Acta Cryst. (1980). B36, 2095–2099

The Structure of the 1-Thyminylacetic Acid and Tyramine (1:1) Complex

BY KEIZO OGAWA, KEIKO TAGO, TOSHIMASA ISHIDA* AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, Yamada-kami, Suita, Osaka 565, Japan

(*Received* 31 *October* 1979; *accepted* 10 *March* 1980)

Abstract

The crystal structure of a 1:1 complex of 1-thyminylacetic acid and tyramine was determined by X-ray diffraction. The complex, $C_7H_7N_2O_4^-.C_8H_{12}NO^+.H_2O$, crystallizes with an equal number of water molecules in the monoclinic space group $C2/c$, with $a = 24{\cdot}392$ (4), $b = 5{\cdot}098$ (1), $c = 27{\cdot}046$ (5) Å, $\beta = 99{\cdot}79$ (1)° and $Z = 8$. The structure was solved by a direct method and refined by a block-diagonal least-squares procedure to $R = 0{\cdot}070$. Because of the acid–base hydrogen bonding of the carboxyl group of the 1-thyminylacetic acid to the amino group of the tyramine, a tetrameric complex unit is formed around a center of symmetry. There are no direct interactions between the pyrimidine and phenol rings, but base-pairing hydrogen bonds between two thymine rings related by a center of symmetry have been found [N(3)—H···O(2): 2·872 Å]. The molecules of water of crystallization and the hydroxyl group also stabilize the molecular packing by hydrogen-bond formation.

Introduction

For the recognition of nucleic acids by proteins, several types of interaction between nucleic acids and proteins have been proposed; these are an electrostatic interaction between the phosphate group of the nucleic acid and the basic side chain of the amino acid, a stacking interaction between the purine or pyrimidine base in the nucleic acid and the aromatic ring in the amino acid, and hydrogen-bond formation between the base, sugar or phosphate and the amino acid. In particular, direct and specific interactions of the nucleic acid base with the amino acid side chain, such as a stacking interaction or hydrogen-bond formation, are considered to be the most important for nucleic acid–protein mutual recognition.

Hélène and co-workers have investigated the interactions of polynucleotides with oligopeptides containing tyrosine or its derivatives (Hélène, Montenay-Garestier & Dimicoli, 1971; Dimocoli & Hélène, 1974; Brun, Toulme & Hélène, 1975; Durand, Maurizot, Borazan & Hélène, 1975) by fluorescence, CD and NMR techniques, and suggested that the nucleic acid actually interacts with the tyrosine residue in two manners; one is a base-to-base stacking interaction involving the phenol rings and the other is the hydrogen bonding of the base, sugar or phosphate with the hydroxyl group of the phenol ring. Furthermore, the fluorescence quenching study of staphylococcal nuclease upon binding of thymidine 3′,5′-diphosphate (Cautrecasas, Edelhoch & Anifinsen, 1967) indicates a direct interaction of the thymine ring with the tyrosine residue.

In order to elucidate the interaction mechanism between thymine and tyrosine at atomic resolution, the crystal structure analysis of the 1-thyminylacetic acid (TAA) and tyramine (TRA) (1:1) complex was carried out.

Experimental

Materials

Potassium 1-thyminylacetate was synthesized by a similar method to that described in a previous paper (Ishida, Inoue & Tomita, 1979). Tyramine hydrochloride was purchased from Nakarai Chemicals Co., Kyoto.

Crystallization and data collection

An aqueous solution of potassium 1-thyminylacetate was loaded on to a small ion-exchange resin column (Amberlite IRA-401, 5 × 10 mm) and eluted by an aqueous solution (1%) of tyramine hydrochloride. Transparent platelet crystals were obtained from the eluent by slow evaporation at room temperature. Paper electrophoresis, using a single crystal dissolved in a small amount of water, clearly showed that the crystal contained TAA and TRA. Preliminary X-ray photographs indicated the crystal to be monoclinic with the space group Cc or $C2/c$. The density of the crystals, measured by flotation in a benzene–carbon tetrachloride mixture, was very close to the calculated density of an equimolar complex of TAA, TRA and

* Present address: Osaka College of Pharmacy, Kawai, Matsubara, Osaka 560, Japan.

