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Crystal Structures of Tryptamine Picrate and D,L-Tryptophan Picrate–Methanol, Two Indole Donor–Acceptor Complexes

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The crystal structures of the red picric acid salts of tryptamine and of D,L-tryptophan–methanol were determined by X-ray diffraction methods. Crystals of tryptamine picrate ($C_{10}H_{13}N_2.C_6H_2N_3O_7$) are monoclinic, space group $P2_1/c$, with $a=15{\cdot}927$ (2), $b=6{\cdot}913$ (1), $c=21{\cdot}841$ (2) Å, $\beta=133{\cdot}88$ (1)° and $Z=4$. Crystals of D,L-tryptophan picrate–methanol ($C_{11}H_{13}N_2O_2.C_6H_2N_3O_7.CH_4O$) are triclinic, space group $P\bar{1}$, with $a=11{\cdot}733$ (1), $b=11{\cdot}547$ (1), $c=7{\cdot}971$ (1) Å, $\alpha=100{\cdot}34$ (3), $\beta=81{\cdot}31$ (1), $\gamma=97{\cdot}98$ (2)°, and $Z=2$. Three-dimensional X-ray intensity data (2882 reflections for the tryptamine complex and 3458 reflections for the tryptophan complex) were measured with an automated diffractometer by use of nickel-filtered copper radiation. Trial structures, obtained by direct methods, were refined by least-squares calculations to R indices of 0·056 and 0·088 for the tryptamine and tryptophan complexes, respectively. Both crystal structures contain distinct indole–picrate pairs. The indole and picrate planes are stacked, with interplanar spacings of 3·3–3·5 Å. The stacking interaction appears to be of the donor–acceptor (charge-transfer) type. However, contrary to the continous columns of stacked rings usually found in crystal structures of aromatic donor–acceptor complexes, the stacked indole–picrate pairs are relatively isolated and without π-π interactions between adjacent pairs. The stacking patterns are similar in the tryptamine and tryptophan complexes. The tryptamine and tryptophan cations assume the same conformation found for serotonin in the crystal structure of the serotonin picrate monohydrate donor–acceptor complex.

Introduction

Indoles are widely distributed through biological systems, primarily as tryptophan residues in proteins and as derivatives of tryptamine. Indole derivatives form donor–acceptor (charge-transfer) complexes with a variety of aromatic electron acceptors (Harbury & Foley, 1958; Isenberg & Szent-Györgyi, 1958; Fujimori, 1959; Alivisatos, Ungar, Jibril & Mourkides, 1961; Cilento & Tedeschi, 1961; Foster & Hanson, 1964; Wilson, 1966; Shifrin, 1968; Shinitzky & Katchalski, 1968; Montenay-Garestier & Hélène, 1971), and charge-tranfer interactions have been implicated in such biological processes as the binding of nicotinamide (Alivisatos, Ungar, Jibril & Mourkides, 1961; Cilento & Tedeschi, 1961; Shifrin, 1968) and flavin (Harbury & Foley, 1958; Isenberg & Szent-Györgyi, 1958; Wilson, 1966) coenzymes to tryptophan residues of enzymes; interactions of indoles with nucleotides and with nucleic acids (Shinitzky & Katchalski, 1968; Montenay-Garestier & Hélène, 1971); and binding of serotonin and hallucinogenic tryptamines to synaptic receptor sites (Szent-Györgyi, 1960). To obtain information about the structural factors involved in indole interactions with aromatic acceptors, we are currently examining a series of crystal structures in which indole derivatives are complexed with picric acid. In this paper we describe the crystal structures of the picrate complexes of tryptamine and tryptophan (Fig. 1).

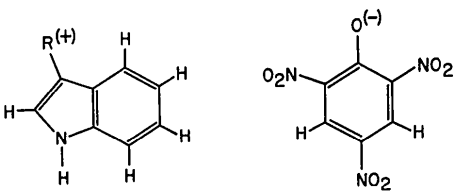

Fig. 1. Structural formulas of the substituted-indole cations tryptamine ($R=CH_2CH_2NH_3$) and tryptophan ($R=CH_2CH(CO_2H)NH_3$) and of the picrate anion.

