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Structure of the Complex 3-Indoleacetic Acid: Tyramine (1:1)*

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Abstract. $C_{10}H_8NO_2^-.C_8H_{12}NO^+$, monoclinic, $P2_1/c$, $a = 9{\cdot}069\ (1)$, $b = 11{\cdot}745\ (2)$, $c = 16{\cdot}136\ (2)$ Å, $\beta = 100{\cdot}33\ (1)^\circ$, $U = 1690{\cdot}8\ (4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}225\ (1)$, $D_x = 1{\cdot}227$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·7988 mm^{-1}. The structure was solved by a direct method and refined to $R = 0{\cdot}054$ for 2889 independent reflections. No prominent interaction between the indole and phenol rings is observed in the crystal. Both molecules are held together by the hydrogen bonds between the carboxyl group of 3-indoleacetic acid and the amino group of tyramine, forming a tetrameric complex unit.

Introduction. Electron transfer within proteins is of general importance in biological oxidation–reduction systems. It has been thought possible that aromatic amino acids such as tryptophan and tyrosine could be implicated in such a process (Prütz, Butler, Land & Swallow, 1980; Winfield, 1965). On the other hand, it has been shown that a tyrosine residue is involved in the specific indole binding site of human serum albumin (Fehske, Müller & Wollert, 1979). In order to elucidate

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* Structural Studies of the Interaction between Indole Derivatives and Biologically Important Aromatic Compounds. VIII.

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the mode of interaction between indole and phenol rings, we determined the crystal structure of the title complex by X-ray analysis.

The title complex crystallized as transparent plates from 50% aqueous ethanol solution containing equimolar amounts of 3-indoleacetic acid (IAA) and tyramine (TRA). Preliminary oscillation and Weissenberg photographs showed that the crystals were monoclinic (space group $P2_1/c$ from systematic absences). Unit-cell dimensions were determined on a Rigaku four-circle diffractometer using 40 reflections and were refined by least squares. The intensities of 2889 independent reflections were measured by the ω–2θ scan technique using Cu $K\alpha$ radiation ($\sin\theta/\lambda \leq$ 0·588 Å^{-1}), and the usual Lorentz and polarization corrections were applied.

The structure was solved by the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The E map based on the phases of 192 reflections ($|E| \geq 1{\cdot}84$) revealed all the non-hydrogen atoms. The positions of all 20 H atoms were obtained from a difference map. Block-diagonal least-squares refinements converged to $R = 0{\cdot}054$.[*] The final atomic coordinates are given in Table 1. All numerical calculations were carried out on an ACOS-900 computer of the Computation Center of Osaka University using *The Universal Crystallographic Computing System* (1979). The scattering factors cited in *International Tables for X-ray Crystallography* (1974) were used for all atoms.

Discussion. The bond lengths and angles for non-hydrogen atoms with their standard deviations are shown in Fig. 1. The bond lengths involving H atoms range from 0·85 (3) [N(9)–H(9*a*)] to 1·13 (4) Å [C(10)–H(10*a*)]. The bonding parameters for the indole ring of IAA agree with those found in other IAA molecules (Ishida, 1979). The indole ring is planar with a maximum deviation of 0·012 (4) Å at C(2) and the atoms attached to the ring lie almost on the plane. The carboxyl group is in an anionic resonance form. The dihedral angle between the indole ring and the carboxyl group is 105·4 (1)°. The torsion angles χ [C(2)–C(3)–C(10)–C(11)] and φ [C(3)–C(10)–C(11)–O(12)] are 113·3 (4) and −17·1 (4)° respectively: these values were frequently observed in the other crystal structures, in which the conformations of IAA are all inside the range of (+)clinal for χ (80·4 to 113·4°) and (−)synperiplanar for φ (−6·4 to −29·2°), suggesting the most stable conformation for IAA (Ishida, 1979).

