

The Structure of 1-(4-Imidazolylsulfonyl)-4-phenylimidazole

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The crystal and molecular structures of 1-(4-imidazolylsulfonyl)-4-phenylimidazole have been determined by single-crystal X-ray techniques. Crystals are orthorhombic, space group *Pbca*, with $a=9.808$ (6), $b=7.351$ (5), $c=33.958$ (12) Å, and $Z=8$. The structure was solved by direct methods and refined by least-squares calculations to an R of 0.058 for 1038 reflexions with $F > \sigma(F)$ measured on a diffractometer. The molecules form chains in one dimension linked by asymmetric N-H...N hydrogen bonds with N-H of 0.93 Å, H...N of 1.94 Å, N-N of 2.866 Å, and N-H...N of 172°. The chains are associated in the second dimension by the stacking of parallel bases separated by 3.41 Å.

Introduction

The present X-ray study was initiated to establish the molecular structure of the title compound as a guide to our synthesis program on imidazole derivatives. We were particularly interested in the point of attachment of the phenyl ring, the tautomeric form of the imidazoles, and the nature of the hydrogen bonding.

Experimental

A sample of 1-(4-imidazolylsulfonyl)-4-phenylimidazole was obtained from Dr Ellis of this laboratory. Crystals suitable for X-ray work were obtained by the slow evaporation of an ethyl acetate solution. Crystals were air stable. Crystals are orthorhombic; the space group was uniquely determined from the systematic absences observed on Weissenberg and precession photographs. Cell parameters were obtained from the least-squares refinement of the angular positions for 10 reflections carefully centered on a diffractometer at room temperature. The cell data are summarized in Table 1.

Table 1. *Crystal data*

$C_{12}H_{10}N_4SO_2$	
Space group	<i>Pbca</i>
a	9.808 (6)
b	7.351 (5)
c	33.958 (12)
Cell volume	2448.3 Å ³
Z	8
ρ (calculated)	1.49 g cm ⁻³
ρ (observed)	1.49 g cm ⁻³
μ	2.68 cm ⁻¹

A prismatic crystal of dimensions 0.13 × 0.30 × 0.20 mm was chosen for data collection. The crystal was mounted on a Picker four-circle automatic diffractometer with the b axis along the diffractometer ϕ axis. The data were measured with Zr-filtered Mo radiation

(Mo $K\alpha$, $\lambda=0.7107$ Å) and the θ - 2θ scan technique. The scan range for each reflection was 1.5° plus the $K\alpha_1$ - $K\alpha_2$ separation; backgrounds of 15 s were measured before and after each scan. 1140 reflections were measured out to 40° 2θ . No crystal decomposition was observed from the periodic recording of standard reflections.

The data were corrected for Lorentz and polarization effects, but not for absorption. The structure factor errors were estimated according to a scheme reported earlier (Guggenberger, 1968). Those data with $F < \sigma(F)$ were given zero weight in the final refinements. A special effort was made to examine each reflection for possible overlap from neighboring reflections due to lack of resolution with Mo radiation caused by the large c cell edge. Each reflection was individually scaled and plotted as it was measured (on-line to Calcomp) along with the background approximation for that reflection. On examination it appeared that 46 reflections might involve some overlap; these fell in the class $h \leq 2$, $k \leq 4$, and $l > 10$. These data were remeasured with a 2θ scan range of 0.80°. Now 21 of these were acceptable, but there was still some question about the remaining 25 reflections so they were excluded entirely from the refinement. A structure-factor comparison was made at the end of the refinement for the 21 reflections included and their agreement was acceptable.

Structure determination and refinement

The positions of the nonhydrogen atoms were determined by the symbolic addition procedure with the Fleischer, Dewar & Stone (1967) computer program. The statistical distribution of E 's followed the expected centric distribution; the observed values of 0.81 for $\langle |E| \rangle$ and 0.95 for $\langle |E^2 - 1| \rangle$ are close to the theoretical values of 0.798 and 0.968, respectively (Karle, Hauptman & Christ, 1958). 278 reflections were phased in the \sum_2 process (E 's > 1.0 used). Three reflections were

Table 2. *Final coordinates and thermal parameters for the heavy atoms*

Standard deviations are given in parentheses. Temperature factor has the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Data are $\times 10^4$ ($* \times 10^5$).