Experimental

Tryptamine picrate

Tryptamine picrate was obtained as a reddish precipitate upon mixing aqueous solutions of tryptamine and picric acid. The compound was crystallized as red prisms by evaporating an ethanol solution at room temperature. Oscillation and Weissenberg photographs showed the crystals to be monoclinic, and space group $P2_1/c$ was indicated by the systematic absence of reflections $h0l$ with l odd and $0k0$ with k odd. A crystal with approximate dimensions of 0·20, 0·25, and 0·10 mm was mounted on a Picker FACS-1 diffractometer with its b axis slightly inclined to the φ axis of the goniostat. Unit-cell parameters were calculated by a least-squares refinement of 2θ values (Cu $K\alpha_1$) for 16 reflections in the range $69° < 2\theta < 94°$; Table 1 lists cell parameters and other crystal data.

Intensity data were collected with the diffractometer by use of nickel-filtered copper radiation, a scintillation counter, and a $\theta/2\theta$ scanning technique. The scan speed was 1° min^{-1}, and a 20 s background measurement was performed at each terminus of the scans. Measurements were made for the 2882 independent reflections with $2\theta < 128°$. Three reference reflections that were monitored periodically showed no significant intensity fluctuations during the collection of intensity data. Reflections that had scan counts below back-

Table 1. *Crystal data*

	Tryptamine picrate	D,L-Tryptophan picrate–methanol
Stoichiometry	$C_{10}H_{13}N_2.C_6H_2N_3O_7$	$C_{11}H_{13}N_2O_2.C_6H_2N_3O_7.CH_4O$
Z	4	2
Space group	$P2_1/c$	$P\bar{1}$
a	15·927 (2) Å	11·733 (1) Å
b	6·913 (1)	11·547 (1)
c	21·841 (2)	7·971 (1)
α	–	100·34 (3)°
β	133·88 (1)°	81·31 (1)
γ	–	97·98 (2)
D_m	1·49 g cm^{-3}	1·47 g cm^{-3}
D_x	1·491	1·481
μ(Cu $K\alpha$)	10·4 cm^{-1}	11·0 cm^{-1}

Unit-cell parameters were measured at room temperature. The standard deviations given in parentheses are twice those obtained from the least-squares fits. Densities were measured by flotation.

