vs.* $103 \cdot 8$ and $105 \cdot 1°$ respectively). These

* A list of structure factors and atomic thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32310 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
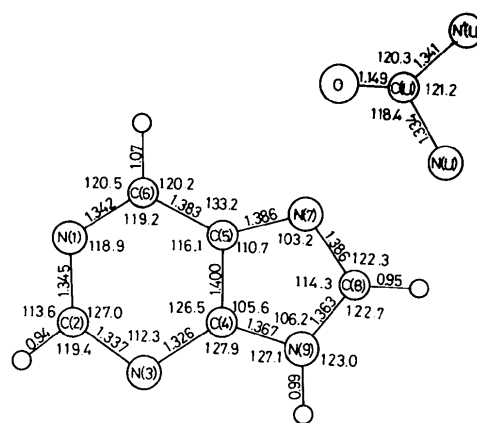
Table 2. *Atomic positional parameters for non-hydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^3$) with the estimated standard deviations in parentheses*

	m^*	x	y	z
N(1)	$1 \cdot 0$	1660 (1)	1431 (1)	3261 (12)
C(2)	$1 \cdot 0$	2207 (1)	1591 (1)	2091 (14)
N(3)	$1 \cdot 0$	2712 (1)	1415 (1)	612 (11)
C(4)	$1 \cdot 0$	2625 (1)	1044 (1)	364 (12)
C(5)	$1 \cdot 0$	2080 (1)	843 (1)	1433 (12)
C(6)	$1 \cdot 0$	1589 (1)	1055 (1)	2944 (14)
N(7)	$1 \cdot 0$	2155 (1)	460 (1)	735 (12)
C(8)	$1 \cdot 0$	2731 (1)	440 (1)	−755 (13)
N(9)	$1 \cdot 0$	3038 (1)	780 (1)	−1018 (11)
C(U)	$0 \cdot 5$	3029 (3)	2441 (2)	6952 (33)
O	$0 \cdot 5$	2487 (23)	2491 (12)	6987 (23)
N(U)	$0 \cdot 5$	3331 (3)	2397 (2)	10171 (27)
N'(U)	$0 \cdot 5$	3341 (3)	2403 (2)	3736 (26)
H(C2)	$1 \cdot 0$	222 (1)	185 (1)	248 (11)
H(C6)	$1 \cdot 0$	114 (2)	92 (1)	366 (14)
H(C8)	$1 \cdot 0$	294 (2)	21 (1)	−123 (13)
H(N9)	$1 \cdot 0$	340 (2)	82 (1)	−272 (19)

* Occupancy factor.

Fig. 1. Interatomic distances and angles in the complex. The e.s.d.'s in the bond lengths are: C—C(or N) 0·004, C(U)—O 0·05, C(U)—N(U) [or N'(U)] 0·01, H—C(or N) 0·04 Å. The e.s.d. in the angle N(U)—C—N'(U) is 0·8° and those for other angles involving only non-hydrogen atoms are 0·3°; those for angles involving H atoms are 2°.

changes in the bond angles reflect the change in the protonation sites, which is in accordance with the effect pointed out by Sundaralingam & Jensen (1965) and Singh (1965). The protonation at N(9) was also confirmed by a difference Fourier synthesis which was calculated after three cycles of least-squares refinement without H(N9), and by a hydrogen-bond system which will be discussed in detail later. Intermolecular contacts are shown in Table 4.

The C—O bond, 1·149 Å, is considerably short in comparison with the molecular dimensions of urea but we cannot place much reliance on the value. As to the ring atoms of purine, they are coplanar within the experimental error. The equation of the plane and the deviations of the atoms from the plane, for the nine

ring atoms of purine, are listed in Table 3 along with the corresponding values in purine itself. Only the H atom at N(9) deviates appreciably from the plane. Purine molecules stack on top of each other as do the molecules of many other purine and pyrimidine compounds. The interplanar spacing between the purines is 3·30 Å, which is smaller than in the purine crystal, 3·39 Å. The overlapping modes of adjacent purine molecules in the complex and in purine are illustrated in Fig. 2. The overlapped purine molecule shifts about 1·86 Å along the long axis of the molecule in the complex as compared with that in the purine crystal. Fig. 3 is another view of the stacking in which the location of the urea molecule is also shown.

