CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

FRITCHIE, C. J. (1966). *Acta Cryst.* 20, 27–36.

HELLER, J., DREIDING, A. S., GRIEB, R. & NIGGLI, A. (1972). *Angew. Chem. Int. Ed. Engl.* 11, 236–238.

HWANG, K. J., DONOHUE, J. & TSAI, C. (1972). *Acta Cryst.* B28, 1727–1732.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KABUTO, C,. YAGIHARA, M., ASAO, T. & KITAHARA, Y. (1973). *Angew. Chem. Int. Ed. Engl.* 12, 836.

KAFTORY, M. (1978). *Acta Cryst.* B34, 952–954.

LANDHEER, I. & GINSBURG, D. (1979). *Recl Trav. Chim. Pays-Bas.* In the press.

LITTKE, W. & DRÜCK, U. (1974). *Angew. Chem. Int. Ed. Engl.* 13, 539–540.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SHELDRICK, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

VOGEL, E., BREUER, A., SOMMERFELD, C. D., DAVIS, R. E. & LIU, L. K. (1977). *Angew. Chem. Int. Ed. Engl.* 16, 169–170.

Structural Studies of the Interaction between Indole Derivatives and Biologically Important Aromatic Compounds.
III. The Crystal and Molecular Structure of Tryptamine: 1-Thyminylacetic Acid (1:1) Complex

BY TOSHIMASA ISHIDA AND MASATOSHI INOUE

Osaka College of Pharmacy, 2-10-65 Kawai, Matsubara-City, Osaka 580, Japan

AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, Yamadakami, Suita-City, Osaka 565, Japan

Abstract

The crystal structure of a 1:1 complex of tryptamine and 1-thyminylacetic acid, $C_{10}H_{13}N_2^+.C_7H_7N_2O_4^-$, has been determined by the X-ray method. The crystal is monoclinic, space group $P2_1/c$ with unit-cell dimensions: $a = 9.793$ (2), $b = 6.122$ (1), $c = 28.160$ (3) Å and $\beta = 95.46$ (2)°. The structure was solved using *MULTAN* and refined by a block-diagonal least-squares method to give a final R value of 0.058. As for the interaction between the acid and the amine, an ion pair (salt bridge) is formed between the positive charge at the terminal amino N atom of tryptamine and the negative charge at the carboxyl O atom of 1-thyminyl-acetic acid. No prominent interaction between the pyrimidine and indole rings is observed in the crystal. Both component molecules are held together by three-dimensional frameworks of hydrogen bonds around the twofold screw axis to form an infinite helical array in the *b* direction.

Introduction

In order to understand the role of the tryptophan residue in protein–nucleic acid interaction, the interactions between tryptophan and nucleic acids have been widely investigated by kinetics, chemical modification, UV, CD and NMR spectroscopies or X-ray structure analysis.

It is of interest to identify which of the four nucleic bases could interact most specifically with the indole ring of the tryptophan residue.

In the present paper, we report the crystal structure of the title complex by the X-ray diffraction method, which is a model for the study of the indole–thymine interaction.

Experimental

The synthesis of potassium 1-thyminylacetate (I) was carried out according to the method previously

described by Browne, Eisinger & Leonard (1968) (Fig. 1). An aqueous solution of (I) was placed in an Amberlite-IRA-401 anion-exchange (OH-type resin) column; the column was then eluted with an equimolar aqueous solution of tryptamine hydrochloride. Transparent platelet-shaped crystals were obtained by slow evaporation of the elution at room temperature. The UV spectrum and thermal analysis of the crystals showed that they consisted of tryptamine (TPA) and 1-thyminylacetic acid (TAA) in a 1:1 molar ratio, but no water of crystallization.

Preliminary oscillation and Weissenberg photographs showed the crystals to be monoclinic and in space group $P2_1/c$ from systematic absences. The crystallographic data are given in Table 1. The density was measured by flotation in a carbon tetrachloride–benzene mixture. The cell dimensions were refined by the least-squares method using 30 reflections measured on a Rigaku–Denki automatic four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, with which three-dimensional intensity data were also collected. A total of 2485 independent reflections within $\sin\theta/\lambda < 0.55$ Å^{-1} were collected using the ω–2θ scan technique and were corrected for Lorentz and polarization factors, but not for absorption, because of the small size of the crystal (dimensions: $0.3 \times 0.2 \times 0.4$ mm). In order to check the stability of the crystal, the intensities of three standard reflections were measured after every 50 reflections. No appreciable change was detected during the run. The scan speed was 4° min^{-1} and background measurements were taken for 5 s.
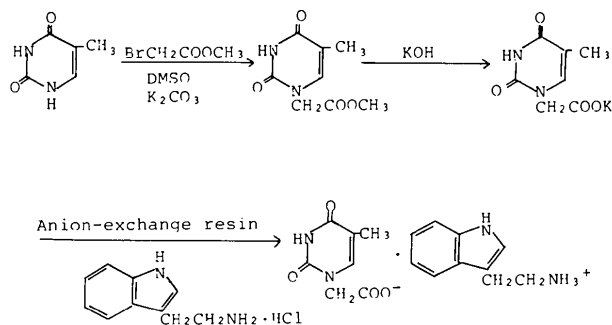
Structure determination and refinement