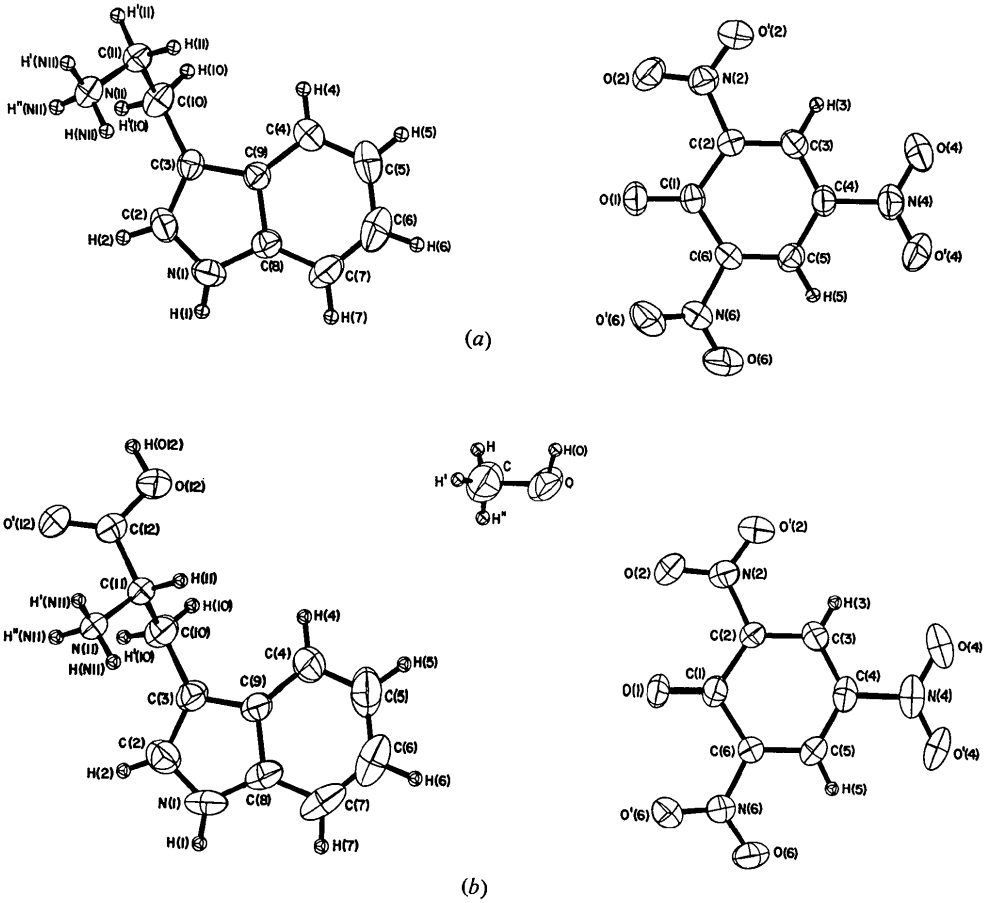

Fig. 2. The conformations and atom labels of the component molecules in (*a*) tryptamine picrate and (*b*) D,L-tryptophan picrate–methanol. The tryptophan molecule shown here is the L-enantiomer. Nonhydrogen atoms are represented by thermal ellipsoids that are defined by the principal axes of thermal vibration and scaled to include 50% probability. Hydrogen atoms are represented by spheres that are defined by an artificial isotropic temperature factor B of 0·75 Å^2. [This drawing and those in Figs. 3 and 4 were prepared by using the computer program *ORTEP* (Johnson, 1965)].

ground level were assigned intensity values of 0·0. Variances of the intensities were estimated according to counting statistics plus a correctional term $(0{\cdot}03S)^2$, where S is the scan count. Intensities and their variances were corrected for Lorentz and polarization factors, and absorption corrections (the factors range from 1·10 to 1·23) were applied by using the computer program *ORABS* (Wehe, Busing & Levy, 1962). The data were then scaled by Wilson's (1942) method.

Table 2. *Starting sets of reflections for the structure determinations by direct methods*

Table entries include h, k, l, $|E|$, and the starting signs. The Σ_1 relationships are from Hauptman & Karle (1953).

	Tryptamine picrate			D,L-Tryptophan picrate–methanol		
Origin-defining reflections	9 4 $\bar{14}$	3·05+		2 $\bar{2}$ $\bar{1}$	5·70+	
	7 2 $\bar{5}$	3·18+		1 5 $\bar{2}$	3·67+	
	6 1 $\bar{19}$	2·98+		$\bar{2}$ 5 $\bar{6}$	3·02+	
$\sum_1$ formula	8 2 $\bar{6}$	2·05+				
	0 0 14	2·60−				
Variable signs	4 1 $\bar{3}$	4·18		3 $\bar{5}$ $\bar{2}$	4·57	
	4 5 2	3·20		$\bar{7}$ $\bar{2}$ $\bar{5}$	3·83	
				$\bar{2}$ 3 0	3·27	
				$\bar{6}$ $\bar{3}$ $\bar{5}$	3·88	

A suitable trial structure was obtained by direct methods by use of the computer program *MULTAN* (Main, Woolfson & Germain, 1971); the starting set of reflections is described in Table 2. The trial structure was refined with a modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w(F_o^2 - F_c^2/k^2)^2$, where k is a scale factor, and the weight w is equal to $1/\sigma^2(F_o^2)$. All reflections, regardless of their $I/\sigma(I)$ ratio, were retained in the refinement. Scattering factors for the nonhydrogen atoms were from *International Tables for X-ray Crystallography* (1962), with anomalous dispersion components ($\Delta f'$ and $\Delta f''$) from Cromer & Liberman (1970). All hydrogen atoms were located in difference Fourier maps that were computed during the latter stages of refinement. Scattering factors for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). Final cycles of refinement included the scale factor k, all positional parameters, anisotropic temperature parameters for the nonhydrogen atoms, isotropic temperature parameters for the hydrogen atoms, and Zachariasen's (1963) isotropic extinction parameter g [as formulated by Coppens & Hamilton (1970)]. Since limited core storage prevented simultaneous variation of all parameters, the atoms of the tryptamine cation were refined together, and the atoms

Table 3. *Final heavy-atom parameters and their estimated standard deviations*

All values have been multiplied by 10^4. Thermal parameters are given according to the expression: $T = \exp(-\sum_{ij} h_i \beta_{ij} h_j)$. The final value of the extinction parameter g is 0·071 (5) for tryptamine picrate and 0·017 (4) for D,L-tryptophan picrate–methanol.