Fig. 4 illustrates the hydrogen-bonding system. Strong N(9)—H $\cdots$ N(1) hydrogen bonds, 2·814 Å in

Table 3. *Deviations of the atoms from the least-squares plane through the ring atoms of purine*

$$0.3928X - 0.1245Y + 0.9112Z = 1.8113.$$

N(1)	0·0007 Å	(−0·007 Å)	C(8)	−0·0095	(−0·001)
C(2)	−0·0063	(−0·004)	N(9)	0·0065	(−0·007)
N(3)	−0·0025	(0·016)	H(C2)	0·019	(−0·17)
C(4)	0·0077	(−0·005)	H(C6)	−0·070	(0·05)
C(5)	0·0005	(−0·006)	H(C8)	0·105	(0·10)
C(6)	0·0032	(0·006)	H(N9)	−0·275	(*0·09)
N(7)	−0·0003	(0·008)			

* The value for H(N7).

Table 4. *Intermolecular distances (Å) less than 3·5 Å between non-hydrogen atoms, and those less than 2·9 Å between hydrogen atoms and non-hydrogen atoms, together with their estimated standard deviations*

Symmetry code

(i)	x, y, z	(ii)	$x, y, 1 + z$
(iii)	$x, y, -1 + z$	(iv)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$
(v)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 + z$	(vi)	$\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$
(vii)	$\frac{1}{4} + x, \frac{1}{4} - y, 1\frac{1}{4} + z$	(viii)	$\frac{1}{4} + x, \frac{1}{4} - y, -\frac{3}{4} + z$
(ix)	$\frac{3}{4} + x, \frac{1}{4} - y, \frac{3}{4} + z$	(x)	$\frac{3}{4} + x, \frac{1}{4} - y, -\frac{1}{4} + z$

N(1)$\cdots$N(9)^{ix}	2·814 (4)*	C(5)$\cdots$C(6)^{iii}	3·326 (6)
N(1)$\cdots$H(N9)^{ix}	1·887 (35)*	C(5)$\cdots$C(8)^{ii}	3·448 (6)
N(U)$\cdots$N(7)^{vii}	3·238 (7)*	C(5)$\cdots$N(9)^{ii}	3·397 (5)
N(U)$\cdots$O^{v}	3·030 (30)*	C(6)$\cdots$C(8)^{iii}	3·495 (5)
N'(U)$\cdots$N(7)^{vi}	3·039 (6)*	C(6)$\cdots$N(9)^{ix}	3·465 (4)
N'(U)$\cdots$O^{v}	3·019 (30)*	C(6)$\cdots$N(9)^{iii}	3·491 (4)
N(1)$\cdots$C(2)^{ii}	3·444 (6)	N(7)$\cdots$C(8)^{ii}	3·311 (6)
N(1)$\cdots$N(3)^{ii}	3·454 (5)	N(7)$\cdots$C(8)^{iv}	3·435 (4)
C(2)$\cdots$N(3)^{ii}	3·320 (6)	H(C2)$\cdots$O^{i}	2·836 (50)
N(3)$\cdots$C(6)^{vi}	3·373 (5)	H(C6)$\cdots$N(3)^{ix}	2·595 (43)
N(3)$\cdots$C(6)^{viii}	3·438 (5)	H(C6)$\cdots$N(3)^{x}	2·857 (44)
N(3)$\cdots$C(8)^{iii}	3·480 (4)	H(C8)$\cdots$N(7)^{iv}	2·606 (37)
C(4)$\cdots$C(6)^{iii}	3·453 (6)	H(N9)$\cdots$C(6)^{viii}	2·705 (47)
C(4)$\cdots$N(9)^{ii}	3·370 (6)		

* These contacts are shown in Fig. 4(a) and (b) as hydrogen bonds.
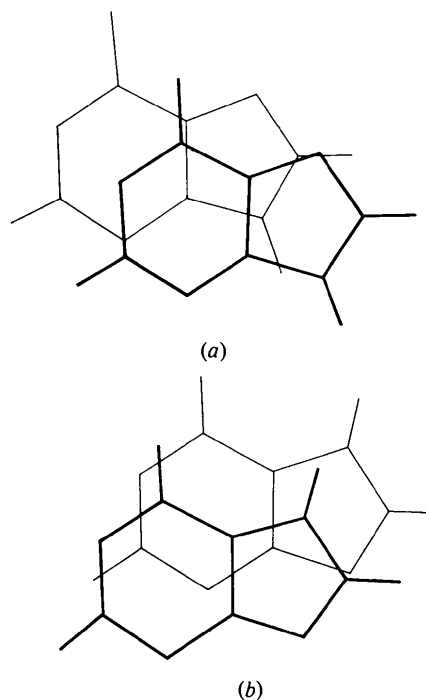

(a)

(b)

