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The Crystal Structure of 6-Methyluracil-5-acetic Acid*

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Crystals of 6-methyluracil-5-acetic acid are monoclinic, space group $P2_1/n$, with $a=4.8929$ (1), $b=12.6368$ (3), $c=12.7455$ (1) Å, $\beta=99.174$ (2)°, $Z=4$. Approximately 1600 intensity data for two different crystals were collected on an automated diffractometer; one crystal was an approximate cube 0.16 mm on an edge and the second was a sphere 0.18 mm in diameter. The structure was derived by direct phasing methods and refined by full-matrix least-squares analysis. The two data sets were treated separately, and both led to the same parameters (within three e.s.d.'s) except for the coefficient of secondary extinction, which was 25% (four e.s.d.'s) smaller for the crystal that had been ground to a sphere. Final refinement, which included anisotropic temperature coefficients for all atoms including hydrogen, led to an R index of 0.036 and standard deviations of about 0.0015 Å in the positions of the heavy atoms. The pyrimidine ring is slightly nonplanar, being folded along the C(2)···C(5) axis to relieve strain between the exocyclic substituents. The structure features an off-set stacking of parallel pyrimidine rings at a separation of about 3.29 Å, and hydrogen bonding across centers of symmetry to form base-pairs.

Introduction

Our crystal structure investigation of 6-methyluracil-5-acetic acid, $C_7H_8N_2O_4$, was begun in 1967. Originally inspired by our continuing interest in the geometry and packing of nucleic acid derivatives, it served as an early test in our Laboratories of the power of direct methods of phase determination and of the accuracy of diffractometer measurements. At the beginning of the analysis, the author who carried out all of the experimentation (RD) knew nothing as to the nature of the compound other than that it contained

no atom heavier than oxygen; it is a testimonial to the power of present-day methods that RD knew the complete make-up of the molecule – including the identities of the various atom types and the locations of the protons – within two weeks after completing the data collection.

Experimental

Crystals in the form of colorless needles, elongated along a , were obtained from Professor James English of Yale University as part of the Treat B. Johnson collection. Unit-cell dimensions were obtained from a least-squares treatment of 84 measurements on zero-level Weissenberg photographs about the a and b axes, taken at 20 (1)°C; the films were held in the asymmetric position, following the Straumanis technique. The space group $P2_1/n$ was indicated by the absence of reflections $h0l$ with $(h+l)$ odd and $0k0$ with k odd. The density was measured by flotation in an aqueous

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potassium iodide solution. Crystallographic data are given in Table 1.

Table 1. *Crystal data*

$C_7H_8N_2O_4$	M.W. 184.14
Monoclinic	Space group $P2_1/n$
$a = 4.8929 \pm 0.0001 \text{ \AA}$	$Z = 4$
$b = 12.6368 \pm 0.0003$	$V = 778 \text{ \AA}^3$
$c = 12.7455 \pm 0.0001$	$F(000) = 384 e^-$
$\beta = 99.174 \pm 0.002^\circ$	$D_m = 1.57 \text{ g.cm}^{-3}$
	$D_x = 1.572 \text{ g.cm}^{-3}$
Cu $K\alpha_1 = 1.54051 \text{ \AA}$	
Cu $K\alpha_2 = 1.54433$	$\mu = 11.41 \text{ cm}^{-1}$
Cu $K\alpha = 1.5418$	

Intensity data were collected on a General Electric diffractometer automated by Datex, using Ni-filtered copper radiation and a proportional counter. A θ - 2θ scan technique was used, the scan range including both the α_1 and α_2 peaks; background was counted for 30 sec at each end of the scan, and the scanning rate was 1° in 2θ per min. A single standard reflection was checked after each 15 intensity measurements; it showed no significant drift in intensity.

Two sets of data were collected, the first set coming from an almost cube-shaped crystal with dimensions $0.17 \times 0.16 \times 0.15$ mm, mounted along the a axis, and the second set from a crystal which had been ground to a sphere (Bond, 1951) of radius 0.09 mm, also mounted along the a axis.

For the first set, each reflection was measured once only. After the data processing, described later, this set consisted of 1582 observed reflections (that is, reflections with net counts greater than zero) out of the 1632 independent reflections out to $2\theta = 153^\circ$.