Table 1. *The final atomic coordinates and isotropic thermal parameters with estimated standard deviations in parentheses*

	x	y	z	B_{eq}/B (Å^2)[*]
IAA molecule				
N(1)	0·4961 (3)	0·3705 (2)	1·1573 (1)	5·0 (1)
C(2)	0·6013 (4)	0·3554 (3)	1·1057 (2)	5·0 (2)
C(3)	0·5283 (4)	0·3489 (2)	1·0240 (2)	3·9 (1)
C(4)	0·2433 (4)	0·3577 (3)	0·9624 (2)	5·6 (2)
C(5)	0·1052 (5)	0·3677 (4)	0·9838 (3)	7·4 (2)
C(6)	0·0897 (5)	0·3812 (3)	1·0671 (3)	7·5 (3)
C(7)	0·2122 (5)	0·3846 (3)	1·1314 (2)	5·7 (2)
C(8)	0·3548 (4)	0·3724 (2)	1·1096 (2)	4·5 (1)
C(9)	0·3720 (3)	0·3592 (2)	1·0247 (2)	4·0 (1)
C(10)	0·5979 (4)	0·3346 (2)	0·9471 (2)	4·3 (1)
C(11)	0·5636 (3)	0·2219 (2)	0·9014 (2)	3·1 (1)
O(12)	0·5148 (2)	0·1404 (1)	0·9383 (1)	3·7 (1)
O(13)	0·5902 (2)	0·2154 (2)	0·8280 (1)	4·2 (1)
H(1)	0·520 (4)	0·378 (3)	1·211 (2)	6 (1)
H(2)	0·726 (4)	0·347 (3)	1·127 (2)	4·1 (8)
H(4)	0·255 (4)	0·344 (3)	0·899 (2)	5·2 (9)
H(5)	−0·000 (4)	0·363 (3)	0·937 (2)	7 (1)
H(6)	−0·026 (4)	0·387 (3)	1·080 (2)	7 (1)
H(7)	0·205 (4)	0·395 (3)	1·190 (2)	5·4 (9)
H(10*a*)	0·724 (4)	0·339 (3)	0·966 (2)	4·9 (9)
H(10*b*)	0·561 (4)	0·405 (3)	0·905 (2)	5·3 (9)
TRA molecule				
C(1)	1·0691 (3)	0·4292 (3)	0·6907 (2)	4·3 (1)
C(2)	0·9552 (3)	0·5013 (3)	0·6552 (2)	4·5 (1)
C(3)	0·8095 (3)	0·4864 (2)	0·6685 (2)	4·0 (1)
C(4)	0·7778 (3)	0·3968 (2)	0·7186 (2)	3·6 (1)
O(4)	0·6339 (2)	0·3869 (2)	0·7328 (1)	3·9 (1)
C(5)	0·8894 (3)	0·3223 (3)	0·7532 (2)	4·1 (1)
C(6)	1·0341 (3)	0·3378 (3)	0·7391 (2)	4·5 (2)
C(7)	1·2291 (3)	0·4470 (3)	0·6779 (2)	5·1 (2)
C(8)	1·2510 (3)	0·4119 (2)	0·5909 (2)	3·4 (1)
N(9)	1·4132 (2)	0·4188 (2)	0·5850 (1)	3·2 (1)
H(2)	0·974 (3)	0·566 (3)	0·619 (2)	3·3 (7)
H(3)	0·729 (3)	0·535 (3)	0·643 (2)	3·0 (7)
H(4)	0·626 (4)	0·328 (3)	0·765 (2)	4·7 (8)
H(5)	0·868 (3)	0·253 (3)	0·788 (2)	3·2 (7)
H(6)	1·118 (3)	0·277 (3)	0·766 (2)	3·4 (7)
H(7*a*)	1·300 (4)	0·403 (3)	0·720 (2)	5·7 (9)
H(7*b*)	1·260 (4)	0·528 (3)	0·688 (2)	4·5 (8)
H(8*a*)	1·187 (3)	0·470 (3)	0·545 (2)	3·4 (7)
H(8*b*)	1·212 (3)	0·326 (3)	0·577 (2)	3·0 (7)
H(9*a*)	1·435 (4)	0·391 (3)	0·540 (2)	4·4 (8)
H(9*b*)	1·441 (3)	0·497 (3)	0·581 (2)	2·7 (7)
H(9*c*)	1·482 (4)	0·400 (3)	0·633 (2)	4·9 (9)

[*] The equivalent isotropic temperature factors for non-H atoms have been calculated by $B_{eq} = \frac{4}{3}(a^2B_{11} + 2ab\cos\gamma B_{12} + \ldots)$.