The structure was solved by the direct method with the program *MULTAN* (Germain, Main & Woolfson, 1971) using 368 reflections with $|E| \geq 1.20$. An E map computed from the phase set with the highest figure of merit revealed the positions of all the non-hydrogen atoms. The structure was refined by the full-matrix least-squares method with isotropic thermal parameters, and then by the block-diagonal least-squares method with anisotropic temperature factors ($R = 0.105$); the weight was taken as unity. A difference map at this stage clearly showed the positions of all twenty H atoms (peak height: 0.3–0.5 e Å^{-3}), which were included in all subsequent refinements with isotropic temperature factors. The final least-squares refinement was computed with the weighting scheme $w = 1.42$ for $F_o = 0.0$, $w = 1.0$ for $0 < F_o \leq 19.0$ and $w = [1.0 + 0.40(|F_o| - 19.0)]^{-1}$ for $F_o > 19.0$. During the last cycle of refinement, none of the positional parameters shifted more than one fifth of their

Fig. 1. Synthesis of the TPA:TAA (1:1) complex.

Table 1. *Crystal data of the TPA:TAA (1:1) complex*

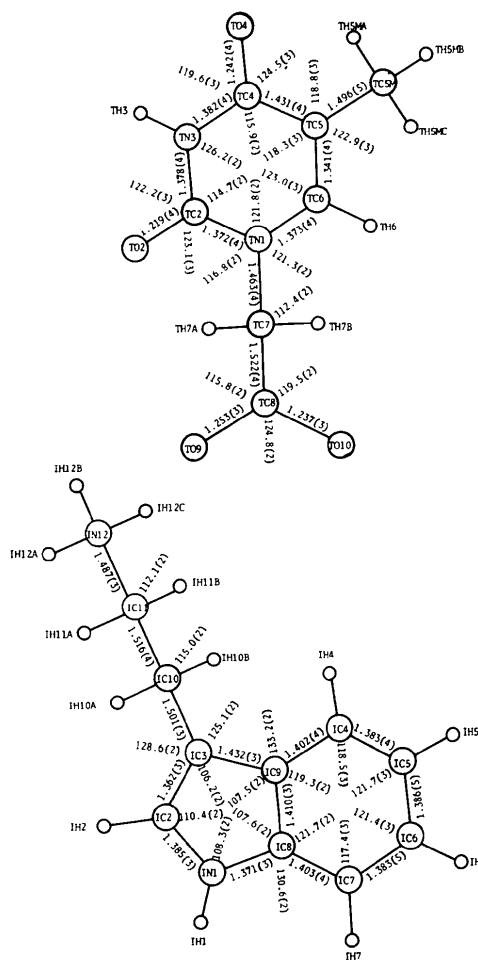| Chemical formula	$C_{17}H_{20}N_4O_4$	β	$95.46\,(2)^\circ$
Molecular weight	344.37	V	1680.6 Å^3
Crystal system	Monoclinic	Z	4
Space group	$P2_1/c$	D_m	$1.354\,(3)$ Mg m^{-3}
a	$9.793\,(2)$ Å	D_x	1.361
b	$6.122\,(1)$	μ (Cu $K\alpha$)	0.953 mm^{-1}
c	$28.160\,(3)$		

Fig. 2. The bond lengths (Å) and angles (°) of the TPA and TAA molecules.

estimated standard deviations. The final R value including $F_o = 0.0$ is 0.058.

All numerical calculations were carried out on an NEAC-2200-700 computer of the Computation Center of Osaka University using programs of *The Universal Crystallographic Computing System* (1973). In the structure factor calculation, the atomic scattering factors cited in *International Tables for X-ray Crystallography* (1974) were used.

Results and discussion

The atomic coordinates from the last refinement are given in Table 2.* The bond lengths and angles for non-hydrogen atoms, with their standard deviations estimated from the least-squares refinement are given in Fig. 2, together with the atomic numbering.