The same number of independent reflections was scanned during the collection of the second set, but here 330 reflections were measured once and the remaining 1302 reflections two or more times. As a check of the alignment and the mosaicity of the crystal the $0kl$ reflections were measured three times and the $0\bar{k}l$ reflections once; the agreement between these two groups of data was nearly within the counting statistics. This second set consisted of 1606 independent observed reflections. The processing of the two sets of data was carried out separately, first correcting all the measured intensities for background and then for Lorentz and polarization factors. No correction for absorption was considered necessary, since μR_{\max} is less than 0.16 for both crystals. Observational variances $\sigma^2(I)$ included, besides counting statistics for the scan and backgrounds, a term $(0.02S)^2$, where S is the scan count. The reflections measured more than once were given weights equal to the arithmetic average of the weights of the individual measurements.

Determination and refinement of the structure

As indicated in the Introduction, the solution of the structure was effected without prior knowledge of the

empirical formula of the compound. It was based on the first data set.

The cell dimensions, measured density, and space group suggested that the unit cell contains four molecules of molecular weight approximately 184. Approximate scale and temperature factors were obtained by Wilson's (1942) method, assuming the molecule to comprise 12 nitrogen atoms. On the basis of this same assumption, the structure factors were converted to E 's (Hauptman & Karle, 1953). The values of the statistical averages $\langle |E| \rangle$ and $\langle |E^2 - 1| \rangle$, 0.795 and 1.084, were satisfactorily consistent with a centrosymmetric structure, as were the results of the $N(z)$ test (Howells, Phillips & Rogers, 1950).

The structure was solved by the symbolic addition method (Zachariasen, 1952). The origin was fixed by assigning positive signs to three large E values which entered into many Sayre (1952) relationships; three additional E 's were assigned arbitrary symbols. The starting set of phases is listed in Table 2.

Table 2. *Set of signs for application of the Sayre relationships*

h	k	l	$ E $	Signs
0	3	11	3.98	+
1	6	9	3.81	+
4	1	6	3.76	+
2	9	2	3.49	a
3	6	4	3.24	b
2	7	8	3.23	c

As the phase determination, which was carried out by hand, progressed, it soon became apparent that a and b (Table 2) were negative and c positive. On this basis, the signs of 214 reflections with $|E|$ greater than 1.5 were determined; all 214 signs ultimately proved to be correct. An E map (Karle, Hauptman, Karle & Wing, 1958) computed from these 214 terms clearly revealed 13 peaks, with very little extraneous detail. A structure-factor calculation, based on 13 nitrogen atoms, gave an R index $(= \sum ||F_o| - |F_c|| / \sum |F_o|)$ of 0.27 for the 1582 observed reflections.

The skeleton of the molecule – a six-membered ring, three individual substituents and four-atom branched side chain – was immediately evident. In addition, the bond distances and angles, as well as the relative heights of the side-chain atoms, strongly suggested an acetic acid grouping, while two of the ring atoms and two substituent atoms were represented by peaks in the E map considerably larger than the remaining atoms, suggesting a pyrimidine ring with, perhaps, nitrogen atoms as substituents. With the atoms identified in this way, two least-squares refinement cycles of the coordinates and isotropic temperature factors were carried out. The R index dropped to 0.17, but anomalously small B values for the two substituent 'nitrogen' atoms suggested that they were, in fact, oxygen. Two subse-

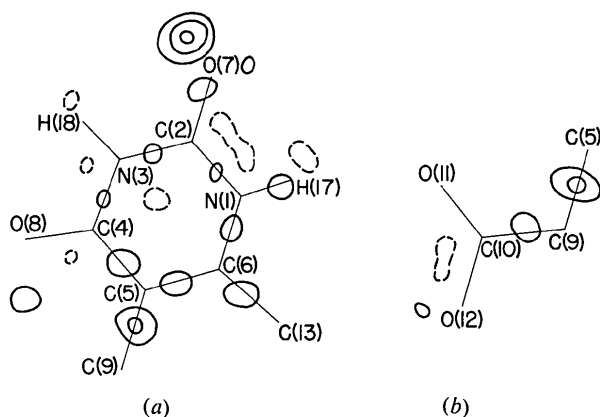


Fig. 1. The final difference electron density, calculated (a) in the plane of the pyrimidine ring; (b) in the plane of the carboxyl group. Contours are at 0.1, 0.2, 0.3 e.Å⁻³.