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	45206 (13)*	61520 (19)*	41310 (4)*	804 (18)*	1539 (33)*	73 (2)*	15 (21)*	39 (4)*	0 (6)*
O(1)	5686 (3)	5340 (5)	43100 (11)*	76 (4)	229 (10)	110 (4)*	51 (5)	47 (11)*	74 (17)*
O(2)	3707 (3)	5258 (5)	38495 (10)*	118 (5)	192 (9)	90 (4)*	-31 (6)	20 (12)*	-95 (17)*
N(1)	5101 (4)	8037 (6)	39123 (12)*	79 (6)	183 (11)	71 (5)*	-15 (7)	17 (13)*	34 (20)*
N(2)	6331 (5)	10513 (7)	38089 (15)*	111 (7)	200 (13)	134 (6)*	-31 (7)	-76 (18)*	156 (24)*
N(3)	1712 (4)	7575 (6)	48612 (12)*	79 (6)	172 (11)	72 (5)*	7 (6)	53 (14)*	34 (20)*
N(4)	3969 (4)	7567 (5)	48495 (12)	78 (6)	164 (11)	69 (5)*	-13 (6)	17 (14)*	9 (19)*
C(1)	6240 (6)	9012 (9)	40083 (17)*	95 (8)	220 (16)	109 (7)*	-31 (10)	-69 (18)*	92 (29)*
C(2)	5183 (5)	10574 (7)	35664 (15)*	78 (7)	154 (14)	71 (6)*	1 (9)	59 (18)*	-50 (26)*
C(3)	4422 (5)	9084 (8)	36337 (15)*	87 (7)	188 (14)	63 (6)*	5 (9)	-22 (16)	52 (25)*
C(4)	2875 (6)	7970 (7)	50575 (15)*	79 (7)	191 (14)	71 (6)*	-21 (9)	26 (20)*	71 (23)*
C(5)	3454 (5)	6929 (7)	44985 (15)*	59 (7)	133 (12)	77 (6)*	-1 (7)	1 (16)*	30 (22)*
C(6)	2065 (5)	6916 (7)	45007 (16)*	84 (8)	156 (13)	82 (6)*	4 (8)	19 (17)*	47 (23)*
C(7)	4968 (6)	12053 (8)	32875 (15)*	96 (8)	177 (14)	73 (6)*	24 (9)	47 (18)*	6 (25)*
C(8)	3753 (6)	12152 (8)	30780 (16)*	134 (9)	202 (15)	77 (6)*	46 (9)	4 (20)*	35 (28)*
C(9)	3538 (6)	13539 (10)	28068 (18)*	124 (8)	268 (18)	98 (7)*	37 (11)	54 (20)*	3 (31)*
C(10)	4545 (9)	14832 (10)	27460 (20)*	179 (11)	316 (21)	111 (8)*	96 (14)	101 (27)*	174 (34)*
C(11)	5729 (7)	14766 (9)	29621 (21)*	173 (11)	209 (16)	129 (9)*	3 (11)	147 (26)*	121 (35)*
C(12)	5945 (6)	13386 (9)	32296 (17)*	122 (8)	227 (16)	96 (7)*	-3 (11)	54 (19)*	68 (28)*

assigned symbols and three were used to fix the origin. All the nonhydrogen atoms were found on the resultant *E* map.

The model was refined by full-matrix least-squares calculations with isotropic thermal parameters giving an R ($= \sum |F_o| - |F_c| / \sum |F_o|$) of 0.115 and R_w ($= [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^2$) of 0.133. The model was refined with anisotropic thermal parameters giving an R of 0.088 and R_w of 0.096. At this point electron density maps were calculated through the planes of the imidazole and benzene rings to locate the hydrogen atoms. All the hydrogen atom positions were located easily and included in the refinement; fixed isotropic thermal parameters of 4.0 \AA^2 were used for the imidazole hydrogens and 5.0 \AA^2 for the benzene hydrogens. The final refinements were done in two sections: (a) all nonhydrogen atom parameters, and (b) the parameters involving the hydrogen atoms. The final R values for the 1038 reflections with $F > \sigma(F)$ are 0.058 for R and 0.060 for R_w . The corresponding values for all the data (1114 reflections) are 0.067 for R and 0.061 for R_w . The final goodness-of-fit $\{ = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} \}$ is 1.35.