0567-7408/80/092095-05$01.00

Table 1. *Crystal data*

Formula	$C_7H_7N_2O_4^-.C_8H_{12}NO^+.H_2O$
M_r	339·35
Crystal system	Monoclinic
a	24·392 (4) Å
b	5·098 (1)
c	27·046 (5)
β	99·79 (1)°
V	3314 (1) Å^3
Space group	$C2/c$
Z	8
D_m	1·352 (1) Mg m^{-3}
D_x	1·360
μ(Mo $K\alpha$)	0·0840 mm^{-1}
F(000)	1440

water molecules. The crystallographic data are listed in Table 1. Three-dimensional intensity data were collected with a crystal of 0·25 × 0·48 × 0·13 mm on a Rigaku computer-controlled four-circle diffractometer using monochromatic Mo $K\alpha$ radiation. With the ω–2θ scan technique, a scan speed of 4° min^{-1} (2θ) and 10 s background measurements at each end of the scan, 1511 independent non-zero reflections were obtained in the range $\sin\theta/\lambda < 0{\cdot}56$ Å^{-1}.

Structure determination and refinement

The structure was solved by a direct method using the program *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) assuming the space group to be $C2/c$. An E map, calculated using 300 reflections ($E \geq 1{\cdot}55$) with the phase set of the highest combined figure of merit (2·96), revealed the locations of all the nonhydrogen atoms except that of the O atom of the water molecule, which was found by a subsequent Fourier synthesis.

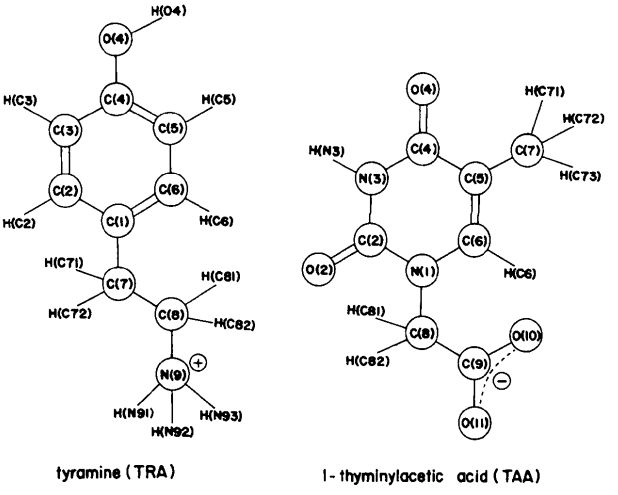

Fig. 1. The chemical structures and the atomic numbering of both components.

Table 2. *The final atomic coordinates with their estimated standard deviations in parentheses*