(*a*) Tryptamine picrate

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tryptamine									
N(1)	1728 (2)	5209 (3)	2478 (1)	75 (2)	148 (4)	44 (1)	20 (2)	37 (1)	−2 (2)
C(2)	1947 (2)	5915 (3)	3163 (1)	61 (2)	158 (5)	29 (1)	4 (2)	21 (1)	12 (2)
C(3)	1373 (2)	7605 (3)	2967 (1)	50 (1)	155 (4)	25 (1)	−11 (2)	23 (1)	−4 (2)
C(4)	34 (2)	9479 (4)	1536 (2)	91 (2)	206 (6)	39 (1)	43 (3)	39 (1)	18 (2)
C(5)	−441 (3)	9390 (5)	722 (2)	131 (3)	328 (8)	37 (1)	68 (4)	44 (2)	45 (3)
C(6)	−211 (3)	7841 (5)	451 (2)	133 (3)	411 (10)	33 (1)	11 (5)	48 (2)	2 (3)
C(7)	501 (2)	6360 (4)	982 (1)	98 (2)	264 (7)	38 (1)	−13 (3)	45 (1)	−30 (2)
C(8)	993 (2)	6460 (3)	1813 (1)	56 (2)	163 (5)	33 (1)	−6 (2)	30 (1)	−9 (2)
C(9)	762 (2)	7991 (3)	2098 (1)	50 (1)	142 (4)	27 (1)	−1 (2)	25 (1)	−2 (1)
C(10)	1320 (2)	8767 (4)	3519 (1)	70 (2)	226 (6)	32 (1)	−22 (3)	35 (1)	−15 (2)
C(11)	2107 (2)	10508 (3)	3953 (1)	69 (2)	165 (5)	29 (1)	6 (2)	33 (1)	−2 (2)
N(11)	3353 (2)	9924 (3)	4543 (1)	63 (2)	188 (4)	26 (1)	−9 (2)	27 (1)	−10 (2)
Picrate									
C(1)	4207 (2)	7877 (3)	3415 (1)	46 (1)	164 (4)	25 (1)	−12 (2)	22 (1)	−7 (2)
O(1)	4495 (1)	8449 (2)	4081 (1)	64 (1)	250 (4)	26 (1)	5 (2)	26 (1)	−15 (1)
C(2)	3437 (2)	8897 (3)	2612 (1)	52 (1)	137 (4)	30 (1)	2 (2)	27 (1)	1 (2)
N(2)	2976 (1)	10778 (3)	2545 (1)	71 (1)	156 (4)	38 (1)	4 (2)	37 (1)	1 (2)
O(2)	3027 (2)	11331 (2)	3098 (1)	150 (2)	204 (4)	62 (1)	47 (2)	80 (1)	12 (2)
O′(2)	2540 (2)	11780 (2)	1924 (1)	153 (2)	211 (4)	48 (1)	66 (2)	59 (1)	34 (2)
C(3)	3099 (2)	8192 (3)	1882 (1)	55 (2)	197 (5)	26 (1)	11 (2)	26 (1)	10 (2)
C(4)	3506 (2)	6427 (3)	1893 (1)	60 (2)	204 (5)	25 (1)	4 (2)	28 (1)	−7 (2)
N(4)	3122 (2)	5665 (3)	1116 (1)	86 (2)	294 (6)	32 (1)	22 (3)	39 (1)	−4 (2)
O(4)	2360 (2)	6531 (3)	453 (1)	148 (2)	453 (7)	30 (1)	96 (3)	44 (1)	18 (2)
O′(4)	3572 (2)	4202 (3)	1147 (1)	129 (2)	343 (5)	48 (1)	60 (3)	57 (1)	−16 (2)
C(5)	4274 (2)	5360 (3)	2635 (1)	59 (2)	163 (5)	32 (1)	5 (2)	31 (1)	−5 (2)
C(6)	4617 (2)	6073 (3)	3361 (1)	53 (1)	163 (5)	25 (1)	7 (2)	23 (1)	9 (2)
N(6)	5443 (2)	4918 (3)	4122 (1)	77 (2)	208 (5)	30 (1)	30 (2)	28 (1)	18 (2)
O(6)	5464 (2)	3186 (3)	4044 (1)	164 (2)	201 (5)	54 (1)	61 (3)	54 (1)	34 (2)
O′(6)	6132 (2)	5715 (3)	4811 (1)	127 (2)	319 (5)	29 (1)	46 (3)	21 (1)	14 (2)

Table 3 (*cont.*)