The scattering factors for the neutral atoms were used (Hanson, Herman, Lea & Skillman, 1964). The sulfur atom was corrected for the real and imaginary parts of the anomalous scattering effect (Templeton, 1962). A final electron-density difference map was calculated and showed no unusual features ($|e| \leq 0.2 \text{ e \AA}^{-3}$).

The final parameters for the heavy atoms are given in Table 2 and those for the hydrogen atoms in Table 3; the hydrogens are identified also by the atoms to which they are attached. The observed and calculated structure factors are listed in Table 4.

Table 3. *Coordinates and thermal parameters for the hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)N(3)	0.0839	0.7622	0.4968	4.0
H(2)C(1)	0.6797	0.8540	0.4205	4.0
H(3)C(3)	0.3533	0.8610	0.3505	4.0
H(4)C(4)	0.2851	0.8392	0.5328	4.0
H(5)C(6)	0.1418	0.6542	0.4322	4.0
H(6)C(8)	0.2977	1.1164	0.3155	5.0
H(7)C(9)	0.2604	1.3538	0.2649	5.0
H(8)C(10)	0.4408	1.5678	0.2690	5.0
H(9)C(11)	0.6437	1.5664	0.2954	5.0
H(10)C(12)	0.6797	1.3261	0.3378	5.0

Discussion

Molecular structure

The molecular structure illustrating the numbering system used here and the thermal ellipsoids plotted at the 50% probability level is shown in Fig. 1. Two points of significant interest to us are established immediately, namely, the point of attachment of the phenyl ring and tautomeric form of the N(3),N(4)-imidazole ring. The phenyl ring is attached to C(2) instead of the other possibility for attachment to C(3). The N(3),N(4)-imidazole ring exists as the N(3)-H tautomeric form as opposed to the N(4)-H form.

The bond distances are shown in Fig. 2 and the bond angles in Fig. 3. In both figures the open bonds signify the double-bond positions of the primary resonance form. Other short intramolecular distances as well as intermolecular distances are given in Table 5. A comparison of imidazole bond distances with some observed structures is given in Table 6 which shows the similarities of imidazole geometries in very different bonding situations, including the metal-bonded case.

Further comparisons are available for imidazole geometries in purines (Sletten & Jensen, 1969) and adenines (Watson, Sutor & Tollin, 1965) and metal-imidazoles (Mighell & Santoro, 1971; Prout, Allison & Rossotti, 1971).

The S-O distances are in the range of frequently observed values (Meyers & Trueblood, 1969, and refer-

Table 5. *Nonbonding distances*

(i) Intramolecular distances (Å)			
O(1)-O(2)	2.493	O(2)-C(3)	2.990
O(1)-N(1)	2.467	O(2)-C(6)	2.995
O(1)-C(5)	2.563	O(2)-H(5)	2.917
O(1)-N(4)	2.979	O(2)-H(3)	2.733
O(1)-C(1)	2.938	N(1)-C(5)	2.690
O(1)-H(2)	2.617	H(3)-H(6)	2.287
O(2)-N(1)	2.468	H(10)-N(2)	2.536
O(2)-C(5)	2.536		
(ii) Intermolecular distances (Å)			
O(1)-H(4) (a)	2.624	H(4)-H(2) (c)	2.365
O(2)-H(3) (b)	2.768	H(3)-H(6) (b)	2.615
N(3)-N(4) (c)	2.866	H(6)-H(7) (b)	2.647
C(9)-H(6) (d)	2.707		

Symmetry operators

- (a) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$ (c) $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$
 (b) $\frac{1}{2} - x, -\frac{1}{2} + y, z$ (d) $\frac{1}{2} - x, \frac{1}{2} + y, z$

Table 4. *Observed and calculated structure factors*

The columns give the running index *h*, 10*F_o*, and 10*F_c*. An asterisk marks an unobserved reflection (see text).