	x	y	z	B_{eq} (Å^2)
Thyminylacetic acid				
N(1)	0·4341 (1)	0·0202 (7)	0·4346 (1)	3·613
C(2)	0·4601 (2)	−0·1880 (8)	0·4609 (1)	3·531
O(2)	0·4882 (1)	−0·2622 (6)	0·5010 (1)	4·102
N(3)	0·5010 (1)	−0·3066 (7)	0·4399 (1)	3·483
C(4)	0·5187 (2)	−0·2286 (9)	0·3964 (2)	3·990
O(4)	0·5585 (1)	−0·3444 (7)	0·3829 (1)	5·907
C(5)	0·4900 (2)	−0·0096 (8)	0·3700 (1)	3·770
C(6)	0·4488 (2)	0·1010 (9)	0·3898 (1)	3·924
C(7)	0·5058 (2)	0·0818 (11)	0·3213 (2)	6·087
C(8)	0·3904 (2)	0·1546 (9)	0·4559 (2)	4·227
C(9)	0·3349 (2)	0·0140 (9)	0·4494 (1)	4·056
O(10)	0·3270 (1)	−0·1835 (6)	0·4215 (1)	5·125
O(11)	0·3004 (1)	0·1135 (7)	0·4732 (1)	6·209
H(N3)	0·529 (2)	−0·478 (8)	0·460 (1)	
H(C71)	0·496 (2)	−0·057 (8)	0·293 (1)	
H(C72)	0·467 (2)	0·114 (8)	0·301 (1)	
H(C73)	0·545 (2)	0·187 (9)	0·329 (1)	
H(C6)	0·425 (1)	0·258 (9)	0·369 (1)	
H(C81)	0·384 (2)	0·343 (8)	0·438 (1)	
H(C82)	0·405 (1)	0·172 (8)	0·497 (1)	
Tyramine				
C(1)	0·1698 (2)	0·4588 (8)	0·2906 (2)	4·378
C(2)	0·1338 (2)	0·2487 (10)	0·2842 (2)	4·787
C(3)	0·1200 (2)	0·1287 (10)	0·2369 (2)	4·761
C(4)	0·1421 (2)	0·2232 (9)	0·1968 (2)	3·933
O(4)	0·1288 (1)	0·1013 (6)	0·1512 (1)	4·941
C(5)	0·1776 (2)	0·4358 (9)	0·2033 (2)	4·359
C(6)	0·1912 (2)	0·5499 (9)	0·2504 (2)	5·046
C(7)	0·1849 (2)	0·5890 (10)	0·3421 (2)	6·103
C(8)	0·2145 (2)	0·4137 (10)	0·3807 (2)	5·747
N(9)	0·2300 (1)	0·5439 (7)	0·4301 (1)	4·214
H(C2)	0·116 (1)	0·179 (8)	0·316 (1)	
H(C3)	0·092 (1)	−0·037 (8)	0·232 (1)	
H(O4)	0·353 (1)	−0·308 (8)	0·379 (1)	
H(C5)	0·194 (2)	0·518 (8)	0·171 (1)	
H(C6)	0·222 (1)	0·719 (8)	0·256 (1)	
H(C71)	0·149 (1)	0·654 (8)	0·354 (1)	
H(C72)	0·211 (2)	0·746 (8)	0·338 (1)	
H(C81)	0·252 (2)	0·350 (8)	0·369 (1)	
H(C82)	0·188 (2)	0·266 (8)	0·384 (1)	
H(N91)	0·217 (2)	0·449 (8)	0·456 (1)	
H(N92)	0·212 (2)	0·722 (9)	0·430 (1)	
H(N93)	0·273 (2)	0·565 (8)	0·440 (1)	
Water				
O(W)	0·3508 (2)	0·4076 (11)	0·0546 (1)	14·838
H(W1)	0·384 (2)	0·460 (8)	0·069 (1)	
H(W2)	0·342 (1)	0·429 (8)	0·021 (1)	

The structure was refined by a full-matrix least-squares method with isotropic temperature factors and then by a block-diagonal least-squares method with anisotropic ones for all the nonhydrogen atoms. All H atoms could be located from a difference Fourier map and these were included in a further refinement with isotropic temperature factors. During the final refinement the following weighting scheme was used: $w = 0{\cdot}0$ for $|F_o| = 0{\cdot}0$ and $w = (\sigma|F_o|^2 - 36{\cdot}491|F_o|^2)^{-1}$

for $|F_o| > 0.0$. The final R value was 0·070 for 1511 non-zero reflections. Numerical calculations were carried out on an ACOS Series NEAC System 900 computer of the computation center of this university using the *Universal Crystallographic Computing System* (1973). The scattering factors cited in *International Tables for X-ray Crystallography* (1974) were used for all atoms.