Molecular structure

TAA molecule

Several X-ray structure analyses on thymine derivatives have been reported: thymine monohydrate (Gerdil, 1961), thymine (Ozeki, Sakabe & Tanaka, 1969), thymine:*p*-benzoquinone (1:1) complex (Sakurai & Okunuki, 1971), 1-methylthymine (Hoogsteen, 1963*a*), 1-methylthymine:9-methyladenine (1:1) complex (Hoogsteen, 1963*b*), 1,1'-trimethylenebisthymine (Frank & Paul, 1973), thymidine (Young, Tollin & Wilson, 1969), 1-β-D-arabinofuranosylthymine (Tougard, 1973), 5'-bromo-5'-deoxythymidine (Huber, 1957), calcium thymidylate (Trueblood, Horn & Luzzati, 1961) and thymidine-5'-carboxylic acid (Suck, Saenger & Rohde, 1974). The observed bond lengths and angles of the TAA molecule in this complex agree well with those of the compounds having a carbon atom substituent on N(1). C(4)—O(4) (1·242 Å) is significantly longer than C(2)—O(2) (1·219 Å), which might be because O(4) participates in hydrogen bonding whereas O(2) does not. This tendency has also been observed in 1-methylthymine, thymidine, thymine-5'-carboxylic acid, 1,1'-trimethylenebisthymine and a number of uracil derivatives.

The general pattern of bond lengths can be explained in terms of valence-bond theory, as has been pointed out by Hoogsteen (1963*a*).

In the difference Fourier map, no H atom was found in the neighborhood of the O atoms [O(9) and O(10)]

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34370 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$)

	x	y	z
$IN(1)$	2772 (2)	6312 (3)	1774 (1)
$IC(2)$	2581 (2)	5186 (4)	2189 (1)
$IC(3)$	3306 (2)	3284 (4)	2209 (1)
$IC(4)$	4891 (3)	1698 (5)	1603 (1)
$IC(5)$	5442 (3)	2185 (5)	1181 (1)
$IC(6)$	5107 (3)	4091 (6)	931 (1)
$IC(7)$	4201 (3)	5592 (5)	1092 (1)
$IC(8)$	3638 (2)	5117 (4)	1520 (1)
$IC(9)$	3981 (2)	3194 (4)	1780 (1)
$IC(10)$	3475 (3)	1639 (4)	2605 (1)
$IC(11)$	2654 (3)	2105 (5)	3024 (1)
$IN(12)$	1174 (2)	1591 (3)	2914 (1)
$TN(1)$	442 (2)	10593 (4)	866 (1)
$TC(2)$	−323 (3)	8724 (5)	795 (1)
$TN(3)$	124 (2)	7319 (4)	460 (1)
$TC(4)$	1246 (3)	7627 (5)	204 (1)
$TC(5)$	2027 (3)	9569 (5)	313 (1)
$TC(6)$	1603 (3)	10945 (5)	639 (1)
$TC(7)$	−3 (3)	12159 (4)	1213 (1)
$TC(8)$	160 (2)	11272 (4)	1720 (1)
$TO(9)$	−443 (2)	12324 (3)	2019 (1)
$TO(10)$	868 (2)	9624 (3)	1811 (1)
$TO(2)$	−1328 (2)	8335 (4)	1004 (1)
$TO(4)$	1506 (2)	6260 (4)	−100 (1)
$TC(5M)$	3278 (3)	9978 (7)	59 (1)
$IH(1)$	226 (4)	755 (6)	174 (1)
$IH(2)$	194 (3)	581 (5)	242 (1)
$IH(4)$	516 (3)	22 (6)	180 (1)
$IH(5)$	617 (3)	108 (6)	105 (1)
$IH(6)$	558 (3)	442 (6)	61 (1)
$IH(7)$	392 (3)	706 (6)	90 (1)
$IH(10A)$	455 (3)	152 (6)	274 (1)
$IH(10B)$	322 (3)	13 (5)	247 (1)
$IH(11A)$	272 (3)	369 (6)	312 (1)
$IH(11B)$	297 (3)	104 (5)	332 (1)
$IH(12A)$	49 (3)	253 (6)	305 (1)
$IH(12B)$	94 (3)	5 (6)	295 (1)
$IH(12C)$	73 (4)	189 (6)	261 (1)
$TH(3)$	−44 (3)	604 (5)	35 (1)
$TH(6)$	216 (3)	1241 (5)	73 (1)
$TH(7A)$	−101 (3)	1258 (6)	114 (1)
$TH(7B)$	57 (3)	1354 (6)	119 (1)
$TH(5MA)$	387 (4)	853 (5)	7 (1)
$TH(5MB)$	369 (4)	1134 (6)	14 (1)
$TH(5MC)$	304 (4)	1062 (6)	−24 (1)

of the TAA molecule, indicating the carboxylic group to be in the anionic form (—COO⁻); C(8)—O(9) (1·253 Å) is somewhat longer than C(8)—O(10) (1·237 Å), which is normal for a double bond (1·23 ± 1 Å) (Kennard, 1968), suggesting that the electronegative charge is predominantly localized on the O(9) atom.