In the TRA molecule, the mean C–C and C(4)–O(4) distances of the phenol ring are 1·386 (4) and 1·369 (3) Å respectively; these values are not significantly different from those observed in TRA.HCl (1·388 and 1·361 Å) (Tamura, Wakahara, Fujiwara & Tomita, 1974). The bond angles are also reasonable. The benzene ring is planar, and O(4) and C(7) lie

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[*] Lists of structure factors, anisotropic thermal parameters and the least-squares planes of the indole, carboxyl, benzene and aminoethyl moieties, together with the displacements of atoms from the planes, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36189 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

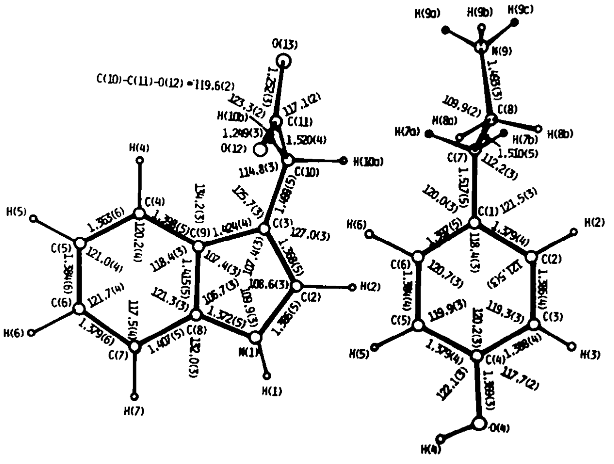

Fig. 1. Bond lengths (Å) and angles (°).

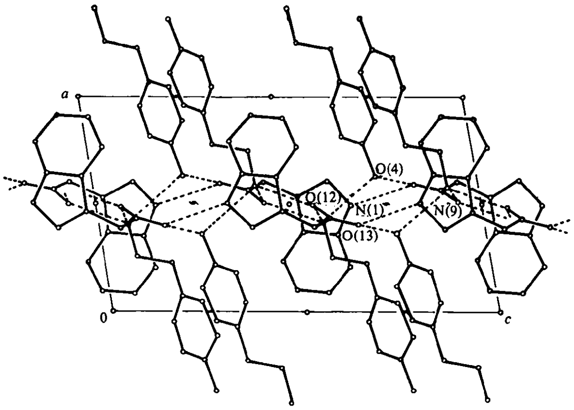

Fig. 2. The molecular packing viewed down **b**.

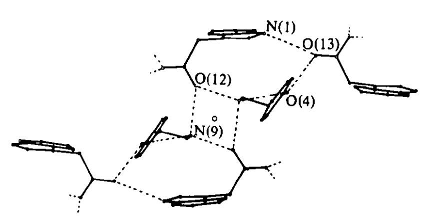

Fig. 3. The hydrogen bonding about a center of symmetry.

almost on the plane. Three H atoms are tetrahedrally bound to N(9), indicating the amino group to be in a cationic form. The dihedral angle between the aminoethyl group and the benzene ring is 107·2 (2)°. The TRA molecule has an extended conformation: the torsion angle θ [C(1)–C(7)–C(8)–N(9)] is $-173{\cdot}7$ (2)°. This extended conformation was also observed in TRA.HCl (θ = 179·7°) and TRA–1-thyminylacetic acid (θ = 178·7°) (Ogawa, Tago, Ishida & Tomita, 1980).

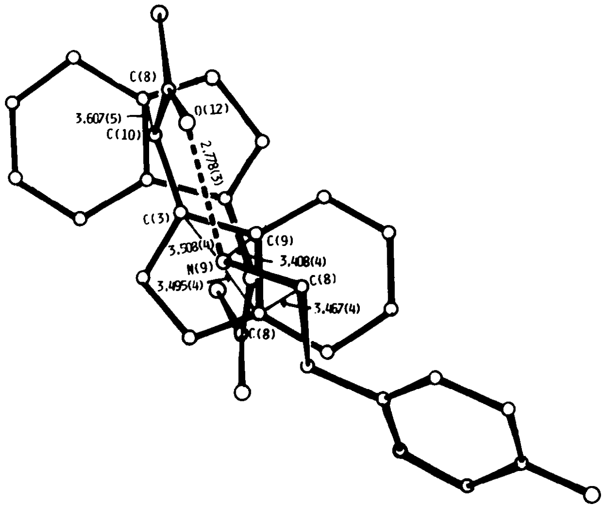

Fig. 4. A projection of IAA and its neighboring IAA and TRA molecules onto the central indole ring, with some short contacts (Å).