quent least-squares cycles reduced R to 0.14. At this point a difference map clearly indicated the positions of all eight hydrogen atoms, and the model was complete. The final least-squares refinement for this data set included, in a single matrix, 151 parameters: coordinates and anisotropic temperature coefficients B_{ij} for the 13 heavy atoms, coordinates and isotropic B 's for the eight hydrogen atoms, a scale factor, and a secondary extinction parameter (Larson, 1967, equation 3; Zachariasen, 1963). The R index was 0.041 for the 1582 reflections of non-zero weight.

This set of parameters was then refined through two full-matrix least-squares cycles based on the second set of data. The only significant parameter change was for the secondary extinction coefficient, g , which was 25% (4σ) smaller for the second set of data. The les-

sening of the extinction effect was presumably due to the grinding of the crystal.

The final refinement, which included anisotropic temperature coefficients for the hydrogen atoms, was based on the second data set. After four full-matrix least-squares cycles, no parameter shift was as much as 10% of its standard deviation, and convergence was assumed. The final R index was 0.036; the goodness-of-fit $\sum w(F_o^2 - F_c^2)^2 / (m - s)$, where $m = 1606$ reflections of non-zero weight and $s = 191$ parameters, was 1.66. The final parameters are listed in Table 3, and the observed and calculated structure factors in Table 4. All calculations were carried out on an IBM 7094 computer under the CRYRM system (Duchamp, 1964). Form factors for C, N, and O were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). No account was taken of anomalous dispersion. The quantity minimized in the least-squares calculations was $\sum w[F_o^2 - (1/k^2)F_c^2]^2$, with $w = \sigma^{-2}(F_o^2)$ (see Experimental section). The 26 reflections with net intensities less than zero were given zero weight; for none of them did the final value of F_c^2 differ (algebraically) from the observed negative value by as much as 3σ .

At the conclusion of the refinement, a complete difference map was calculated; its most important features are shown in Fig. 1. We feel confident that these features are not an artifact of the data, for they appeared, essentially unchanged, on difference maps calculated from the two sets of experimental data separately. They are surely significant, ranging up to approximately ten times the noise level of the map. They presumably reflect the failure of our model to account for such things as bonding electron density, non-ellipsoidal or non-harmonic thermal vibration, or polarization of the electron clouds.

Table 3. *The final atomic parameters and their standard deviations (in parentheses)*

