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Studies on Intermolecular Complex Formation. VII.* Crystal Structure of Adenosine–5-Bromouracil

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The crystal structure of a complex between adenosine and 5-bromouracil has been determined by the heavy-atom method, and refined to $R = 8.3\%$ for 2003 independent reflections. The crystals are monoclinic, space group $P2_1$, with $a = 7.050$ (3), $b = 16.860$ (5), $c = 7.347$ (3) Å, $\beta = 102.98$ (4)°. The adenosine and 5-bromouracil molecules form a planar base pair and are connected to each other by two hydrogen bonds, *i.e.* AN(1)···UHN(1) (2.83 Å) and AN(10)H···UO(2) (3.18 Å). The adenosine molecule in this complex has been found to exist in the *syn* conformation, with an intramolecular hydrogen bond, AO(5')···AN(3) (2.79 Å).

Introduction

The intermolecular-complex-formation ability of nucleotide bases with organic compounds has been extensively surveyed and the cytosine and adenine molecules showed a strong affinity for organic compounds having the cyclic [C(=O)—NH—C(=O)—NH] or —COOH functional groups. However, in the case of

nucleosides this ability is considerably diminished because of the sugar moiety. In order to induce complex-formation ability of nucleosides in crystalline fields we tried crystallizing from several different aqueous organic solvents. The best solvent for obtaining suitable crystals was a chloroform–ethanol–water (50:45:5 v/v%) mixture. Well shaped complex crystals of adenosine with 5-bromouracil were obtained using the above solvent. Many structural investigations of the complexes of nucleosides or nucleotide-base derivatives have been studied to provide a geometrical interaction scheme for nucleic acids [*e.g.* 1-methylthymine–9-methyladenine (Hoogsteen, 1962), de-

* Part I: Tamura, Sakurai & Sato (1971). Part II: Tamura, Hata, Sato & Sakurai (1972). Part III: Tamura, Hata & Sato (1973). Part IV: Tamura, Sato & Hata (1973). Part V: Tamura, Yoshikawa, Sato & Hata (1973). Part VI: Hata, Yoshikawa, Sato & Tamura (1975).

oxyguanosine–5-bromodeoxycytidine (Haschemeyer & Sobell, 1964), and adenosine–5-bromouridine (Haschemeyer & Sobell, 1965)]. The present structure analysis may provide additional information on intermolecular interactions between these homologous molecules which are related to the biological significance and the molecular dynamic processes.

Experimental

Equimolar amounts of adenosine and 5-bromouracil were dissolved in a hot chloroform–ethanol–water (50:45:5 v/v%) mixture. After being allowed to stand for several days at room temperature, the mixture yielded a crystal suitable for X-ray analysis.

Oscillation and Weissenberg photographs showed the crystals to be monoclinic, space group $P2_1$. The

unit-cell parameters, $a = 7.050 \pm 0.003$, $b = 16.860 \pm 0.005$, $c = 7.347 \pm 0.003$ Å, $\beta = 102.98 \pm 0.04^\circ$, were obtained from a least-squares refinement of 15 reflections measured on a Rigaku four-circle automatic diffractometer. The crystal density was measured by the flotation method, giving a value of 1.78 g cm^{-3} . On the assumption of two adenosine–5-bromouracil pairs in the unit cell, the calculated density is 1.78 g cm^{-3} .

2003 independent reflections were collected on the diffractometer up to a 2θ limit of 60° using Mo $K\alpha$ radiation and the $2\theta/\theta$ scan mode at a scan speed of 2° min^{-1} . The data were corrected for the usual Lorentz–polarization factors, but no correction was made for the absorption effect.

The structure was determined by the heavy-atom method. The position of the Br atom was readily interpreted from the Patterson map. The Fourier synthesis based on the Br phases helped to determine the whole structure, and the identities of the C, O and N atoms were assigned from the chemical formula. Five cycles of block-diagonal least-squares refinement reduced the R factor to 0.099. A difference synthesis was then carried out to obtain the coordinates of the H atoms. Eight cycles of further block-diagonal least-squares refinement gave a final R factor of 0.083. The final atomic parameters with their standard deviations are listed in Table 1.*