Results and discussion

The chemical structures of TAA and TRA are shown in Fig. 1 with the atomic numbering. The final positional parameters are listed in Table 2.*

Structure of the TAA molecule

The bond distances and angles are given in Table 3. The bond distances in the pyrimidine ring are normal in comparison with those of other related compounds. However, the C—O distances, 1·232 (5) and 1·241 (6) Å, of the exocyclic carbonyl groups are slightly longer than the standard values (1·211 and 1·234 Å; Frank & Paul, 1973) found in the other thymine derivatives; this tendency is probably due to the participation of the O atoms in hydrogen bonding. In a difference Fourier map, no peak corresponding to the H atom attached to O(10) or O(11) was observed, indicating that the carboxyl group is in the anionic form.

The equation of the best plane of the pyrimidine ring and deviations of each atom from this plane are given in Table 4. In this crystal, the N(3) and C(6) atoms deviate by 0·025 and 0·022 Å, respectively, on the same side of the plane through the atoms N(1), C(2), C(4) and C(5); *i.e.* this pyrimidine ring takes the boat conformation frequently observed in the structures of thymine derivatives.

As shown in Table 5, the torsion angles around the bonds N(1)—C(8) [C(2)—N(1)—C(8)—C(9)] and C(8)—C(9) [N(1)—C(8)—C(9)—O(10)] are 77·1 and 9·3°, respectively, while those in the TAA–tryptamine complex crystal are 66·9 and 14·4° (Ishida, Inoue & Tomita, 1979). These values fall within the synclinal region about the N(1)—C(8) bond and within the synperiplanar region about the C(8)—C(9) bond, which seems to be one of the most stable TAA conformations.

Structure of the TRA molecules

The bond distances and angles are given in Table 3; they are in agreement with those in related compounds (tyramine hydrochloride: Tamura, Wakahara, Fujiwara & Tomita, 1974; Podder, Dattagupta, Saha & Saenger, 1979; tyrosine and tyrosine hydrochloride: Frey, Koetzle, Lehmann & Hamilton, 1973). Three H atom peaks bound tetrahedrally to the N atom were found in a difference Fourier map, showing the amino group to be in the cationic form. The phenol ring is almost planar; the equation of the best plane is given in

Table 3. *Bond distances* (Å) *and angles* (°) *with their estimated standard deviations in parentheses*

1-Thyminylacetic acid (TAA)

N(1)—C(2)	1·371 (5)	N(1)—C(6)	1·383 (5)
N(1)—C(8)	1·466 (6)	C(2)—O(2)	1·232 (5)
C(2)—N(3)	1·369 (5)	N(3)—C(4)	1·380 (6)
C(4)—O(4)	1·241 (6)	C(4)—C(5)	1·442 (6)
C(5)—C(6)	1·341 (6)	C(5)—C(7)	1·509 (7)
C(8)—C(9)	1·515 (6)	C(9)—O(10)	1·253 (6)
C(9)—O(11)	1·250 (6)	N(3)—H(N3)	1·09 (4)
C(7)—H(C71)	1·04 (4)	C(7)—H(C72)	1·03 (4)
C(7)—H(C73)	1·08 (5)	C(6)—H(C6)	1·09 (5)
C(8)—H(C81)	1·08 (4)	C(8)—H(C82)	1·11 (4)
C(2)—N(1)—C(6)	121·2 (4)	C(2)—N(1)—C(8)	117·5 (3)
C(6)—N(1)—C(8)	121·3 (3)	N(1)—C(2)—O(2)	122·5 (4)
N(1)—C(2)—N(3)	115·7 (4)	O(2)—C(2)—N(3)	121·8 (4)
C(2)—N(3)—C(4)	125·6 (4)	N(3)—C(4)—O(4)	119·9 (4)
N(3)—C(4)—C(5)	116·6 (4)	O(4)—C(4)—C(5)	124·2 (4)
C(4)—C(5)—C(6)	117·6 (4)	C(4)—C(6)—C(7)	119·7 (4)
C(7)—C(5)—C(6)	122·7 (4)	C(5)—C(6)—N(1)	123·2 (4)
N(1)—C(8)—C(9)	115·3 (4)	C(8)—C(9)—O(10)	119·6 (4)
C(8)—C(9)—O(11)	114·4 (4)	O(10)—C(9)—O(11)	126·0 (4)
C(2)—N(3)—H(N3)	116 (2)	C(4)—N(3)—H(N3)	118 (2)
C(5)—C(7)—H(C71)	112 (2)	C(5)—C(7)—H(C72)	100 (2)
C(5)—C(7)—H(C73)	109 (2)	C(5)—C(6)—H(C6)	118 (2)
N(1)—C(6)—H(C6)	118 (2)	N(1)—C(8)—H(C81)	108 (2)
N(1)—C(8)—H(C82)	108 (2)	C(9)—C(8)—H(C81)	108 (2)
C(9)—C(8)—H(C82)	106 (2)	H(C81)—C(8)—H(C82)	112 (3)