An indication of the planarity of the pyrimidine ring and the equation of the least-squares plane are given in Table 3, together with details of the other planes of the TPA:TAA complex. The deviations from the best plane through the six ring atoms range between −0·024 and 0·013 Å. The planarity is reasonable in comparison with other thymine derivatives. The C(7) atom deviates slightly from the pyrimidine ring (0·044 Å).

The relatively large deviation of the H(3) atom attached to N(3) (0·10 Å) may be attributed to the hydrogen bond formed with atom TO(4) which is related by a center of symmetry. The carboxyl group is almost planar (maximum deviation: 0·004 Å), being approximately at a right angle to the pyrimidine ring [dihedral angle: 105·7 (1)°]. The conformation of the TAA molecule, where the torsion angles τ[C(2)—N(1)—C(7)—C(8)] and ω[N(1)—C(7)—C(8)—O(10)] are 66·9 (3) and 14·4 (3)°, is also observed in the related compounds 9-adeninylacetic acid [$\tau = 81·5$ (4), $\omega = -3·9$ (4)° (Ishida, Senda, Inoue & Tomita, 1978) and $\tau = 84·3$, $\omega = 7·7°$ (Voet, 1973)] and 7,8-dimethylisoalloxazine-10-acetic acid [$\tau = 73$ (1), $\omega = 12$ (2)° (Ishida, Inoue, Fujiwara & Tomita, 1978)]. It is interesting to note that in both compounds the torsion angles τ and ω lie in the synclinal and synperiplanar

Table 3. *Deviations* (Å) *of atoms from the least-squares planes*

Equations of the best planes with the form $m_1 X + m_2 Y + m_3 Z = d$ in orthogonal space

Plane	m_1	m_2	m_3	d
Indole ring	0·7317	0·4697	0·4940	5·9167
Aminoethyl group	0·1344	−0·9337	0·3319	1·8512
Pyridinium ring	−0·5001	0·4774	−0·7225	1·2177
Carboxyl group	0·7946	0·5727	0·2019	4·6874

Deviations from the best planes

TPA Indole ring		TAA Pyridinium ring	
IN(1)*	0·008 (2)	TN(1)*	−0·024 (2)
IC(2)*	−0·026 (3)	TC(2)*	0·012 (3)
IC(3)*	−0·022 (2)	TN(3)*	0·009 (2)
IC(4)*	0·019 (3)	TC(4)*	−0·015 (3)
IC(5)*	−0·015 (3)	TC(5)*	0·006 (6)
IC(6)*	−0·026 (4)	TC(6)*	0·013 (3)
IC(7)*	0·001 (3)	TC(7)	−0·044 (3)
IC(8)*	0·032 (2)	TO(2)	0·031 (2)
IC(9)*	0·030 (2)	TO(4)	−0·064 (2)
IC(10)	−0·142 (3)	TC(5M)	0·019 (4)
IH(1)	0·05 (4)	TH(3)	−0·10 (3)
IH(2)	−0·01 (3)	TH(6)	0·02 (3)
IH(4)	0·03 (3)	Carboxyl group	
IH(5)	−0·07 (4)	TC(7)*	−0·001 (3)
IH(6)	−0·08 (3)	TC(8)*	0·004 (2)
IH(7)	0·01 (3)	TO(9)*	−0·001 (2)
Aminoethyl group		TO(10)*	−0·002 (2)
IC(10)*	0·0	TN(1)	0·324 (2)
IC(11)*	0·0	TH(7A)	0·66 (3)
IN(12)*	0·0	TH(7B)	−0·93 (4)
IC(3)	1·317 (2)		
IH(10A)	−0·32 (3)		
IH(10B)	−0·71 (3)		
IH(11A)	0·81 (3)		
IH(11B)	−0·91 (3)		
IH(12A)	0·50 (4)		
IH(12B)	−0·88 (3)		
IH(12C)	0·50 (4)		

* Atoms defining the plane.

regions, respectively, which thus avoids collision with the neighboring atoms.

TPA molecule

Three H atoms found in the difference map are tetrahedrally bound to the N atom of the aminoethyl side chain, indicating the amino group to be in the cationic form ($-NH_3^+$).