Table 1. Final atomic parameters ($\times 10^4$, for H $\times 10^3$) with e.s.d.'s in parentheses

	x	y	z
AN(1)	7640 (16)	6231 (7)	1967 (19)
AC(2)	8265 (17)	5484 (8)	1758 (22)
AN(3)	10075 (15)	5208 (6)	2443 (16)
AC(4)	11302 (17)	5772 (7)	3439 (18)
AC(5)	10808 (17)	6541 (7)	3728 (20)
AC(6)	8892 (16)	6769 (7)	2900 (17)
AN(7)	12377 (16)	6957 (6)	4668 (17)
AC(8)	13863 (19)	6436 (7)	4980 (21)
AN(9)	13243 (16)	5694 (6)	4297 (16)
AN(10)	8186 (19)	7514 (8)	3054 (20)
AC(1')	14498 (15)	5020 (11)	4375 (17)
AC(2')	13878 (21)	4280 (8)	4515 (20)
AC(3')	14815 (19)	3611 (8)	4459 (21)
AC(4')	14580 (21)	3896 (7)	2444 (21)
AC(5')	12777 (21)	3572 (8)	1129 (20)
AO(1')	14388 (15)	4767 (5)	2531 (14)
AO(2')	14607 (19)	4317 (7)	7359 (16)
AO(3')	16804 (14)	3578 (6)	5371 (16)
AO(5')	11067 (15)	3650 (6)	1747 (18)
Br	-504 (2)	5000 (2)	-2780 (2)
UN(1)	3762 (16)	6464 (7)	-72 (16)
UC(2)	2916 (18)	7200 (8)	-98 (19)
UN(3)	1011 (17)	7253 (7)	-1004 (18)
UC(4)	-144 (19)	6634 (8)	-1841 (19)
UC(5)	899 (16)	5875 (8)	-1730 (20)
UC(6)	2788 (20)	5827 (8)	-844 (21)
UO(2)	3859 (16)	7772 (6)	698 (16)
UO(4)	-1832 (15)	6745 (7)	-2668 (18)
AH(C2)	900 (20)	802 (12)	324 (20)
AH(C8)	720 (26)	507 (12)	96 (25)
AH(N10a)	667 (26)	748 (12)	295 (26)
AH(N10b)	1525 (22)	657 (9)	563 (21)
AH(C1')	1616 (25)	522 (12)	489 (25)
AH(C2')	1226 (18)	424 (8)	520 (17)
AH(O2')	1591 (22)	403 (9)	760 (21)
AH(C3')	1335 (26)	334 (11)	449 (25)
AH(C4')	1553 (18)	382 (8)	204 (18)
AH(C5'a)	1238 (22)	376 (10)	37 (21)
AH(C5'b)	1306 (21)	300 (9)	109 (20)
UH(N1)	517 (31)	641 (14)	55 (30)
UH(N3)	36 (29)	782 (10)	-106 (26)
UH(C6)	347 (26)	534 (11)	-118 (25)

Results and discussion

The bond lengths and angles are listed in Table 2 and the atomic numbering scheme is in Fig. 1. All bond lengths are in good agreement with values found in other general nucleosides, except for the glycosidic bond of 1.43 Å which is slightly shorter than the average value of 1.47 Å (Saenger, 1971). Some of the bond angles, however, differ significantly. In particular, AC(8)–AN(9)–AC(1') in the adenosine residue is 6° smaller than that in a single molecule of crystalline adenosine, and AC(4)–AN(9)–AC(1') is 5° larger. Adenosine in this complex has C(2')-endo puckering and a torsion angle of 239.6° , indicating a *syn* conformation. Although the above difference in bond angles around AN(9) is not observed in the case of other *syn*-2'-endo adenosine derivatives, such as 8-bromoadenosine (Tavale & Sobell, 1970) and 3'-O-acetyladenosine (Rao & Sundaralingam, 1970), the result in this case may be attributed to the different molecular environments of these structures. The conformation and puckering data of some purine systems are given in Table 3.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33159 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Intramolecular bond lengths (Å) and angles (°) with their standard deviations in parentheses*