Table 4 contains a large grid of numerical data for structure factors, including indices *h*, 10*F_o*, and 10*F_c*. The data is organized in columns corresponding to different *h* values, with some columns marked with an asterisk to indicate unobserved reflections.

ences therein). The distances and angles around the sulfur atom are similar to those observed in the sulfathiazole polymorphs (Kruger & Gafner, 1972) when allowances are made for the different types of nitrogen atoms (>N- vs. >N) and the internal compensation in the S-C bond. The S-C(5) and S-N(1) distances are shorter than expected for S-Csp² and S-Nsp² 'single' bonds [see Ammon, Watts & Stewart (1970) for a listing of S-C bonds]. These data are consistent with some (possibly appreciable) delocalization of the imidazole π systems with the SO₂ group. Some of the angular distortion [N(1)-S-C(5) is 104.7 (2)°, O(1)-S-O(2) is 123.2 (2)°] may result from this interaction, but it is difficult to separate this from steric effects. The C-H distances are normal for an X-ray determination as are the benzene C-C distances. The C(2)-C(7) distance of 1.457 (7) is short for a Csp²-Csp² distance; this along with the planarity of the adjacent rings is consistent with some delocalization of the two ring systems.

The interatomic angles in the N(3), N(4)-imidazole are consistent with the N(3)-H tautomeric form established by the electron density maps. In particular the larger internal angle subtended at N(3) compared to N(4) is typical for the protonated N site (Singh, 1965; Sletten, Sletten & Jensen, 1968). The same tautomer was observed in the histamine imidazole ring in 6-histaminopurine (Thewalt & Bugg, 1972).

The data for the least-square planes through the different ring systems are given in Table 7. Each of the individual rings is planar to 0.01 Å while the combined phenylimidazole ring is planar to 0.09 Å. The angle between the two imidazole rings is 100.2° (79.8° between normals, Table 7) and the angle between the imidazole and attached phenyl ring is 7.2° (planes II and IV).

The thermal motion appears to be normal for the geometries involved. The root-mean-square amplitudes of vibration vary from 0.164 to 0.365 Å. The most anisotropic atom is O(1) (0.164-0.285 Å).

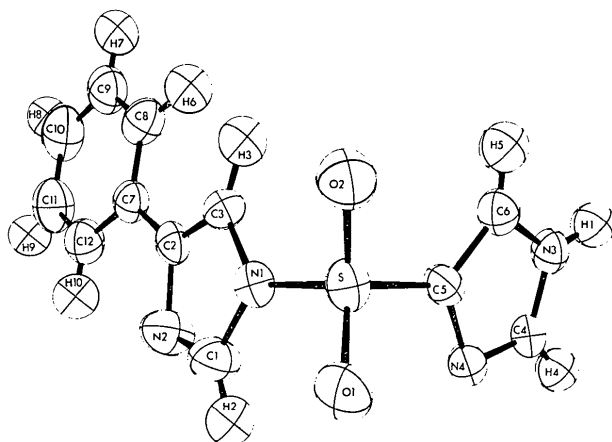
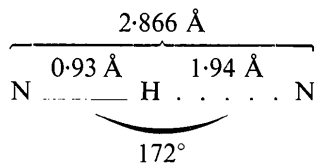


Fig. 1. Molecular structure illustrating thermal ellipsoids and numbering system.

Packing and hydrogen bonding

The most important features of the crystal packing are hydrogen bonding and base stacking. Both of these features are commonly found in nucleic acid constituents and polynucleotides both in the solid and solution states (Ts'o, 1968). Numerous examples of base stacking with purine and pyrimidine bases can be found in the literature (Thewalt & Bugg, 1972; Bugg, Thomas, Sundaralingam & Rao, 1971, and references therein). While the N(3),N(4)-imidazole is involved in hydrogen bonding and base stacking, the N(1),N(2)-imidazole and phenyl ring are involved in the conventional herringbone packing of planar aromatic rings.