Fig. 2. The overlapping mode of the purine rings, (a) for the purine and urea (2:1) complex crystals, (b) for the purine crystals.
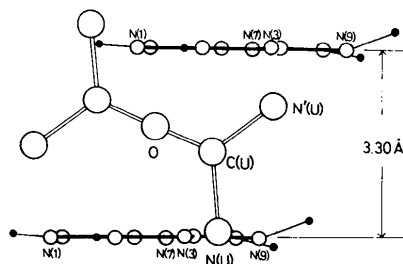

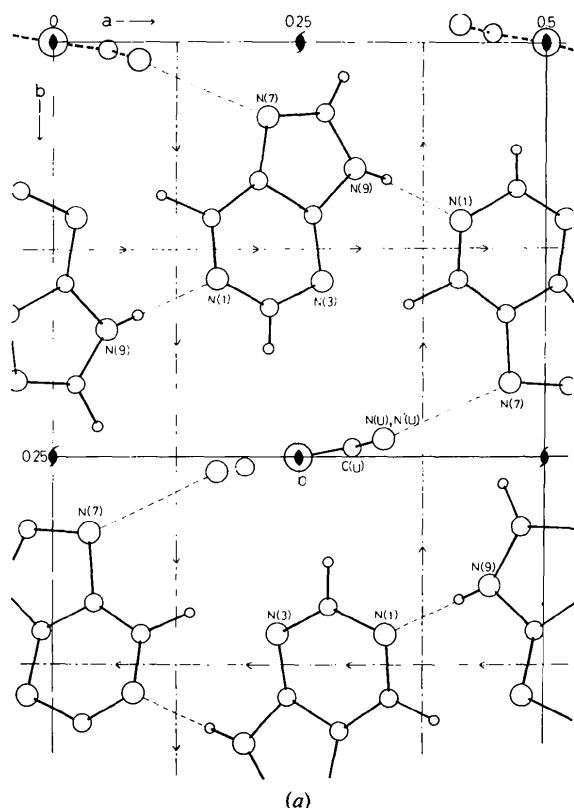Fig. 3. Projection of the molecule onto the mean plane of the urea.

Fig. 4. (a) The crystal structure viewed along the c axis showing the hydrogen bonds as dashed lines. The distances between the hydrogen-bonded atoms are listed in Table 4.

length, hold the purine molecules together to form an infinite sheet along (301). Assuming the urea molecules to be arranged as shown by the bold molecules (drawn with bold filled bonds) in Fig. 4(b) around the diad at ($\frac{1}{4}$, $\frac{1}{4}$, z), a network of hydrogen bonds could reasonably be formed between the urea molecules (two NH···O bonds of 3·02 and 3·03 Å) as well as between the urea and purine molecules [two N—H···N(7) bonds of 3·039 and 3·238 Å]. If this were the case, the repeat distance of the urea molecules along the c axis of this structure would be twice as long as that actually found in the present complex and the symmetry of the space group would be violated. The model should therefore be considered as disordered, as described earlier. In the average structure, the urea molecules are distributed with equal probability at the positions shown in Fig. 4(b) by the faint molecules (drawn with faint open bonds) around the diad at ($\frac{1}{4}$, $\frac{1}{4}$, z). It is not possible to find both the bold and faint molecules simultaneously around the diad. Very diffuse intermediate layer lines corresponding to the identity period 2c clearly appeared on the heavily exposed c-axis oscillation photographs and indicate that the urea molecules do not adopt a completely disordered structure.

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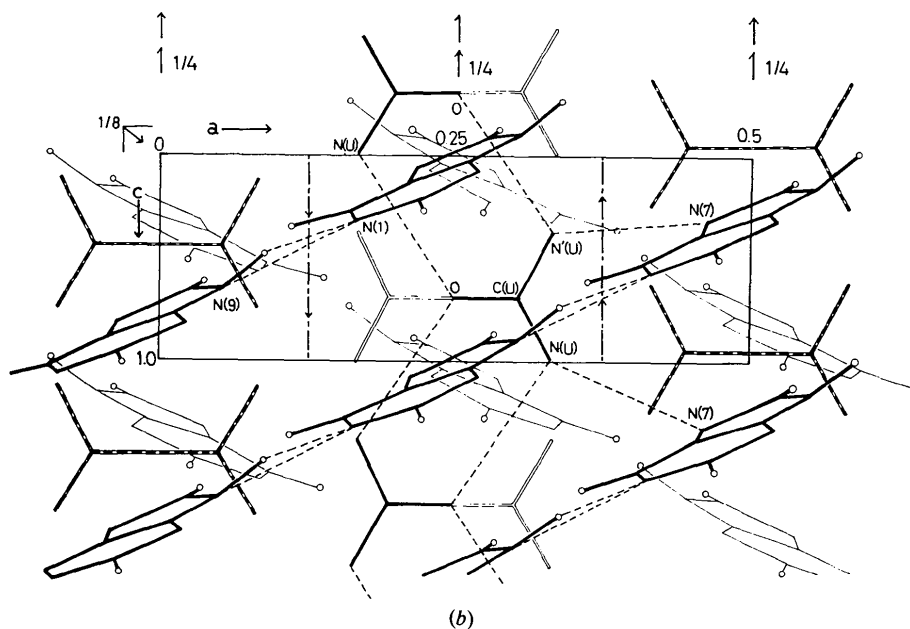International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Fig. 4 (cont.). (b) Crystal structure viewed along the b axis. The striped molecules represent urea molecules whose positions are not fixed, owing to the disorder. For clarity, Fig. 4(b) shows the molecules between $y = 0$ and $y = \frac{1}{2}$.