AN(1)–AC(2)	1.355 (17)	AC(6)–AN(10)	1.364 (17)	AC(2')–AO(2')	1.406 (18)	UN(1)–UC(6)	1.332 (18)
AN(1)–AC(6)	1.341 (16)	AN(7)–AC(8)	1.347 (14)	AC(3')–AC(4')	1.530 (21)	UC(2)–UN(3)	1.361 (14)
AC(2)–AN(3)	1.345 (14)	AC(8)–AN(9)	1.382 (15)	AC(3')–AO(3')	1.413 (14)	UC(2)–UO(2)	1.240 (16)
AN(3)–AC(4)	1.380 (15)	AN(9)–AC(1')	1.434 (17)	AC(4')–AC(5')	1.516 (18)	UN(3)–UC(4)	1.381 (17)
AC(4)–AC(5)	1.371 (17)	AC(1')–AC(2')	1.575 (20)	AC(4')–AO(1')	1.477 (15)	UC(4)–UC(5)	1.468 (17)
AC(4)–AN(9)	1.379 (13)	AC(1')–AO(1')	1.405 (16)	AC(5')–AO(5')	1.387 (14)	UC(4)–UO(4)	1.223 (14)
AC(5)–AC(6)	1.405 (14)	AC(2')–AC(3')	1.553 (18)	Br–UC(5)	1.847 (12)	UC(5)–UC(6)	1.347 (15)
AC(5)–AN(7)	1.360 (15)			UN(1)–UC(2)	1.375 (17)		
AC(2)–AN(1)–AC(6)	119.6 (15)	AC(4)–AN(9)–AC(8)	106.3 (7)	AC(3')–AC(2')–AO(2')	113.3 (12)		
AN(1)–AC(2)–AN(3)	125.7 (18)	AC(4)–AN(9)–AC(1')	129.4 (12)	AC(1')–AO(1')–AC(4')	110.9 (9)		
AC(6)–AC(5)–AN(7)	132.2 (11)	AN(9)–AC(1')–AO(1')	107.6 (12)	UC(5)–UC(4)–UO(4)	125.6 (14)		
AC(4)–AC(5)–AN(7)	111.1 (12)	AN(9)–AC(1')–AC(2')	114.3 (9)	UN(3)–UC(4)–UO(4)	121.0 (10)		
AC(4)–AC(5)–AC(6)	116.4 (14)	AC(2')–AC(1')–AO(1')	105.5 (8)	UN(3)–UC(4)–UC(5)	113.3 (14)		
AC(5)–AC(4)–AN(9)	106.2 (11)	AC(1')–AC(2')–AO(2')	112.3 (11)	UC(2)–UN(3)–UC(4)	126.0 (10)		
AN(3)–AC(4)–AN(9)	128.1 (10)	AN(1')–AC(2')–AC(3')	99.4 (9)	UN(3)–UC(2)–UO(2)	123.1 (13)		
AN(3)–AC(14)–AC(5)	125.7 (17)	AC(4')–AC(5')–AO(5')	115.1 (16)	UC(4)–UC(5)–UC(6)	120.6 (11)		
AC(2)–AN(3)–AC(4)	112.9 (6)	AC(5')–AC(4')–AO(1')	108.3 (12)	UN(1)–UC(2)–UO(2)	120.6 (18)		
AN(1)–AC(6)–AC(5)	119.6 (8)	AC(3')–AC(4')–AO(1')	105.2 (12)	UN(1)–UC(2)–UN(3)	116.3 (12)		
AN(7)–AC(8)–AN(9)	111.0 (15)	AC(3')–AC(4')–AC(5')	113.3 (10)	UC(2)–UN(1)–UC(6)	122.8 (16)		
AC(5)–AN(7)–AC(8)	105.2 (6)	AC(4')–AC(3')–AO(3')	110.5 (11)	Br–UC(5)–UC(4)	117.2 (10)		
AC(5)–AC(6)–AN(10)	123.3 (14)	AC(2')–AC(3')–AO(3')	106.9 (13)	Br–UC(5)–UC(6)	122.2 (6)		
AC(8)–AN(9)–AC(1')	124.2 (15)	AC(2')–AC(3')–AC(4')	104.1 (8)	UN(1)–UC(6)–UC(5)	121.1 (12)		
AN(1)–AC(6)–AN(10)	117.0 (14)						

Table 3. *The conformational and puckering data of some purine systems*

	Conformation	Puckering	Reference
Adenosine	<i>anti</i>	C(3')-endo	(a)
2'-Deoxyadenosine	<i>anti</i>	C(3')-endo	(b)
2'-Amino-2'-deoxyadenosine	<i>anti</i>	C(2')-endo	(c)
3'-Deoxy-3'-(dihydroxyphosphinylmethyl)adenosine	<i>anti</i>	C(3')-endo	(d)
Adenosine 3'-phosphate	<i>anti</i>	C(3')-endo	(e)
Adenosine 5'-phosphate	<i>anti</i>	C(3')-endo	(f)
Adenosine-5-bromouridine	<i>anti</i>	C(3')-endo	(g)
8-Bromoadenosine	<i>syn</i>	C(2')-endo	(h)
3'-O-Acetyladenosine	<i>syn</i>	C(2')-endo	(i)
Adenosine cyclic 3',5'-monophosphate	<i>syn, anti</i>	C(4')-exo, C(3')-endo	(j)
5'-Methyladenosine cyclic 3',5'-monophosphate	<i>syn</i>	C(3')-endo, C(4')-exo	(k)
5'-Methylammonio-5'-deoxyadenosine iodide monohydrate	<i>syn</i>	C(2')-endo	(l)
Adenosine-5-bromouracil	<i>syn</i>	C(2')-endo	This study

References: (a) Lai & Marsh (1972). (b) Watson, Sutor & Tollin (1965). (c) Rohrer & Sundaralingam (1970). (d) Hecht & Sundaralingam (1972). (e) Sundaralingam (1966). (f) Kraut & Jensen (1963). (g) Haschemeyer & Sobell (1964). (h) Tavale & Sobell (1970). (i) Rao & Sundaralingam (1970). (j) Watenpaugh, Dow, Jensen & Furberg (1968). (k) Sundaralingam & Abola (1972). (l) Saenger (1971).