(*b*) D,L-Tryptophan picrate–methanol

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tryptophan									
N(1)	1029 (3)	8484 (3)	5460 (4)	97 (3)	107 (3)	163 (6)	24 (2)	−74 (3)	−4 (3)
C(2)	−32 (3)	7882 (3)	5237 (4)	108 (3)	75 (3)	168 (7)	15 (3)	−36 (4)	24 (4)
C(3)	−381 (3)	8111 (2)	3792 (4)	69 (3)	53 (2)	164 (6)	2 (2)	−42 (3)	7 (3)
C(4)	697 (3)	9454 (3)	1626 (5)	88 (3)	78 (3)	234 (8)	8 (2)	−41 (4)	50 (4)
C(5)	1685 (4)	10195 (3)	1295 (6)	103 (4)	98 (4)	346 (11)	−4 (3)	−11 (5)	94 (5)
C(6)	2534 (4)	10412 (3)	2389 (7)	84 (4)	86 (4)	414 (13)	−15 (3)	7 (6)	23 (6)
C(7)	2408 (3)	9901 (3)	3829 (6)	70 (3)	88 (3)	331 (11)	8 (3)	−64 (5)	−54 (5)
C(8)	1401 (3)	9125 (3)	4163 (4)	72 (3)	68 (3)	199 (7)	12 (2)	−53 (4)	−16 (4)
C(9)	532 (2)	8901 (2)	3070 (4)	63 (2)	51 (2)	172 (6)	7 (2)	−44 (3)	7 (3)
C(10)	−1515 (3)	7648 (3)	3128 (4)	72 (3)	71 (3)	206 (7)	1 (2)	−35 (4)	10 (4)
C(11)	−1438 (2)	6586 (2)	1687 (4)	56 (2)	65 (2)	147 (6)	−9 (2)	−29 (3)	33 (3)
N(11)	−1062 (2)	5579 (2)	2286 (3)	48 (2)	60 (2)	134 (4)	−6 (2)	−23 (2)	19 (2)
C(12)	−2610 (3)	6177 (3)	1047 (4)	62 (3)	70 (3)	163 (6)	−3 (2)	−32 (3)	18 (3)
O(12)	−2793 (2)	6766 (2)	−110 (4)	101 (2)	119 (3)	319 (7)	−28 (2)	−114 (3)	98 (3)
O′(12)	−3276 (2)	5407 (2)	1593 (3)	55 (2)	107 (2)	224 (5)	−24 (2)	−38 (2)	54 (3)
Picrate									
C(1)	2098 (2)	6483 (2)	1242 (3)	47 (2)	61 (2)	112 (5)	3 (2)	−16 (3)	7 (3)
O(1)	1210 (2)	5818 (2)	847 (2)	51 (2)	84 (2)	125 (4)	−15 (1)	−26 (2)	13 (2)
C(2)	2728 (2)	7350 (2)	245 (3)	65 (2)	62 (2)	114 (5)	−2 (2)	−30 (3)	20 (3)
N(2)	2282 (2)	7551 (2)	−1275 (3)	94 (3)	79 (2)	142 (5)	−9 (2)	−43 (3)	36 (3)
O(2)	1299 (2)	7136 (2)	−1549 (3)	113 (3)	133 (3)	260 (6)	−31 (2)	−112 (3)	83 (3)
O′(2)	2912 (2)	8143 (3)	−2243 (3)	139 (3)	157 (3)	218 (6)	−44 (2)	−64 (3)	121 (4)
C(3)	3736 (3)	8023 (3)	640 (4)	68 (3)	71 (3)	144 (6)	−15 (2)	−15 (3)	25 (3)
C(4)	4200 (2)	7881 (3)	2063 (4)	55 (2)	80 (3)	166 (6)	−9 (2)	−31 (3)	15 (3)
N(4)	5263 (3)	8598 (3)	2503 (4)	73 (3)	117 (3)	272 (8)	−34 (2)	−59 (4)	36 (4)
O(4)	5710 (3)	9325 (3)	1593 (5)	115 (3)	172 (4)	424 (9)	−89 (3)	−80 (4)	116 (5)
O′(4)	5661 (2)	8434 (3)	3749 (4)	113 (3)	214 (4)	348 (8)	−63 (3)	−142 (4)	87 (5)
C(5)	3660 (3)	7098 (3)	3117 (4)	64 (2)	79 (3)	141 (6)	1 (2)	−41 (3)	22 (3)
C(6)	2640 (2)	6431 (2)	2738 (3)	56 (2)	62 (2)	116 (5)	−1 (2)	−17 (3)	21 (3)
N(6)	2110 (2)	5633 (2)	3907 (3)	62 (2)	85 (2)	141 (5)	1 (2)	−19 (3)	39 (3)
O(6)	2679 (2)	5421 (2)	4953 (3)	89 (2)	171 (3)	210 (5)	−4 (2)	−41 (3)	120 (3)
O′(6)	1106 (2)	5204 (3)	3895 (4)	94 (2)	186 (4)	299 (7)	−56 (2)	−66 (3)	155 (4)
Methanol									
C	4595 (4)	3509 (4)	3173 (5)	122 (4)	149 (5)	224 (9)	9 (4)	−50 (5)	44 (5)
O	4580 (2)	4005 (2)	1670 (3)	73 (2)	154 (3)	249 (6)	−25 (2)	−67 (3)	71 (3)

of the picrate anion were refined in the alternate cycles.