The molecules form chains in one dimension by N-H...N hydrogen bonds characterized by



These chains are stacked in the second dimension with 3.41 Å between parallel molecules. The hydrogen bonding and base stacking are shown in Fig. 4; the top view is normal to the plane of the hydrogen bonded imidazole ring. The overlap is partial but specific in the sense that N(3) and C(5) of each imidazole overlap above and below with C(5) and N(3), respectively, of stacked imidazoles. The orientation of

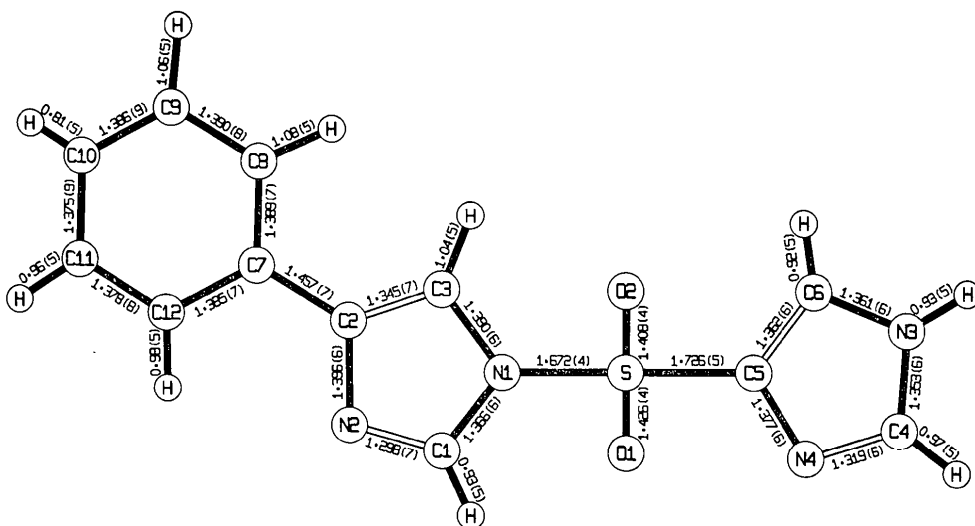


Fig. 2. Bond distances (Å).

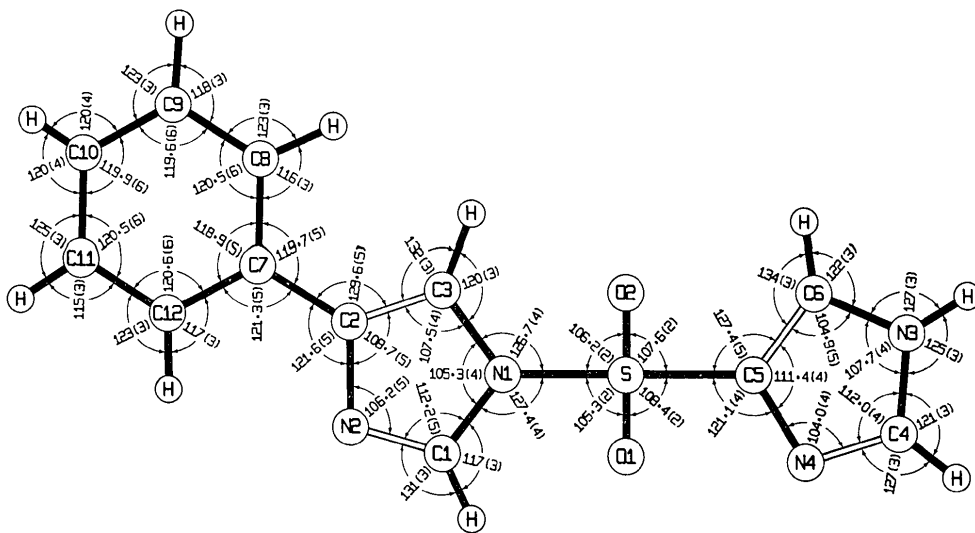


Fig. 3. Bond angles (°).