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4-Dimethylaminopyridine Hydrochloride Dihydrate*

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$C_7H_{11}N_2^+.Cl^-.2H_2O$ is triclinic $P\bar{1}$ with $a = 16·162$ (4), $b = 7·066$ (4), $c = 9·584$ (4) Å, $\alpha = 104·51$ (9), $\beta = 90·01$ (8), $\gamma = 94·44$ (8)°, $M_r = 194·66$, $Z = 4$, $D_m = 1·218$ g cm^{-3}, $D_x = 1·223$ g cm^{-3}. The amino group is essentially planar with a N(7)–C(4) bond length of about 1·340 Å. Protonation takes place at the ring N. There are two independent molecules in the structure with significantly different geometries, apparently related to the formation of a very short N–H $\cdots$ Cl hydrogen bond (3·081 Å) in one case, and a N–H $\cdots$ O bond (2·675 Å) in the other.

Introduction

^{14}N NQR studies of 2-aminopyridine (Marino, Guibé & Bray, 1968) and 2-aminopyrimidine (Schempp & Bray, 1971) have suggested that the two *ortho* ring N atoms in the pyrimidine are almost twice as effective as one ring N in withdrawing charge from the amino group. The C–NH$_2$ bond reflects this situation; the bond length is 0·009 Å longer in 2-aminopyridine than in 2-aminopyrimidine (Scheinbeim & Schempp, 1976). NQR study of 4-aminopyridine hydrochloride (Chao, 1975) shows that the quadrupole coupling constant (3315·6 kHz) and the asymmetry parameter (0·431) for the amino group change from their values in 4-aminopyridine (3506·3 kHz and 0·385) (Marino *et al.*, 1968) toward those in 2-aminopyrimidine (3270·3 kHz and 0·406); this seems to signal a limit to the amino group's electron-donating power. We then expect that the C–N(amino) bond length will reflect this (Chao & Schempp, 1977); unfortunately the structure of 4-aminopyridine hydrochloride has not been determined. The present structure determination was undertaken as part of planned NQR and X-ray studies of 4-dimethylaminopyridine and its hydrochloride.

A clear needle-shaped crystal of 4-dimethylaminopyridine.HCl dihydrate was obtained by adding dilute hydrochloric acid to an ethanol solution of the parent pyridine and letting this solution evaporate to dryness. The crystals lose water of hydration to form a white powder when they are exposed to the air for 1–2 days. A single crystal with approximate dimensions 0·2 × 0·3 × 0·3 mm was sealed in a Lindemann glass capillary. The unit-cell constants and the three-dimensional intensity data were measured by using a four-circle computer-controlled diffractometer (Nonius CAD-4) in the variable $\theta/2\theta$ scan mode. There were 4334 independent reflections measured with $\theta \leq 75°$, of which 1227 had an integrated intensity less than $2\sigma(I)$. These were assigned an intensity $I = \sigma(I)/2$ and given zero weight during the least-squares refinement.

The structure was solved by the heavy-atom method and the atomic positional parameters were refined with a block-diagonal least-squares program (Shiono, 1971). H atoms were located in a difference electron density map, although the methyl H atoms turned out to have large temperature factors which did not converge during refinement. The ten strongest reflections gave large ratios of F_c/F_m and were given zero weight in the subsequent refinement. The reflections were weighted according to the Cruickshank (1965) scheme where $w = 0·9447 - 0·0073 |F_m| - 0·0008 |F_m|^2$ for the final refinement. The atomic scattering factors used were those of Cromer & Waber (1965) for Cl, O, N and C