Values for the heavy atoms have been multiplied by 10^5 , and those for the hydrogen atoms by 10^4 . The temperature factor has the form $\exp(-b_{11}h^2 \dots - b_{12}hk \dots)$. The final value for the secondary extinction parameter g (Larson, 1967) is $15.4(1.4) \times 10^{-6}$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	-27854 (23)	47336 (9)	39671 (8)	2470 (48)	386 (7)	344 (7)	188 (29)	658 (28)	1 (11)
C(2)	-22113 (25)	39268 (10)	46767 (9)	2419 (52)	402 (8)	312 (7)	-63 (31)	500 (32)	-64 (11)
N(3)	-2983 (25)	32186 (10)	44379 (9)	2762 (49)	420 (8)	300 (7)	377 (33)	615 (29)	101 (11)
C(4)	9841 (25)	32426 (10)	35506 (9)	2295 (49)	411 (8)	300 (7)	-145 (34)	388 (30)	-107 (12)
C(5)	1958 (25)	40934 (10)	28104 (9)	2269 (50)	401 (8)	284 (7)	-230 (32)	390 (30)	-43 (12)
C(6)	-16268 (25)	48283 (10)	30515 (9)	2423 (52)	410 (8)	307 (7)	-272 (32)	395 (31)	-22 (12)
O(7)	-32867 (20)	38455 (7)	54873 (7)	3323 (46)	519 (7)	405 (6)	415 (28)	1201 (27)	-6 (10)
O(8)	27270 (20)	25558 (8)	34399 (7)	3210 (44)	504 (6)	360 (6)	740 (28)	778 (25)	14 (10)
C(9)	13859 (30)	41081 (13)	17980 (11)	2497 (57)	483 (9)	338 (8)	-217 (39)	669 (34)	1 (14)
C(10)	-4937 (27)	35912 (10)	8922 (10)	2775 (57)	421 (8)	328 (7)	90 (33)	679 (33)	-17 (12)
O(11)	-26857 (22)	31891 (10)	9799 (8)	3238 (48)	962 (10)	464 (7)	-1295 (35)	1094 (29)	-550 (13)
O(12)	5203 (24)	36166 (9)	-84 (8)	3993 (58)	576 (7)	307 (6)	-670 (32)	931 (29)	-93 (10)
C(13)	-25002 (42)	57904 (14)	24071 (15)	3816 (74)	472 (10)	484 (10)	264 (46)	878 (47)	196 (17)
H(14)	-1027 (46)	6313 (15)	2515 (17)	742 (139)	62 (15)	131 (24)	-329 (83)	-226 (89)	95 (29)
H(15)	-4103 (51)	6114 (16)	2588 (16)	930 (168)	75 (18)	84 (19)	36 (92)	345 (95)	101 (28)
H(16)	-2716 (48)	5656 (14)	1694 (16)	1025 (167)	58 (16)	60 (16)	318 (79)	77 (86)	14 (26)
H(17)	-4159 (34)	5224 (14)	4161 (12)	460 (103)	83 (16)	46 (13)	86 (64)	-40 (58)	39 (23)
H(18)	288 (37)	2718 (14)	4912 (15)	414 (102)	66 (16)	86 (17)	32 (62)	333 (72)	-44 (25)
H(19)	3136 (37)	3720 (13)	1877 (12)	380 (96)	88 (16)	42 (12)	36 (67)	111 (57)	-11 (22)
H(20)	1692 (36)	4836 (14)	1562 (11)	634 (116)	72 (15)	25 (11)	-169 (66)	177 (56)	-9 (21)
H(21)	-642 (43)	3199 (20)	-530 (17)	477 (125)	182 (28)	95 (21)	-18 (94)	91 (81)	145 (39)

Table 4. Observed and calculated structure factors (x 10)

The 26 reflections indicated with an asterisk (*) were measured as having net intensities less than zero; they were given zero weight in the least-squares refinement.

Main body of the document containing a large grid of numerical data representing structure factors for various reflections. The grid is organized into columns with reflection indices (h, k, l) and corresponding observed (Fo) and calculated (Fc) intensity values.

Table 5. Bond distances and angles involving the hydrogen atoms

Standard deviations are about 0.02 Å and 1°.

Table of bond distances and angles involving hydrogen atoms. It lists distances in Å and angles in degrees for various atom pairs and configurations.

Description and discussion of the structure

The standard deviations in the atomic coordinates (Table 3), as calculated from the diagonal elements of the least-squares inverse matrix, correspond to positional uncertainties of about 0.0012 Å for atoms N(1)~O(12), 0.0018 Å for atom C(13) and 0.02 Å for the H atoms. Standard deviations in distances and angles between heavy atoms, then, are in the neighborhood of 0.002 Å and in the bond angles about 0.10°; standard deviations involving hydrogen atoms are about 0.02 Å in the bond distances and about 1° in the bond angles.

A stereoscopic view of the molecule is shown in Fig. 2. Bond distances and angles involving the heavy atoms are shown in Fig. 3; those involving hydrogen atoms are listed in Table 5. In general, the bond distances are in excellent agreement with the values found in 5-ethyl-6-methyluracil (Reeke & Marsh, 1966) and in thymine (5-methyluracil; Gerdil, 1961). The most significant discrepancies among the three determinations are in the C(4)–C(5) and N(3)–C(4) distances, for which the values 1.455 (5) and 1.391 (5) Å found in 5-ethyl-6-methyluracil differ from our values of 1.442 (2) and 1.378 (2) Å by less than three times the pooled standard deviations. Differences between the bond angles, particularly the exterior angles at C(4), C(5) and C(6), are somewhat more significant and appear to reflect slightly different ways of relieving the crowding between the substituent groups. The relatively large difference between the bond angles N(3)–C(4)–O(8) and C(5)–C(4)–O(8), which is common to all three of these compounds, cannot be blamed on crowding, as essentially the same values (119 and 125°) are found in crystals of uracil itself (Stewart & Jensen, 1967).