Table 6. Comparison of imidazole distances

	N(3), N(4) ring	N(1), N(2) ring	Imidazole	1,3-Diphosphor- ylimidazole	6-Histamino- purine*	Purine	Hexakis(imida- zole)nickel(II) nitrate
C(5)-N(4)	1.377 (6)	1.396 (6)	1.378 (5)	1.372 (8)	1.366 (8)	1.374 (8)	1.372 (7)
N(4)-C(4)	1.319 (6)	1.298 (7)	1.326 (5)	1.345 (7)	1.326 (8)	1.312 (8)	1.316 (7)
C(4)-N(3)	1.353 (6)	1.366 (6)	1.349 (5)	1.344 (8)	1.318 (8)	1.330 (8)	1.329 (7)
N(3)-C(6)	1.361 (6)	1.390 (6)	1.369 (5)	1.385 (7)	1.366 (8)	1.374 (8)	1.352 (7)
C(6)-C(5)	1.362 (6)	1.345 (7)	1.358 (5)	1.362 (9)	1.340 (8)	1.403 (8)	1.366 (7)
Reference	Present work		Martinez- Carrera (1966)	Beard & Lenhert (1968)	Thewalt & Bugg (1972)	Watson, Sweet & Marsh (1965)	Santoro, Mighell, Zocchi & Reimann (1969)

* The histamine imidazole ring used.

the hydrogen bonding and base stacking were established explicitly by fixing an orthogonal coordinate system to the imidazole ring and determining its orientation relative to the cell edges. Two vectors originating from the midpoint of N(3) and N(4) were used to establish the local coordinate system, u in the direction of the midpoint to N(3) and v in the direction of the midpoint to C(4). The three local axes were taken according to

$$\begin{aligned} \mathbf{h} &= \mathbf{u} \\ \mathbf{m} &= (\mathbf{u} \times \mathbf{v}) \times \mathbf{u} \\ \mathbf{s} &= \mathbf{u} \times \mathbf{v} \end{aligned}$$

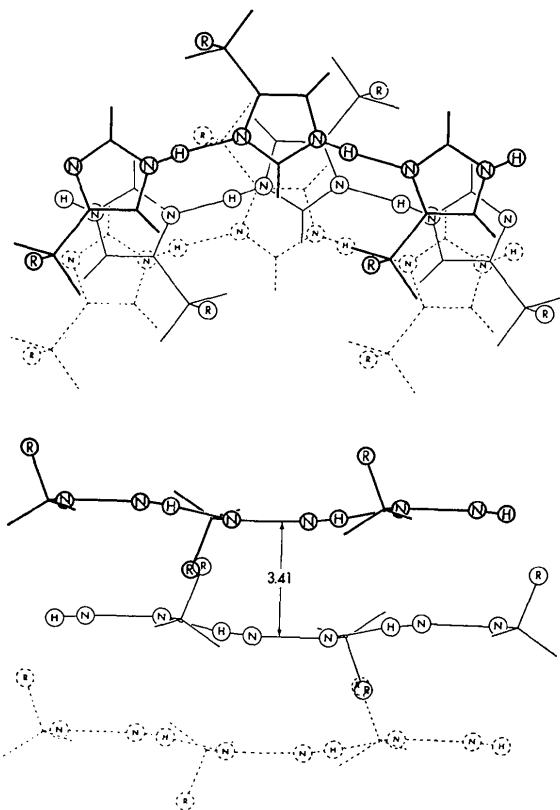


Fig. 4. Front and top views of the base stacking and hydrogen bonding in 1-(4-imidazolylsulfonyl)-4-phenylimidazole (R represents the phenylimidazole group).

Table 7. Least-squares planes through rings

(a) Equations of planes in Cartesian coordinates relative to a, b, c .

$$\begin{aligned} \text{I} & -0.0055X + 0.9277Y - 0.3732Z + 9.993 = 0 \\ \text{II} & -0.5022X + 0.4774Y + 0.7211Z - 9.897 = 0 \\ \text{III} & -0.4457X + 0.5317Y + 0.7202Z - 1.057 = 0 \\ \text{IV} & -0.4106X + 0.5620Y + 0.7180Z - 1.101 = 0 \end{aligned}$$

(b) Deviations (Å) from the planes (asterisks mark atoms included in the plane calculation)

	I	II	III	IV
S	-0.066	0.150	-0.034	-0.213
O(1)	-0.853	-0.271	-0.423	-0.582
O(2)	-0.314	-0.452	-0.716	-0.941
N(3)	-0.006*			
N(4)	-0.008*			
C(4)	0.009*			
C(5)	0.005*			
C(6)	0.000*			
H(1)	-0.104			
N(1)		-0.010*	-0.086*	-0.202
N(2)		0.000*	0.091*	0.074
C(1)		0.006*	0.032*	-0.023
C(2)		-0.007*	0.024*	-0.030
C(3)		0.010*	-0.061*	-0.175
C(7)		-0.065	0.014*	-0.012*
C(8)		0.055	0.071*	0.007*
C(9)		-0.016	0.044*	0.006*
C(10)		-0.207	-0.040*	-0.014*
C(11)		-0.284	-0.055*	0.009*
C(12)		-0.220	-0.034*	0.004*