The final R index ($\sum||F_o|-|F_c||/\sum|F_o|$), based on the complete set of reflections, is 0·056; and the goodness-of-fit $\{[\sum(F_o^2-F_c^2)^2/(m-s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined} is 1·99. During the last cycle of refinement, no parameter shifted more than one-fifth of its estimated standard deviation. A final difference Fourier map showed no peaks or troughs with magnitudes exceeding 0·44 e Å^{-3}.

D,L-*Tryptophan picrate–methanol*

Red, needle-like crystals of the D,L-tryptophan picrate–methanol complex were obtained by slowly evaporating a methanol solution that contained an equimolar mixture of D,L-tryptophan and picric acid. Weissenberg and oscillation photographs showed the crystals to be triclinic, space group $P1$ or $P\bar{1}$. A crystal fragment with approximate dimensions of 0·17, 0·08, and 0·08 mm was sliced from a needle, then mounted on the diffractometer with the c axis of the crystal slightly inclined to the φ axis of the goniostat. Unit-cell parameters were determined by a least-squares analysis of 2θ values for 12 high-angle reflections (Cu $K\alpha_1$) measured with the diffractometer. Crystal data are listed in Table 1. Intensity measurements were made for the 3458 independent reflections with $2\theta < 128°$; the experimental procedure and the treatment of data were like those described for tryptamine picrate. The absorption correction factors range from 1·07 to 1·13.

A Howells, Phillips & Rogers (1950) plot and the average properties of the experimental normalized structure factors suggested that the structure was centrosymmetric, and the measured density (Table 1) indicated that the unit cell contained two formula units of the compound. We therefore presumed the space group to be $P\bar{1}$; this assumption was corroborated by the final structure analysis. A trial structure was obtained by direct methods, with the use of Long's (1965) computer program for centrosymmetric crystals; the starting set of reflections is described in Table 2. The structure was refined by the procedure described for tryptamine picrate, except that no anomalous dispersion corrections were applied to the scattering factors. The atoms of the tryptophan cation were refined

together, and the atoms of the picrate anion plus the methanol molecule were refined in the alternate cycles.

During the last cycles of refinement no parameter shifted more than one-fifth of its estimated standard deviation. The final R index, including all reflections, is 0·088, and the goodness-of-fit is 1·70. A final difference Fourier map, in which hydrogen-atom contributions were omitted, showed residual peaks ranging from 0·34 e Å^{-3} to 0·63 e Å^{-3} at the hydrogen positions; no other peaks or troughs exceeding 0·44 e Å^{-3} in magnitude were present in this map.

Results

Table 3 lists the final heavy-atom parameters and their estimated standard deviations. Table 4 gives the final hydrogen-atom parameters and their estimated standard deviations. In positional coordinates, the estimated standard deviations are approximately 0·003 and 0·04 Å for the nonhydrogen and hydrogen atoms, respectively.*

Table 4. *Final hydrogen-atom parameters and their estimated standard deviations*

Positional parameters have been multiplied by 10^3. Temperature factors are given according to the expression $T = \exp(-B\sin^2\theta/\lambda^2)$.

(*a*) Tryptamine picrate

	x	y	z	B (Å^2)
Tryptamine				
H(1)	198 (2)	419 (4)	246 (2)	5·6 (6)
H(2)	244 (2)	525 (3)	365 (1)	4·3 (5)
H(4)	−010 (2)	1057 (4)	172 (2)	6·8 (7)
H(5)	−091 (2)	1038 (4)	037 (2)	6·8 (7)
H(6)	−061 (2)	782 (4)	−012 (2)	7·2 (7)
H(7)	064 (2)	526 (3)	079 (1)	4·1 (5)
H(10)	051 (2)	929 (4)	318 (2)	5·9 (6)
H′(10)	145 (2)	788 (4)	393 (1)	5·2 (6)
H(11)	195 (2)	1143 (3)	354 (1)	3·1 (4)
H′(11)	196 (2)	1116 (3)	427 (1)	3·7 (4)
H(N11)	357 (2)	941 (4)	425 (1)	5·0 (5)
H′(N11)	389 (2)	1096 (4)	492 (2)	6·7 (7)
H″(N11)	350 (2)	894 (3)	489 (1)	3·9 (5)
Picrate				
H(3)	255 (2)	893 (3)	137 (1)	3·8 (5)
H(5)	453 (2)	416 (4)	262 (1)	4·4 (5)