Tyramine (TRA)

C(1)—C(2)	1·377 (7)	C(1)—C(6)	1·364 (6)
C(1)—C(7)	1·531 (7)	C(2)—C(3)	1·406 (7)
C(3)—C(4)	1·378 (7)	C(4)—C(5)	1·381 (6)
C(4)—O(4)	1·370 (5)	C(5)—C(6)	1·387 (7)
C(7)—C(8)	1·469 (7)	C(8)—N(9)	1·480 (6)
C(2)—H(C2)	1·08 (4)	C(3)—H(C3)	1·08 (4)
O(4)—H(O4)	1·10 (4)	C(5)—H(C5)	1·10 (4)
C(6)—H(C6)	1·14 (4)	C(7)—H(C71)	1·05 (4)
C(7)—H(C72)	1·05 (4)	C(8)—H(C81)	1·06 (4)
C(8)—H(C82)	1·01 (4)	N(9)—H(N91)	0·95 (4)
N(9)—H(N92)	1·01 (4)	N(9)—H(N93)	1·00 (4)
C(2)—C(1)—C(6)	119·1 (4)	C(2)—C(1)—C(7)	120·1 (4)
C(6)—C(1)—C(7)	120·8 (4)	C(1)—C(2)—C(3)	120·2 (5)
C(2)—C(3)—C(4)	119·9 (4)	C(3)—C(4)—O(4)	119·1 (4)
C(3)—C(4)—C(5)	119·7 (4)	O(4)—C(4)—C(5)	121·2 (4)
C(4)—C(5)—C(6)	119·6 (4)	C(1)—C(6)—C(5)	121·7 (4)
C(1)—C(7)—C(8)	113·4 (4)	C(7)—C(8)—N(9)	112·8 (4)
C(1)—C(2)—H(C2)	120 (2)	C(3)—C(2)—H(C2)	120 (2)
C(2)—C(3)—H(C3)	120 (2)	C(4)—C(3)—H(C3)	120 (2)
C(4)—O(4)—H(O4)	114 (2)	C(4)—C(5)—H(C5)	120 (2)
C(6)—C(5)—H(C5)	121 (2)	C(5)—C(6)—H(C6)	121 (2)
C(1)—C(6)—H(C6)	119 (2)	C(1)—C(7)—H(C71)	110 (2)
C(1)—C(7)—H(C72)	108 (2)	C(8)—C(7)—H(C71)	108 (2)
C(8)—C(7)—H(C72)	107 (2)	C(7)—C(8)—H(C81)	109 (2)
C(7)—C(8)—H(C82)	105 (2)	N(9)—C(8)—H(C81)	108 (2)
N(9)—C(8)—H(C82)	110 (2)	C(8)—N(9)—H(N91)	112 (2)
C(8)—N(9)—H(N92)	111 (3)	C(8)—N(9)—H(N93)	111 (3)

Water

O(*W*)—H(*W*1)	0·87 (4)	H(*W*1)—O(*W*)—H(*W*2)	117 (4)
O(*W*)—H(*W*2)	0·89		

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35272 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *The best planes and deviations* (Å) *of atoms from them*

Asterisks indicate atoms included in the calculation of the planes. The plane equations are: $-0{\cdot}5876x - 0{\cdot}6256y - 0{\cdot}5132z + 11{\cdot}0458 = 0{\cdot}0$ for the pyrimidine ring, and $-0{\cdot}7505x + 0{\cdot}6186y - 0{\cdot}2324z + 2{\cdot}4486 = 0{\cdot}0$ for the phenol group.