Six X-ray crystal structure determinations of tryptamine and its complexes have been reported so far: tryptamine (Inoue, Sakaki, Wakahara & Tomita, 1978), tryptamine picrate (Gartland, Freeman & Bugg, 1974), tryptamine phenylacetate (Inoue, Sakaki, Fujiwara & Tomita, 1978), tryptamine 9-adeninylacetate (Ishida, Senda, Inoue & Tomita, 1978), tryptamine hydrochloride (Wakahara, Fujiwara & Tomita, 1973) and tryptamine 7,8-dimethylisoalloxazine-10-acetate (Ishida, Inoue, Fujiwara & Tomita, 1978).

The observed bond lengths and angles of the TPA molecule in this complex are normal and are in the range found for TPA and its other complexes; exceptions are the lengths of N(1)—C(2) (1·385 Å), C(4)—C(5) (1·383 Å) and C(7)—C(8) (1·403 Å) which are slightly longer than normal. Probably due to the conformational specificity of the TPA molecule in this complex the angle C(2)—C(3)—C(10) (128·6°) is larger but C(9)—C(3)—C(10) (125·1°) is smaller than those in the other TPA molecules.

Although the indole ring is reasonably planar, the C(10) atom deviates considerably from the plane (0·142 Å), probably because of crystal-packing effects. The dihedral angle between indole ring and aminoethyl group is 100·2 (2)°.

The torsion angles of the hitherto analyzed TPA molecules are listed in Table 4. Their conformations are all very similar [shown by a molecular-orbital study to be the most stable (Inoue, Sakaki, Wakahara & Tomita,

Table 4. *Conformations of the hitherto determined tryptamines*

	χ	φ
TPA	90·1°	−63·4°
	[(+)anticlinal]	[(−)synclinal]
TPA picrate	100·8	−62·0
	[(+)anticlinal]	[(−)synclinal]
TPA phenylacetate	107·2	−59·8
	[(+)anticlinal]	[(−)synclinal]
TPA 9-adeninylacetate	108·5	−65·7
	[(+)anticlinal]	[(−)synclinal]
TPA hydrochloride	110·9	−60·6
	[(+)anticlinal]	[(−)synclinal]
TPA 7,8-dimethyliso-alloxazine-10-acetate	114·6	−65·9
	[(+)anticlinal]	[(−)synclinal]
TPA 1-thyminylacetate	4·2	75·5
	[(+)synperiplanar]	[(+)synclinal]

1978)], except for the conformation found in this complex: torsion angle χ[C(2)–C(3)–C(10)–C(11)] lies in the anticlinal and φ[C(3)–C(10)–C(11)–N(12)] in the (−)synclinal region. The influence of crystal-packing forces on the intramolecular conformation may explain why the TPA conformation in this complex differs significantly from the stable one. As is the case for serotonin and 5-methylbufotenine complexes (Caillet, Claverie & Pullman, 1977) the observed conformation is preferable to that predicted by MO theory.

Crystal structure

Fig. 3 shows a packing diagram viewed down the b axis; possible hydrogen bonds and intermolecular short contacts less than 3·5 Å are given in Table 5. The complex molecules are mutually linked by hydrogen bonds between the carboxyl group of TAA and the amino group of the TPA molecule around the twofold screw axis: the IN(12) atom of the TPA molecule is connected to the two oxygen atoms [TO(9) and TO(10)] of the neighboring TAA molecule by three hydrogen bonds [IN(12)···TO(9) 2·880, IN(12)··· TO(9) 2·720 and IN(12)···TO(10) 2·888 Å]. The TO(10) atom is also hydrogen bonded to the IN(1)

atom of the indole ring, which strengthens the hydrogen bonding between the anionic carboxyl group and cationic amino group [TO(10)···IN(1) 2·763 Å]. The complex molecules are packed around the twofold screw axis parallel to the b axis to form an infinite helical array with two complex pairs per turn (see Fig. 4).

This packing mode seems to be one of the most stable and is found frequently in crystalline salts formed between amines and acids; *e.g.* TPA:9-adeninylacetic acid (1:1) complex, 5-methoxy-tryptamine:5-methoxyindole-3-acetic acid (1:1) complex and 5-methoxytryptamine:indole-3-acetic acid (Sakaki, Sogo, Wakahara, Kanai, Fujiwara & Tomita, 1976).

Two TAA molecules around a center of symmetry form a dimer connected by two O(4)···H(3)–N(3)

Table 5. *Hydrogen bonds and short contacts less than 3·5 Å*

Superscripts represent the following symmetry operations: (1) x,y,z; (2) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (3) $-x, 1 - y, -z$; (4) $x, 1 + y, z$; (5) $-x, 1\frac{1}{2} + y, \frac{1}{2} - z$; (6) $1 - x, 2 - y, -z$; (7) $-x, 2 - y, -z$.