(*b*) D,L-Tryptophan picrate–methanol

	x	y	z	B (Å^2)
Tryptophan				
H(1)	149 (3)	842 (3)	622 (5)	7·0 (9)
H(2)	−034 (3)	742 (3)	602 (4)	5·8 (8)
H(4)	010 (3)	927 (3)	080 (4)	5·8 (8)
H(5)	185 (3)	1059 (3)	028 (4)	5·4 (7)
H(6)	328 (3)	1093 (3)	209 (5)	7·1 (9)
H(7)	290 (2)	998 (2)	469 (4)	4·2 (6)
H(10)	−179 (2)	829 (3)	268 (4)	4·8 (7)
H′(10)	−212 (3)	742 (3)	403 (4)	6·1 (8)
H(11)	−085 (2)	680 (2)	066 (3)	2·8 (5)
H(N11)	−029 (3)	577 (3)	252 (4)	5·7 (8)
H′(N11)	−108 (3)	491 (3)	146 (4)	5·8 (8)
H″(N11)	−158 (3)	534 (3)	326 (4)	5·5 (8)
H(O12)	−345 (4)	642 (4)	−053 (6)	11 (1)
Picrate				
H(3)	404 (2)	855 (2)	003 (4)	4·5 (7)
H(5)	393 (2)	699 (2)	407 (3)	3·8 (6)
Methanol				
H	453 (4)	413 (4)	429 (6)	11 (1)
H′	519 (7)	308 (6)	309 (9)	19 (2)
H″	376 (6)	313 (5)	342 (8)	17 (2)
H(O)	521 (3)	451 (3)	148 (5)	8 (1)

Fig. 2 depicts the conformations, atom labels, and thermal ellipsoids. The L-enantiomer of tryptophan is shown in Fig. 2, and all subsequent discussion of conformational angles will be applicable to this enantiomer. The structures consist of tryptamine–picrate and tryptophan–picrate ion pairs, with the locus of positive charge residing on the terminal N(11) amino groups of the ethylamine sidechains. The conformations of the ethylamine sidechains are similar in the two structures. Conformational torsion angles are listed in Table 5. The conformation about the C(3)–C(10) bond is such that the plane defined by atoms C(3), C(10), and C(11) is nearly perpendicular to the plane of the indole ring. The conformation about the C(10)–C(11) bond, in which C(11)–N(11) is –synclinal to C(10)–C(3), results in a folding of the ethylamine side chain over the indole plane, while maintaining a staggered arrangement about C(10)–C(11).

Table 5. *Selected torsion angles for the tryptamine and tryptophan moieties*

The sign convention used is that of Klyne & Prelog (1960). Signs of the tryptophan angles correspond to the L-tryptophan enantiomer. The estimated standard deviations are about 0·4°.

	Tryptamine picrate	D,L-Tryptophan picrate–methanol
C(2)—C(3)—C(10)–C(11)	100·8°	99·4°
C(9)—C(3)—C(10)–C(11)	−83·7	−82·5
C(3)—C(10)–C(11)–N(11)	−62·0	−61·1
C(10)–C(11)–N(11)–H(N11)	68·0	67·3
C(3)—C(10)–C(11)–C(12)	–	178·8
C(10)–C(11)–C(12)–O(12)	–	−85·0
C(10)–C(11)–C(12)–O′(12)	–	94·0
N(11)–C(11)–C(12)–O(12)	–	153·2
N(11)–C(11)–C(12)–O′(12)	–	−27·7

In the tryptophan complex, the *gauche* conformation about C(10)–C(11) [Cβ–Cα according to the usual notation for amino acids] places C(10)–C(3) [Cβ–Cγ] and C(11)–C(12) [Cα–C carboxyl] in antiplanar arrangement. An antiplanar conformation about Cβ–Cα was also found for the tryptophan residues in the crystal structures of glycyl-L-tryptophan dihydrate (Pasternak, 1956), 5-hydroxy-D,L-tryptophan (Wakahara, Kido, Fujiwara & Tomita, 1970), and D,L-tryptophan formate (Bye, Mostad & Rømming, 1971). In contrast, Cβ–Cγ is –synclinal to Cα–C carboxyl in the crystal