(c) Dihedral angles (°)

[S, O(1), O(2)]-			
[S, N(1), C(5)]	89.4	II-III	4.5
I-II	79.8	II-IV	7.2
I-III	76.9	III-IV	2.7
I-IV	75.2		

Then h is the direction of the hydrogen-bonded chains, s is the stacking direction (imidazole plane normal) and m completes the orthogonal coordinate system. The matrix of angles describing the orientation of the local coordinate system and the cell edges is

	a	b	c
h	179.0°	89.9°	90.0°
m	87.4	66.9	23.3
s	90.3	23.1	113.1

Thus the hydrogen-bond direction h is parallel to a and the stacking direction s is normal to a , but in a general orientation with respect to b and c .

Other examples of base stacking of simple imidazoles are imidazolium dihydrogen orthophosphate (Blessing & McGandy, 1972) and 1,3-dimethyl-2(3*H*)-imidazole-thione (Ansell, Forkey & Moore, 1970) for which stacking views are provided by the authors. Stacking views for imidazole (Martínez-Carrera, 1966) and 1,3-diphosphorylimidazole (Beard & Lenhart, 1968) were drawn and are shown in Fig 5. The overall hydrogen bonding and base stacking appear to be more extensive in 1-(4-imidazolylsulfonyl)-4-phenylimidazole than in other simple imidazoles, but the number of available structures is too small to make any generalizations. It is noteworthy, however, that the stacking pattern found here is consistent with the idea that dipole-induced dipole forces (Bugg *et al.*, 1971, and references therein) are responsible for solid-state base stacking in purine and pyrimidine bases.

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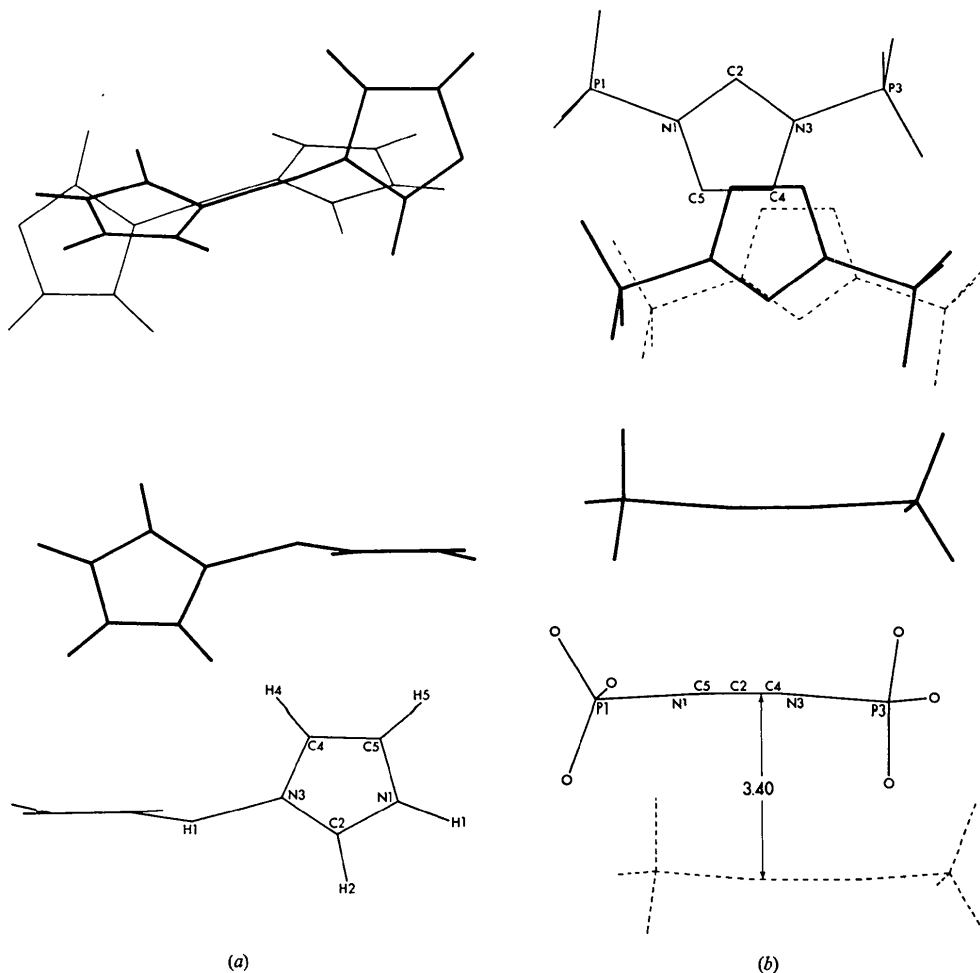