Hydrogen bonds

Donor	Acceptor	$D\cdots A$ (Å)	$H\cdots A$ (Å)	$\angle D-H\cdots A$ (°)
IN(1)[1]	TO(10)[1]	2·763 (3)	1·89 (4)	161 (3)
IN(12)[2]	TO(10)[1]	2·888 (3)	1·91 (4)	168 (3)
TN(3)[1]	TO(4)[3]	2·840 (3)	1·85 (3)	175 (3)
IN(12)[4]	TO(9)[1]	2·880 (3)	1·95 (4)	171 (3)
IN(12)[5]	TO(9)[1]	2·720 (3)	1·75 (3)	176 (3)

Short contacts

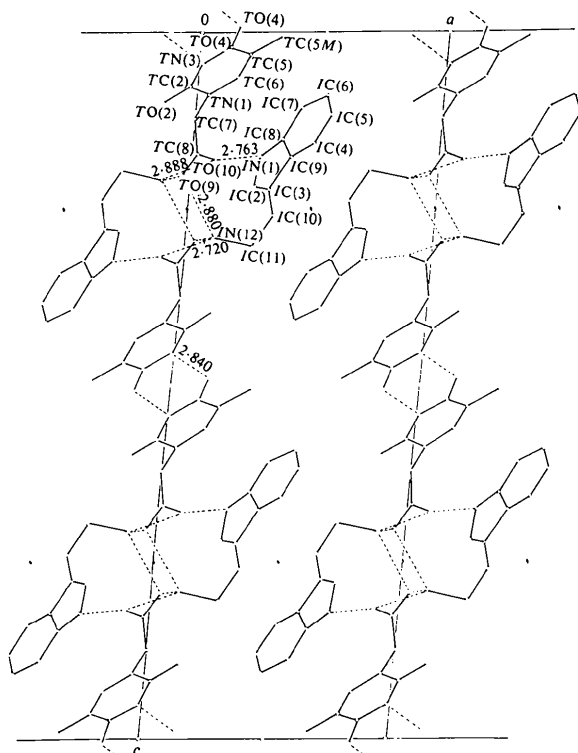|			
IC(2)[1]–TO10[1]	3·315 (3) Å	TC(8)[1]–TO(2)[1]	2·976 (3) Å
TN(1)[1]–TO10[1]	2·719 (3)	TO(2)[1]–TO(10)[1]	3·078 (3)
IC(2)[1]–IN12[1]	3·383 (3)	TC(2)[1]–TO(10)[1]	3·037 (3)
TC(6)[1]–TC(8)[1]	3·480 (4)	TO(2)[1]–IN(12)[2]	3·219 (3)
TO(9)[1]–IC(2)[2]	3·458 (3)	TC(8)[1]–IN(12)[2]	3·353 (3)
TO(2)[1]–IC(11)[2]	3·227 (4)	TO(4)[1]–TO(4)[3]	3·422 (4)
TO(10)[1]–IN(12)[4]	3·317 (3)	TC(8)[1]–IC(3)[4]	3·478 (3)
TC(8)[1]–IN(12)[4]	3·419 (3)	TO(9)[1]–IC(2)[4]	3·435 (3)
TO(10)[1]–IC(10)[4]	3·458 (3)	TO(10)[1]–IC(3)[4]	3·386 (3)
TC(5M)[1]–TC5M[6]	3·422 (8)	TC(5)[1]–TN(3)[7]	3·454 (4)
TC(4)[1]–TN(1)[7]	3·473 (4)	TO(4)[1]–TN(1)[7]	3·350 (3)

Fig. 3. Molecular packing of the TPA:TAA complex viewed along the b axis. The dotted lines represent possible hydrogen bonds.
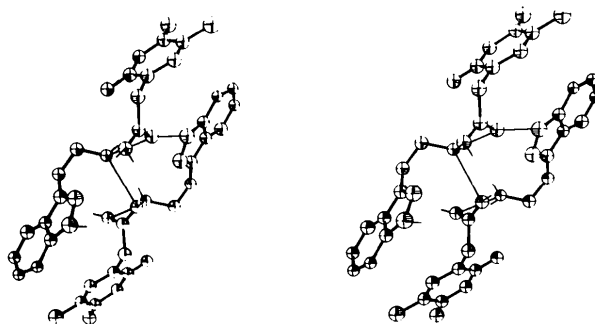

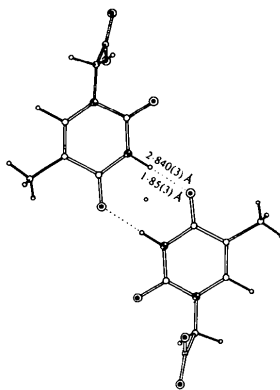Fig. 4. A stereoscopic view of the crystal packing around the twofold screw axis parallel to the b axis.