Pyrimidine ring		Phenol ring	
	Deviation		Deviation
N(1)*	−0·002 (3)	C(1)*	−0·002 (4)
C(2)*	0·002 (4)	C(2)*	0·005 (4)
O(2)	−0·032 (3)	C(3)*	0·001 (4)
N(3)	0·025 (3)	C(4)*	−0·003 (3)
C(4)*	−0·002 (5)	O(4)	−0·031 (2)
O(4)	−0·053 (3)	C(5)*	0·005 (5)
C(5)*	0·002 (4)	C(6)*	−0·001 (5)
C(6)	0·022 (4)	C(7)	0·002 (5)
C(7)	0·017 (6)		

Table 5. *Torsion angles* (°)

TAA molecules

	C(2)–N(1)–C(8)–C(9)	N(1)–C(8)–C(9)–O(10)	References
TAA	77·1 (5)	9·3 (6)	This work
TAA	66·9	14·4	Ishida *et al.* (1979)

TRA molecule and its related compounds

	C(2)–C(1)–C(7)–C(8)	C(1)–C(7)–C(8)–N(9)	References
TRA	63·3 (6)	178·7 (4)	This work
TRA.HCl	71·2	179·4	Tamura *et al.* (1974)
TRA.HCl	69	178	Podder *et al.* (1979)
Dopamine	79·2	174·2	Bergin & Carlström (1968)
Phenylethylamine	72·6	188·9	Tsoucaris (1961)

Table 6. *Hydrogen-bond distances* (Å) *with their estimated standard deviations in parentheses*

Donor	Acceptor	Distance	Symmetry code for acceptor
N(3) (TAA)	O(2) (TAA)	2·872 (5)	$1-x, -1-y, 1-z$
O(4) (TRA)	O(10) (TAA)	2·637 (5)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
N(9) (TRA)	O(10) (TAA)	2·787 (5)	$x, 1+y, z$
N(9) (TRA)	O(*W*)	2·787 (7)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
N(9) (TRA)	O(11) (TAA)	2·948 (5)	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$
N(9) (TRA)	O(11) (TAA)	2·907 (5)	x,y,z
O(*W*)	O(2) (TAA)	3·075 (6)	$x, -y, \frac{1}{2}+z$
O(*W*)	O(4) (TAA)	2·844 (7)	$1-x, 1+y, \frac{1}{2}-z$

Table 4. The conformation of this molecule is very similar to those in related compounds, as shown in Table 5. These conformations are in the most stable region proposed by Pullman & Courpiere (1973) from their energy map.

Crystal structure

Fig. 2 shows the molecular packing projected along the *b* axis. The hydrogen bonds (the dotted lines in Fig. 2) are given in Table 6. As represented in Fig. 2 by the thick lines, two TAA molecules and two TRA molecules around a center of symmetry are mutually

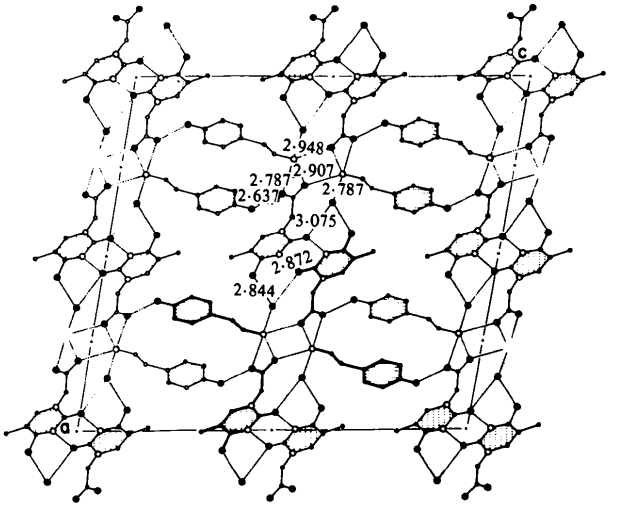

Fig. 2. The molecular packing viewed along the *b* axis. The small dots and dotted lines indicate the centers of symmetry and hydrogen bonds, respectively. The molecules represented by thick lines show one unit of the tetrameric arrangement.