Table 2. *Hydrogen-bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Donor (*D*)	Acceptor (*A*)	*D*···*A*	H···*A*	∠*D*–H···*A*
O(4)(TRA)^{i}	O(13)(IAA)^{i}	2·607 (3)	1·73 (3)	174 (3)
N(9)(TRA)^{i}	O(4)(TRA)^{ii}	2·850 (3)	1·93 (4)	171 (3)
N(9)(TRA)^{i}	O(12)(IAA)^{iii}	2·778 (3)	1·95 (3)	166 (3)
N(9)(TRA)^{i}	O(12)(IAA)^{iv}	2·725 (3)	1·78 (3)	173 (3)
N(1)(IAA)^{i}	O(13)(IAA)^{v}	2·913 (4)	2·19 (4)	144 (3)

Symmetry code

(i)	x,	y,	z	(iv)	$2-x$,	$0{\cdot}5+y$,	$1{\cdot}5-z$
(ii)	$1+x$,	y,	z	(v)	x,	$0{\cdot}5-y$,	$0{\cdot}5+z$
(iii)	$1+x$,	$0{\cdot}5-y$,	$-0{\cdot}5+z$				

The molecular packing of the complex projected along the *b* axis is shown in Fig. 2, in which the broken lines represent the hydrogen bonds. The hydrogen-bonding parameters are given in Table 2. All the N and O atoms participate in hydrogen bonds: these atoms are arranged approximately around the twofold screw axes and centers of symmetry located at $x = \frac{1}{2}$; they are hydrogen-bonded to each other along the *c* axis. The mode of hydrogen bonding around a center of symmetry is shown in Fig. 3. O(12) is involved in a bifurcated hydrogen bond to two N(9) atoms, consequently forming the cyclic tetramer consisting of two IAA and two TRA molecules. N(9) is further hydrogen-bonded to O(4), forming the three hydrogen bonds tetrahedrally. O(13) is also involved in a bifurcated hydrogen bond to N(1) and O(4).

Fig. 4 shows a projection of IAA and its neighboring IAA and TRA molecules onto the central indole ring, with some short contacts. The dihedral angle between the indole and phenol rings is 59·9 (1)°, and no immediate hydrogen bond between both rings was observed. The aminoethyl plane of TRA lies above the plane of the central indole ring [dihedral angle 15·1 (2)°], with an average separation of 3·528 Å.

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SHORT COMMUNICATION

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Acta Cryst. (1981). B**37**, 2120

Room- and high-pressure neutron structure determination of tetrathiafulvalene–7,7,8,8-tetracyano-*p*-quinodimethane (TTF–TCNQ). Thermal expansion and isothermal compressibility. Errata.

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Abstract

Three errors in the paper by Filhol, Bravic, Gaultier, Chasseau & Vettier [*Acta Cryst.* (1981), B**37**, 1225–1235] are corrected. On page 1230, right-hand column, line 7 should read: 'In fact the C(2)···N(2) distance given in Table 6 of Kistenmacher *et al.* (1974) and wrongly used by Chasseau *et al.* (1978), is clearly not in the above directions. It is thus of importance for the discussion below to note the following point: the C(2)—H···N(2) distance referred to by these latter authors is in error (3·36 instead of 3·53 Å) and this hydrogen bond does not exist at room pressure and temperature'. In Table 6, line N(2)···D(2): the values 1·00 and 0·94 (2) should be replaced by 2·62 and 2·59 (2) respectively. In the caption of Fig. 7 the expression for α_i should read $\alpha_i = (1/l_i)(dl_i/dT)$.

All information is given in the *Abstract*.

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