Fig. 5. Front and top views of the stacking in: (a) imidazole (Martínez-Carrera, 1966), (b) 1,3-diphosphorylimidazole (Beard & Lenhart, 1968).

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The Molecular and Crystal Structure of the Sodium Salt of Deoxyadenosine-5'-phosphate Hexahydrate

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The crystal structure of the sodium salt of deoxyadenosine-5'-phosphate hexahydrate has been determined by X-ray diffraction techniques. The unit cell is orthorhombic, space group $P2_12_12_1$, with cell dimensions $a=43.64$ (2), $b=6.908$ (4), $c=6.826$ (4) Å and $Z=4$. The data (1806 reflexions) were collected photographically by equi-inclination Weissenberg geometry and estimated visually. The structure was solved by the symbolic addition procedure and refined to an R value of 0.060. 24 out of 25 hydrogen atoms were located. The sugar ring has the conformation $C(2')$ -endo, $C(3')$ -endo and the glycosidic torsional angle (χ_{C-N}) is 63.4° . The sugar ring oxygen $O(1')$ seems to participate in a hydrogen bond with the amino nitrogen of the base, a feature hitherto not clearly shown in similar structures. The stacking of adenine bases at 3.45 Å with considerable overlap is another interesting feature. The sodium ion has a nearly octahedral coordination with water oxygen atoms at distances of 2.374 to 2.454 Å. The crystal structure may be viewed as consisting of alternate channels of water molecules (sodium ion polyhedra) and nucleotides.

Introduction

Recently, Jacob and colleagues at our Institute have prepared many nucleic acid reactive antibodies for immunological studies, specific to deoxyribonucleotide antigens and in particular to deoxyadenosine-5'-monophosphate (5'-dAMP) (Humayun & Jacob, 1973). This paper reports the complete molecular and crystal structure of this nucleotide.* The present analysis continues our earlier studies on the conformations of DNA constituents (Viswamitra, Reddy, Lin & Sundaralingam, 1971).

Experimental

Crystal growth and crystal data

The material used in the present work was obtained from Sigma Chemical Company (U.S.A.) as a disodium salt of 2'-deoxyadenosine-5'-monophosphoric acid. It

was crystallized by slow diffusion of dioxane into water solutions of the sample. The crystal data were obtained from rotation, Weissenberg and precession photographs using $Cu K\alpha$ radiation (Table 1). The density measured by the flotation method using a mixture of carbon tetrachloride and acetone is 1.53 g cm^{-3} , suggesting a chemical formula of the molecule in the asymmetric unit as $C_{10}H_{13}N_5Na_2O_6P \cdot 5H_2O$ ($d_{calc} = 1.511$ g cm^{-3}). However, detailed structure analysis showed that the molecule exists as $C_{10}H_{13}N_5NaO_6P \cdot 6H_2O$, in the crystal. The crystal data are presented in Table 1 and the numbering scheme for the molecule is shown in Fig. 1.

Intensity data

The intensity data were collected with $Cu K\alpha$ radiation from a crystal of size $0.5 \times 0.4 \times 0.25$ mm, by the equi-inclination Weissenberg technique for layers $hk0$ – $hk6$ and $h0l$. In all, 1806 reflexions were estimated visually by using a calibrated film strip prepared with the experimental crystal. The data were corrected for

* A preliminary communication on this structure has already appeared (Reddy & Viswamitra, 1973).