linked by hydrogen bonds between the TAA carboxyl group and the TRA amino group. One H atom [H(N91)] in the amino group forms a bifurcated hydrogen bond, with O(10) [in a TAA molecule at the position $(x, 1+y, z)$] and O(11) [in a TAA molecule at the position (x,y,z)] as acceptors. A similar tetrameric arrangement, achieved by acid–base hydrogen-bond formation, is observed in the TAA–tryptamine complex (Inoue, Sakaki, Fujiwara & Tomita, 1978). Two TAA molecules related by a center of symmetry form a base pair through two N(3)–H···O(2) hydrogen bonds. The two pyrimidine rings are almost coplanar; the best planes of the two rings are separated by only 0·039 Å. This rare type of hydrogen-bond base-pairing was also observed in 6-methyl-5-nitrouracil (Parthasarathy & Srikrishnan, 1977). The water molecule is located between the base-paired TAA molecules and the amino group of the TRA molecule, stabilizing the molecular packing by relatively strong hydrogen bonds.

Fig. 3 shows a partial projection of the molecular packing on to the TAA(1) pyrimidine ring, with the hydrogen-bond distances and some short contacts. The intermolecular distance between O(2) of TAA(1) and C(2) of TAA(2) is 3·249 Å. A dipole–dipole interaction due to the antiparallel C(2)–O(2) bond moments is considered to be the most important interaction between the TAA(1) and TAA(2) molecules. The O(10) atom of TAA(1) forms a hydrogen bond with the hydroxyl group of the neighboring TRA molecule {O(4)–H(TRA)···O(10) [TAA(1)]: 2·637 Å}. The O(4) atom of the TRA molecule is located above the TRA(1) pyrimidine ring and the dihedral angle between pyrimidine [TAA(1)] and phenol (TRA) rings is 19·0°. The charge densities for O(4) (TRA) and C(6) [TAA(1)], calculated by the

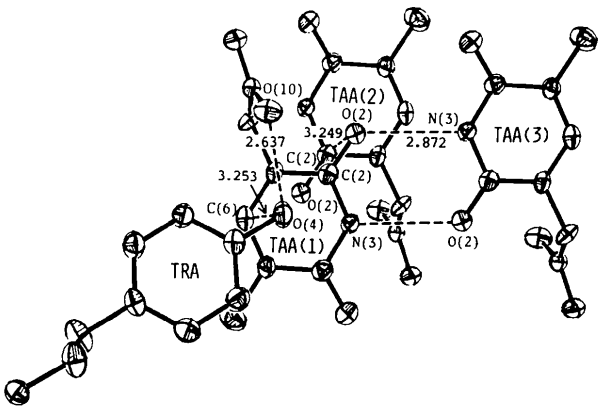

Fig. 3. Partial projection of the molecular packing on to the plane of the TAA(1) pyrimidine ring. The symmetry operations for the TAA(1), TAA(2), TAA(3) and TRA molecules are (x,y,z), $(1-x,-y,1-z)$, $(1-x,-1-y,1-z)$ and $(\frac{1}{2}-x,\frac{1}{2}+y,-z)$, respectively.

CNDO/2 method, are −0·23 and +0·15 e Å^{-3}, respectively, so the atoms come close together (3·253 Å) because of an electrostatic interaction.