The pyrimidine ring is significantly nonplanar (Table 6); it is folded about the line C(2)···C(5) into

a boat conformation. Each half of the boat – C(2), N(3), C(4), C(5) and C(5), C(6), N(1), C(2) – is planar within 0.002 Å, and the dihedral angle between the two halves is 2.5°. This folding helps to relieve the crowding between the substituent groups O(8), C(9), and C(13) while maintaining approximate planarity of the bonding about the individual ring atoms. The same type of folding occurs in 5-ethyl-6-methyluracil (Reeke & Marsh, 1966), where the dihedral angle is 3°; on the other hand, in thymine (Gerdil, 1961), which has a hydrogen atom rather than a methyl group at C(6), the ring atoms are closely coplanar.

Table 6. Deviations from the least-squares plane of the pyrimidine ring

The direction cosines of the least-squares plane of atoms N(1)–C(6), weighted equally, are 0.6724, 0.5491, and 0.3828 relative to the crystal axes *a*, *b*, and *c*; the origin-to-plane distance is 4.295 Å.

	Deviation		Deviation		Deviation
N(1)	0.009 Å	O(7)	–0.031 Å	H(14)	0.98 Å
C(2)	–0.016	O(8)	0.054	H(15)	–0.14
N(3)	0.006	C(9)	–0.111	H(16)	–0.44
C(4)	0.011	C(10)	–1.530	H(19)	0.23
C(5)	–0.019	C(13)	0.075	H(20)	0.38
C(6)	0.009	H(17)	–0.01	O(7)*	–0.031
		H(18)	0.08	O(11)†	0.640

* At $-1-x, 1-y, 1-z$; acceptor of hydrogen bond from N(1)–H(17).

† At $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; acceptor of hydrogen bond from N(3)–H(18).

The four atoms C(9), C(10), O(11), and O(12) of the carboxyl group are coplanar within 0.004 Å; this plane makes a dihedral angle of 85.5° with the plane of the pyrimidine ring. The hydrogen atom H(21) is displaced from the plane of the carboxyl group by 0.12 Å, which is about five e.s.d.'s. The direction of the displacement is the same as that of the hydrogen-bond acceptor atom O(8) (at $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$), which

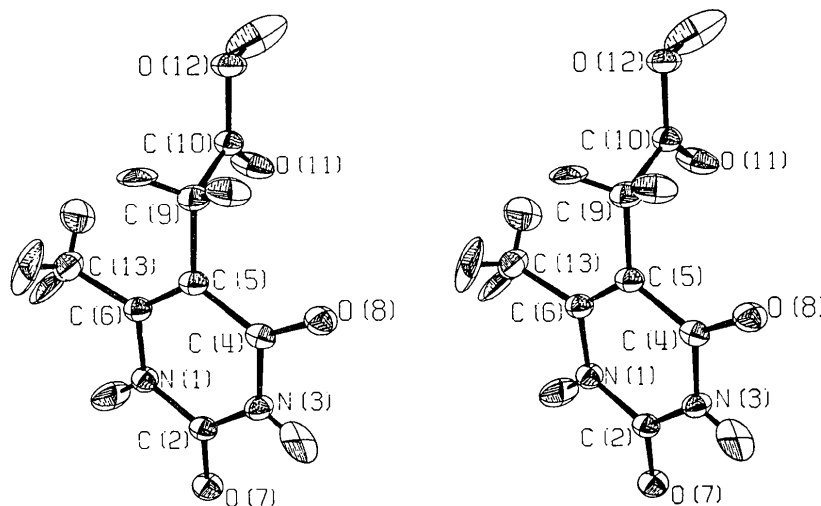


Fig. 2. A stereoscopic view of the molecule (Johnson, 1965). The anisotropic temperature parameters are represented by 50% probability ellipsoids.

lies 0.401 Å from the plane of the carboxyl group. A somewhat smaller deviation of atom H(18) from the plane of the pyrimidine ring (see Table 6) can similarly be blamed on the influence of its hydrogen-bond acceptor, O(11).