Haschemeyer & Rich (1967) have carefully examined the steric barrier to rotation about the glycosidic bond, and have suggested that, particularly in purine nucleosides, the barriers to interconversion between the *syn* and *anti* conformations are not high. In 8-bromo-adenosine (Tavale & Sobell, 1970) it has been suggested that the close contacts introduced by the bulky Br atom at the 8-position on the purine skeleton may act to exclude the *anti* conformation. The occurrence of the unusual *syn* conformation in 5'-methylammonio-5'-deoxyadenosine iodide monohydrate (Saenger, 1971) can be explained by the Coulombic attraction between the positive charge located at N(5') and the lone pair of electrons at N(3).

This might be understood by the short intramolecular atomic distance of 2.88 Å. In the crystals of adenosine cyclic 3',5'-monophosphate (Watenpaugh, Dow, Jensen & Furberg, 1968), both *syn* and *anti* conformations have been found simultaneously in a unit cell. Furthermore, 5'-methyladenosine cyclic 3',5'-monophosphate (Sundaralingam & Abola, 1972) takes the *syn*, whereas adenosine 3'-phosphate (Sundaralingam, 1966), adenosine 5'-phosphate (Kraut & Jensen, 1963) and 3'-deoxy-5'-(dihydroxyphosphinylmethyl)adenosine (Hecht & Sundaralingam, 1972) take the *anti* conformation. So far, adenosine molecules can take the *syn* conformation in the crystalline state when the molecules are modified with a cyclic phosphate, a 3'-O-

acetyl group (Rao & Sundaralingam, 1970), a Br at the 8 position or 5'-methylammonio. Thus, the adenosine compound in this study is the first to be observed in the *syn* conformation with no direct modifiers connected to the adenosine molecule. The reason why the adenosine takes the *syn* conformation in this complex is not clear, but in view of the above data it may be strongly associated with the molecular-packing or the hydrogen-bonding systems in crystalline fields. There are two conformational isomers and two puckering systems in purine nucleoside systems; the most common nucleosides, adenosine and deoxyadenosine, prefer the *anti* conformation with C(3')-*endo* puckering, but the

present compound is *syn* with C(2')-*endo* puckering. Generally, the sugar residue shows a marked preference for C(3')-*endo* puckering in the *anti*, but C(2')-*endo* puckering in the *syn* conformation.

Fig. 2 shows the crystal structure of the complex viewed down *c*. The principal hydrogen bonds between the adenosine and 5-bromouracil molecules are AN(1)···UHN(1) (2.835 Å) and AN(10)H···UO(2) (3.181 Å). An intramolecular hydrogen bond connects the O(5') hydroxyl group with N(3) of the adenine ring. The hydrogen-bonding scheme using AN(1) and AN(10) in the adenosine residue is of the so-called Watson-Crick type, but the uracil residue using the glycosidic UN(1) is not. A similar hydrogen-bonding scheme can be seen in the 9-ethyl-8-bromoadenosine-phenobarbital complex (Kim & Rich, 1968).

The complex-formation ability of adenosine with nucleotide-base homologues has been investigated and it was found that the halouracil derivatives form intermolecular hydrogen bonds with adenosine, while the uracil or thymine molecules, which are expected to bind to one another, do not form complexes in the same crystallizing conditions. The strong complex-formation ability of the halouracil derivatives with adenosine may be due to the overall effect of the electrical charges on the uracil molecule. Some other uracil derivatives, such as 5-nitouracil, barbital and barbituric acid, also have difficulty forming complexes with adenosine.