The structural study of the staphylococcal nuclease–thymidine 3′,5′-diphosphate–Ca^{2+} complex at 1·5 Å resolution (Cotton, Hazen & Legg, 1979) indicates that the thymine ring and the phenol ring of Tyr-113 are almost parallel but are not stacked with each other. On the other hand, as mentioned in the *Introduction*, studies of the interactions between nucleic acids and tyrosine, made by Hélène and co-workers and Cautrecasas *et al.* (1967), suggest the occurrence of stacking and hydrogen-bonding interactions. In the present structural study of the TAA–TRA complex, no hydrogen bond between the thymine ring and the phenolic hydroxyl group was observed, but a hydrogen bond occurs between the carboxyl and hydroxyl groups. It is also interesting to note that the weak interaction between the thymine and phenol rings is probably due to electrostatic or π–π interactions.

References

BERGIN, R. & CARLSTRÖM, D. (1968). *Acta Cryst.* B**24**, 1506–1510.

BRUN, F., TOULME, J. & HÉLÈNE, C. (1975). *Biochemistry*, **14**, 558–563.

CAUTRECASAS, P., EDELHOCH, H. & ANIFINSEN, C. B. (1967). *Proc. Natl Acad. Sci. USA*, **58**, 2043–2050.

COTTON, F. A., HAZEN, E. E. JR & LEGG, M. J. (1979). *Proc. Natl Acad. Sci. USA*, **76**, 2551–2555.

DIMICOLI, J. & HÉLÈNE, C. (1974). *Biochemistry*, **13**, 724–730.

DURAND, M., MAURIZOT, J., BORAZAN, H. N. & HÉLÈNE, C. (1975). *Biochemistry*, **14**, 563–570.

FRANK, J. K. & PAUL, I. C. (1973). *J. Am. Chem. Soc.* **95**, 2324–2331.

FREY, M. N., KOETZLE, T. F., LEHMANN, M. S. & HAMILTON, W. C. (1973). *J. Chem. Phys.* **58**, 2547–2556.

HÉLÈNE, C., MONTENAY-GARESTIER, T. & DIMICOLI, J. (1971). *Biochim. Biophys. Acta*, **254**, 349–365.

INOUE, M., SAKAKI, T., FUJIWARA, T. & TOMITA, K. (1978). *Bull. Chem. Soc. Jpn*, **51**, 1123–1127.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

ISHIDA, T., INOUE, M. & TOMITA, K. (1979). *Acta Cryst.* B**35**, 1642–1648.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN* 74. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PARTHASARATHY, R. & SRIKRISHNAN, T. (1977). *Acta Cryst.* B**33**, 1749–1753.

PODDER, A., DATTAGUPTA, J. K., SAHA, N. N. & SAENGER, W. (1979). *Acta Cryst.* B**35**, 649–652.

PULLMAN, B. & COURPIERE, P. (1973). *Conformation of Biological Molecules and Polymers*, edited by E. D. BERGMANN & B. PULLMAN, pp. 547–568. The Israel Academy of Sciences and Humanities.

TAMURA, K., WAKAHARA, A., FUJIWARA, T. & TOMITA, K. (1974). *Bull. Chem. Soc. Jpn*, **47**, 2682–2685.

TSOUCARIS, G. (1961). *Acta Cryst.* **14**, 909–914.

Universal Crystallographic Computing System (1973). Library of Programs, Computing Center of Osaka Univ.

Acta Cryst. (1980). B**36**, 2099–2103

The β Form of Piperidinium 1-Piperidinecarbodithioate

BY ANDERS WAHLBERG

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21, *Uppsala* 1, *Sweden*

(*Received* 12 *March* 1980; *accepted* 1 *April* 1980)

Abstract

$[C_5H_{12}N]^+$ $[C_6H_{10}NS_2]^-$, monoclinic, $P2_1$, with a = 12·395 (2), b = 15·459 (2), c = 14·320 (2) Å, β = 93·35 (2)°, Z = 8, V = 2739·3 Å^3, D_x = 1·195 Mg m^{-3}. The non-centrosymmetric structure has been refined to $R(F^2)$ = 0·110 for 4991 reflexions and 892 parameters. The structure is built up of two indepen-

0567-7408/80/092099-05$01.00