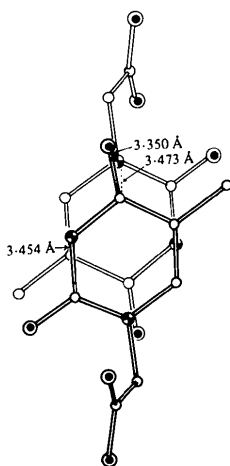Fig. 5. Dimer formation of TAA molecules by two hydrogen bonds around a center of symmetry.

Fig. 6. The stacking of TAA molecules projected on the pyrimidine ring. The molecule at x,y,z overlaps with that at $-x,-y,-z$.

layers held together in the a direction by van der Waals contacts.

At present, two theories exist about the type of interaction which occurs between the indole rings of tryptophan residues in proteins and bases in nucleic acids: one is the stacking interaction attributable to the charge-transfer force of the indole ring (donor) and the base (acceptor) (see, for example, Brun, Toulmé & Hélène, 1975; Hélène & Charlier, 1977; Wray & Wagner, 1977; Kolodny, Neville, Coleman & Zamecnik, 1977; Reuben, 1978; Maurizot, Boubault & Hélène, 1978). The other is the hydrogen-bonding interaction between the pyrrole N atom of the indole and the acceptor atom of the base (Kaneda & Tanaka, 1976; Ohki, Takenaka, Shimanouchi & Sasada, 1977). These forces could be important in the specific interaction between proteins and nucleic acids. However, we could not find any specific interaction between the indole and the thymine base in this complex. In the crystal packing of this complex, the hydrogen bonding between acid and amine could be preferable to a specific interaction between the indole ring and the thymine base, though a weak interaction might be present.

References

BROWNE, D. T., EISINGER, J. & LEONARD, N. J. (1968). *J. Am. Chem. Soc.* 90, 7302–7323.

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

CAILLET, J., CLAVERIE, P. & PULLMAN, B. (1977). *Acta Cryst.* A33, 885–889.

FRANK, J. K. & PAUL, I. C. (1973). *J. Am. Chem. Soc.* 95, 2324–2332.

GARTLAND, G. L., FREEMAN, G. R. & BUGG, C. E. (1974). *Acta Cryst.* B30, 1841–1849.

GERDIL, R. (1961). *Acta Cryst.* 14, 333–344.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

HÉLÈNE, C. & CHARLIER, M. (1977). *Photochem. Photobiol.* 25, 429–434.

HOOGSTEEN, K. (1963a). *Acta Cryst.* 16, 28–38.

HOOGSTEEN, K. (1963b). *Acta Cryst.* 16, 907–916.

HUBER, M. (1957). *Acta Cryst.* 10, 129–133.

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

INOUE, M., SAKAKI, T., WAKAHARA, A. & TOMITA, K. (1978). *Biochim. Biophys. Acta*, 543, 123–135.

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

ISHIDA, T., INOUE, M., FUJIWARA, T. & TOMITA, K. (1978). Unpublished work.

ISHIDA, T., SENDA, S., INOUE, M. & TOMITA, K. (1978). Unpublished work.

KANEDA, T. & TANAKA, J. (1976). *Bull. Chem. Soc. Jpn*, 49, 1799–1804.

KENNARD, O. (1968). *International Tables for X-ray Crystallography*, Vol. III, pp. 275–276. Birmingham: Kynoch Press.

KOLODNY, N. H., NEVILLE, A. C., COLEMAN, D. L. & ZAMECNIK, P. C. (1977). *Biopolymers*, 16, 259–275.

hydrogen bonds of length 2·840 Å (Fig. 5), similar to those found in 1-methylthymine, 1,1'-trimethylene-bisthymine and the uracil derivatives (summarized in Voet & Rich, 1970). However, O(2) does not take part in any hydrogen bonding, but has a short contact with the IN(12) atom of the adjacent TPA molecule related by the twofold screw axis (3·219 Å), probably a result of electrostatic interactions.

The stacking of the TAA molecular planes is shown in Fig. 6; the average interplanar spacing is 3·383 (6) Å which is somewhat shorter than the normal van der Waals separation.

There is no indole ring–pyrimidine ring interaction, because the dihedral angle between these planes is 60·1 (1)° and there is no hydrogen bonding or any contact of less than 3·5 Å between these rings.

The complex molecules are connected by hydrogen bonds formed around a twofold screw axis and a center of symmetry lying on the c axis, and form a layered structure parallel to the b and c directions, with the

MAURIZOT, J., BOUBAULT, G. & HÉLÈNE, C. (1978). *Biochemistry*, **17**, 2096–2101.

OHKI, M., TAKENAKA, A., SHIMANOUCHI, H. & SASADA, Y. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2573–2578.