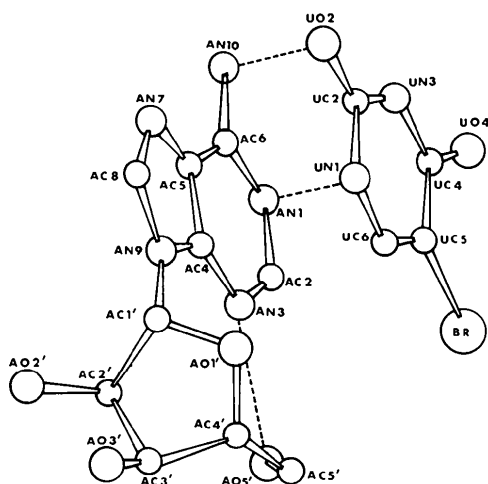


Fig. 1. A projected view of the complex, showing the hydrogen-bonding scheme.

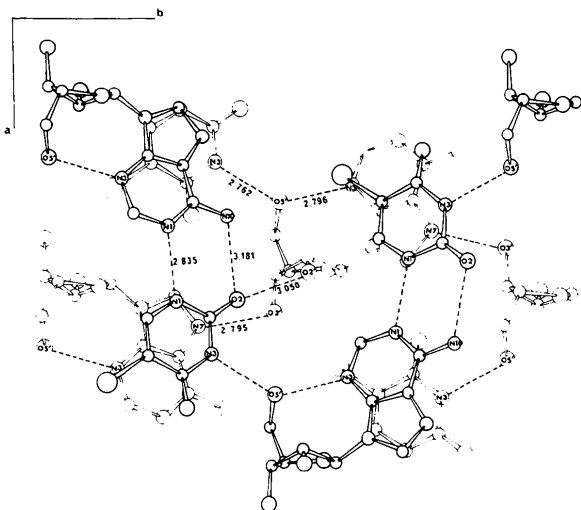


Fig. 2. The crystal structure viewed down *c*.

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Acta Cryst. (1978). B34, 1263–1270

Structural Chemistry of Layered Cyclophanes.

III. Molecular Structures of [2.2](2,7)Pyrenophane-1,1'-diene and Pyrene (Redetermined) at -160°C

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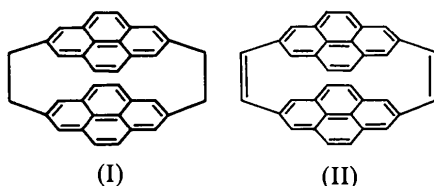
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The molecular structure of [2.2](2,7)pyrenophane-1,1'-diene was determined from X-ray diffraction data collected on a four-circle diffractometer at -160°C . Crystals belong to the monoclinic space group $P2_1/c$ with two molecules per unit cell; $a = 9.829$ (2), $b = 12.631$ (2), $c = 10.001$ (2) Å and $\beta = 113.82$ (1) $^{\circ}$. The structure was solved by the direct method and refined by block-diagonal least squares to an R of 0.064 for 2917 observed reflexions. The pyrene moieties have shallow-boat conformations connected by ethylenic bridges of length 1.344 (3) Å and with angles of 118.5 (2) and 119.3 (2) $^{\circ}$. The molecular structure of pyrene was redetermined to compare its structure with that of [2.2](2,7)pyrenophane-1,1'-diene. The X-ray data were measured at -160°C to obtain standard data of high accuracy for the condensed aromatic compounds. The final R value was 0.063 for 2361 observed reflexions. Good agreement was observed between the chemically equivalent parts of the molecule.

Introduction

Studies of a wide variety of condensed aromatic [2.2]carbophanes have been extensively undertaken from the viewpoint of transannular interaction. Recently, Umemoto, Satani, Sakata & Misumi (1975) have synthesized a [2.2](2,7)pyrenophane (I) and its diene derivative (II), which are typical models for excimer fluorescence studies.



The molecular structure of [2.2](2,7)pyrenophane-1,1'-diene (II) has been determined from X-ray diffraction data collected on a four-circle diffractometer at -160°C . The molecular structure of (I) has been reported by Irngartinger, Kirrstetter, Krieger,

Rodenwald & Staab (1977) in the course of our X-ray studies on (I). A comparison of the molecular structures of (I) and (II) is made in this paper.

The molecular structure of pyrene has been determined hitherto by the X-ray method by Robertson & White (1947), Camerman & Trotter (1965) and Allmann (1970), and by the neutron diffraction method by Hazell, Larsen & Lehmann (1972). Hazell *et al.* compared the molecular structures determined by neutron and X-ray methods. They stressed the marked differences between the bond distances obtained by the two methods and attributed them to the nonsphericities of the electron clouds. It is well known that rather short bond distances are observed because of the effect of thermal vibration in the molecular structure determined by the X-ray method. In fact, the results of Camerman & Trotter and of Allmann are significantly different. To make a strict comparison of the X-ray with the neutron structure we have carried out a redetermination of the molecular structure of pyrene at -160°C . The redetermination was also stimulated by the expectation of basic differences between the