If we define the conformation about the exocyclic bonds C(5)–C(9) and C(6)–C(13) as being 'eclipsed' when one of the bonds to the exocyclic atom lies in the plane of the pyrimidine ring and *gauche* when one of the bonds lies in a plane perpendicular to the ring, the conformation about the C(5)–C(9) bond is within 5° of *gauche* and the conformation about the C(6)–C(13) bond is about midway between *gauche* and 'eclipsed'. These conformations are clearly dictated by the crowding between the substituent groups. The closest approaches between these groups are:

O(8)···H(19), 2.51 Å; H(20)···H(16), 2.42 Å; H(15)···H(17), 2.30 Å.

A drawing of the hydrogen-bond arrangement is shown in Fig. 4. Rather surprisingly, the carboxylic acid groupings do not form dimers across centers of symmetry; rather, the O–H group donates a hydrogen bond to a ring carbonyl group O(8) while the oxygen atom O(11) accepts a hydrogen bond from a ring nitrogen atom N(3). Centers of symmetry are utilized in forming base-pairs linked by N(1)–H(17)···O(7) hydrogen bonds, a feature also found in crystals of thymine monohydrate (Gerdil, 1961) and of 5-ethyl-6-methyluracil (Reeke & Marsh, 1966). Base-pairing across a center of symmetry between pairs of N(3)–H(18)···O(8) hydrogen bonds is found in crystals of 5-ethyl-6-methyluracil and of uracil itself (Parry, 1954; Stewart & Jensen, 1967).

Distances and angles involving the hydrogen bonds are given in Table 7.

Molecules related to one another by translation along the *a* axis form a column of stacked base-pairs; the stacking distance is 3.29 Å. Adjacent base-pairs within the stack are off-set, so that maximum overlap is between unlike atoms. The closest stacking contacts between heavy atoms are: C(2)···O(8), 3.221 Å; C(2)···N(1), 3.238 Å; O(7)···C(6), 3.260 Å. A drawing of one of these columns, as viewed perpendicular to the planes of the bases, is shown in Fig. 5.

The shortest contacts between atoms in different stacks involve molecules related to one another by an *n*-glide plane. They include: O(7)···O(12), 3.210 Å; N(3)···O(12), 3.244 Å; O(7)···C(10), 3.330 Å.

The anisotropic temperature factors of the heavy atoms (see Fig. 2) were examined using the rigid-body treatment of Schomaker & Trueblood (1968). When all 13 atoms were included, the fit to a rigid-body model was unsatisfactory. Deletion of the carboxyl

oxygen atoms, O(11) and O(12), led to a considerably improved but not entirely satisfactory fit; although the quantity $[\sum(\Delta U_{ij})^2/n-s]^{1/2}$ had the relatively low value of 0.0017, many of the individual values of ΔU_{ij} (particularly for $i \neq j$) were greater than three times

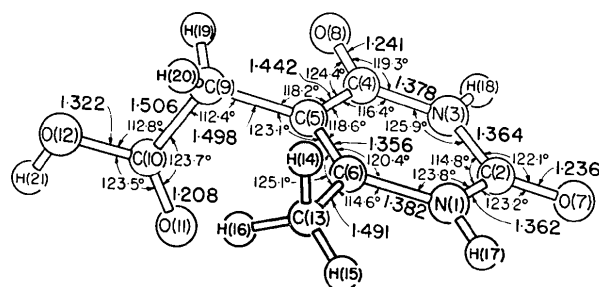


Fig. 3. Bond distances and angles involving the heavy atoms. Standard deviations are about 0.002 Å and 0.10°.

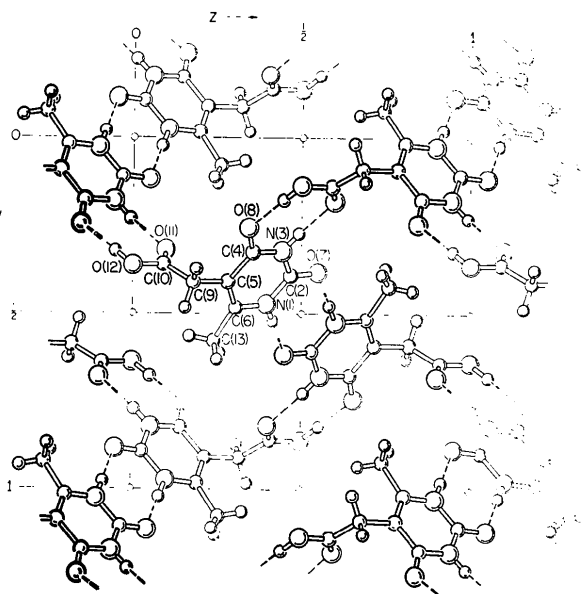


Fig. 4. A drawing of the structure as viewed down the *a* axis. Dashed lines represent hydrogen bonds.