OZEKI, K., SAKABE, N. & TANAKA, J. (1969). *Acta Cryst.* B**25**, 1038–1045.

REUBEN, J. (1978). *FEBS Lett.* **94**, 20–24.

SAKAKI, T., SOGO, A., WAKAHARA, A., KANAI, T., FUJIWARA, T. & TOMITA, K. (1976). *Acta Cryst.* B**32**, 3235–3242.

SAKURAI, T. & OKUNUKI, M. (1971). *Acta Cryst.* B**27**, 1445–1453.

SUCK, D., SAENGER, W. & ROHDE, W. (1974). *Biochim. Biophys. Acta*, **361**, 1–10.

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

TOUGARD, P. (1973). *Acta Cryst.* B**29**, 2227–2231.

TRUEBLOOD, K. N., HORN, P. & LUZZATI, V. (1961). *Acta Cryst.* **14**, 965–982.

VOET, D. (1973). *J. Am. Chem. Soc.* **95**, 3763–3770.

VOET, D. & RICH, A. (1970). *Nucleic Acid Research and Molecular Biology*, Vol. 10, pp. 220–229. New York: Academic Press.

WAHAKAHA, A., FUJIWARA, T. & TOMITA, K. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2481–2486.

WRAY, V. & WAGNER, K. G. (1977). *Z. Naturforsch. Teil C*, **32**, 315–320.

YOUNG, D. W., TOLLIN, P. & WILSON, H. R. (1969). *Acta Cryst.* B**25**, 1423–1432.

The Crystal Structures of Free Radical Salts and Complexes.
XIV. (1,1'-Dimethyl-4,4'-bipyridylium)²⁺ (7,7,8,8-Tetracyano-p-quinodimethanide)₃²⁻

BY G. J. ASHWELL* AND S. C. WALLWORK

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

Abstract

(1,1'-Dimethyl-4,4'-bipyridylium)²⁺ (7,7,8,8-tetracyano-p-quinodimethanide)₃²⁻, $C_{12}H_{14}N_2^{2+} \cdot (C_{12}H_4N_4)_3^{2-}$, (DMBP)²⁺(TCNQ)₃²⁻, is triclinic, space group $P\bar{1}$ with $a = 7·862$ (3), $b = 10·008$ (4), $c = 13·453$ (4) Å, $\alpha = 73·84$ (2), $\beta = 102·36$ (2), $\gamma = 96·70$ (2)°, $Z = 1$. The structure was refined to $R = 0·094$ for 2770 reflexions. The TCNQ's are stacked plane-to-plane in groups of three with no direct overlap between adjacent triads. Within triads there is a favourable exocyclic double bond to quinonoid ring overlap of adjacent molecules with short mean perpendicular spacings of 3·16 Å.

Introduction

The crystal structure of (DMBP)²⁺(TCNQ)₃²⁻ has been determined as part of a series of structure determinations on conducting bipyridylium–TCNQ salts. In most of these complexes the TCNQ's are stacked plane-to-plane in stoichiometric groups of three or four molecules with little or no direct overlap between adjacent groups. Such non-uniformity of spacing and

overlap gives rise to semiconducting behaviour. The conductivity of compacted pellets of (DMBP)²⁺(TCNQ)₃²⁻ is 10^{-1} Ω^{-1} m^{-1} at 300 K and the activation energy is 0·25 eV.

Experimental

Crystal data

$C_{12}H_{14}N_2^{2+} \cdot (C_{12}H_4N_4)_3^{2-}$, $M_r = 798·8$, triclinic, $a = 7·862$ (3), $b = 10·008$ (4), $c = 13·453$ (4) Å, $\alpha = 73·84$ (2), $\beta = 102·36$ (2), $\gamma = 96·70$ (2)°, $U = 991·16$ Å³, $Z = 1$, $D_m = 1·34$, $D_c = 1·34$ Mg m⁻³, $F(000) = 412$, Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å), $\mu = 0·091$ mm⁻¹; space group $P\bar{1}$ (assumed).

A microcrystalline complex with majority composition (DMBP)²⁺(TCNQ)₃²⁻ was deposited when a warm acetonitrile solution (200 ml) of 1,1'-dimethyl-4,4'-bipyridylium diiodide (0·2 g) and TCNQ (0·4 g) was allowed to cool slowly to room temperature. Small crystals of (DMBP)²⁺(TCNQ)₃²⁻ were isolated from the microcrystalline products. The space group and cell dimensions were obtained initially from oscillation and Weissenberg photographs with Cu $K\alpha$ radiation. The cell constants were subsequently refined and intensities collected on a Hilger & Watts computer-controlled four-circle diffractometer, with a $\theta/2\theta$ scan, a scintil-