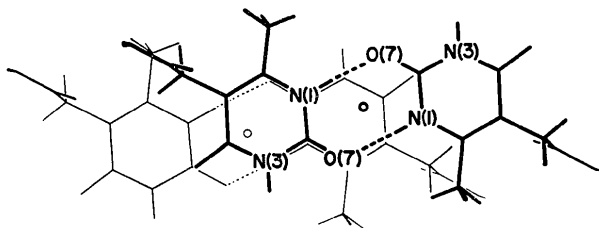


Fig. 5. A drawing of the base stacking, as viewed perpendicular to the planes of the pyrimidine rings.

Table 7. Hydrogen bonds

From A–H	To B	Molecule at	$D(A \cdots B)$	$D(H \cdots B)$	$\angle H-A \cdots B$
N(1)–H(17)	O(7)	$-1-x, 1-y, 1-z$	2.798 Å	1.82 Å	0°
N(3)–H(18)	O(11)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	2.804	1.93	9
O(12)–H(21)	O(8)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	2.667	1.71	6

their standard deviations. The lengths of principal axes of the L tensor were 16, 7, and $4(^{\circ})^2$, and implied corrections to the interatomic distances were in the range 0.002–0.004 Å. We have ignored these corrections.

While the relatively large standard deviations in the anisotropic temperature parameters of the hydrogen atoms preclude detailed discussion of their significance, we are comforted to note that the implied libration ellipsoids (Fig. 2) are not totally unreasonable.

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A Neutron Diffraction Study of the Crystal Structure of Pyrene, $C_{16}H_{10}$

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The crystal structure of pyrene, $C_{16}H_{10}$, has been redetermined at room temperature by means of neutron diffraction. Least-squares refinement of positional, thermal, scale, and extinction parameters gave an R value of 0.034 for 1008 reflexions [with $F^2 > 2\sigma(F^2)$] and 236 parameters; the weighted R value is 0.032. The bond distances agree with those predicted by molecular orbital calculations; the discrepancy between earlier observations and the theoretical values stems from the fact that the earlier values were determined by X-ray diffraction, which locates the centre of the charge cloud rather than the centre of the atom. A correlation has been found for the differences between bond distances determined by X-rays and by neutrons with a function of the bond orders.

Introduction

The crystal structure of pyrene has been previously determined by Robertson & White (1947) from two-dimensional data, and by Camerman & Trotter (1965), henceforth referred to as C & T, from three-dimensional data. Both studies were made by means of X-ray diffraction.

The bond distances obtained by C & T differ considerably from those calculated by SCF-LCAO- π -MO methods [e.g. Warren & Yandle (1968)]. We have therefore determined the structure yet again, this time by means of neutron diffraction so as to obtain more accurate measurements of the bond lengths. The present determination was carried out at room temperature.

Whilst this work was being carried out we learnt from Allmann (1970) that he had repeated the X-ray work on pyrene. There are marked differences between the X-ray results and those obtained by neutron

diffraction. We attribute the difference to the non-sphericity of the electron clouds and correlate the differences between the bond distances as obtained by the two methods with a function of the bond order.

Crystal data

Pyrene, $C_{16}H_{10}$; $M=202.2$; m.p. $150^{\circ}C$. Monoclinic, $a=13.649 \pm 0.01$, $b=9.256 \pm 0.01$, $c=8.470 \pm 0.01$ Å, $\beta=100.28^{\circ} \pm 0.04^{\circ}$, $U=1052.9$ Å³. The cell dimensions are those of C & T. $D_M=1.27$, $Z=4$. The linear absorption coefficient for neutrons ($\lambda=1.025$ Å) = 1.55 cm⁻¹. The systematic absences are: $h0l$ with h odd, $0k0$ with k odd; the space group is $P2_1/a$ (C_{2h}^5 , No. 14).

Experimental

The crystal used for data collection was approximately cylindrical, with the cylinder axis along the [001] direc-