* The following tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30384 (36 pp., 1 microfiche): observed and calculated structure factors, bond lengths and angles of the picrate anions, and atomic deviations from least-squares planes through the indole and picrate rings. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

structure of L-tryptophan hydrochloride (Takigawa, Ashida, Sasada & Kakudo, 1966). The carboxyl group and atom C(11) [Cα] are coplanar and the torsion angle N(11)–C(11)–C(12)–O′(12), which is a measure of the deviation of the amino nitrogen atom from the carboxyl plane, is −28°. In other crystal structures of amino acids and peptides there is considerable variation in the angle of twist about C–Cα, with the N–Cα–C–O conformations ranging from synplanar to –synclinal (Marsh & Donohue, 1967).

Table 6 lists bond lengths and angles that involve only nonhydrogen atoms of the indole derivatives. A table of bond lengths and angles involving nonhydrogen atoms of the picrate anions has been deposited.* Covalent bond lengths and angles involving hydrogen atoms have not been tabulated, but are in their usual range; *e.g.* the C–H bond lengths range from 0·85 to 1·04 Å with an average value of 0·96 Å; the N–H bond lengths range from 0·82 to 0·98 Å with an average value of 0·93 Å; and the O–H bond lengths in the carboxyl group and the methanol molecule of the tryptophan complex are 0·90 and 0·89 Å, respectively. Corresponding bond lengths and angles in the two indole derivatives agree within experimental error, except for some minor differences in the vicinity of C(11) (which contains the carboxyl group in tryptophan). The values are in agreement with those found for serotonin picrate (Thewalt & Bugg, 1972) and D,L-tryptophan formate (Bye, Mostad & Rømming, 1971). There is satisfactory agreement between the picrate dimensions in the tryptamine and tryptophan complexes, and in serotonin picrate. The C–O bond length (1·421 Å) in the methanol molecule of the tryptophan

* See footnote page 1845.

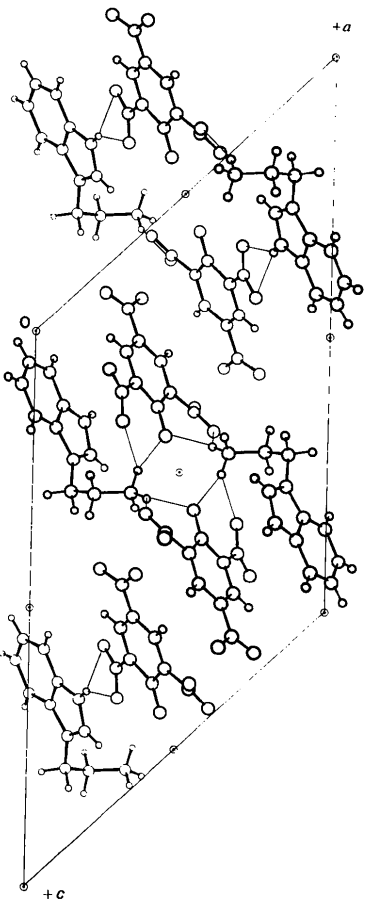

Fig. 3. The crystal structure of tryptamine picrate as viewed down **b**. Covalent and hydrogen bonds are represented by heavy and light lines, respectively.

Table 6. *Bond lengths and angles involving only nonhydrogen atoms of the tryptamine and tryptophan cations*

The estimated standard deviations are about 0·004 Å and 0·3°.

Bond lengths	Tryptamine	Tryptophan
C(8)—N(1)	1·368 Å	1·362 Å
N(1)—C(2)	1·370	1·359
C(2)—C(3)	1·357	1·359
C(3)—C(9)	1·434	1·429
C(9)—C(4)	1·392	1·389
C(4)—C(5)	1·369	1·363
C(5)—C(6)	1·390	1·389
C(6)—C(7)	1·363	1·362
C(7)—C(8)	1·394	1·403
C(8)—C(9)	1·401	1·406
C(3)—C(10)	1·500	1·500
C(10)–C(11)	1·507	1·525
C(11)–N(11)	1·489	1·476
C(11)–C(12)	–	1·522
C(12)–O(12)	–	1·298
C(12)–O′(12)	–	1·197

Bond angles	Tryptamine	Tryptophan
C(8)—N(1)—C(2)	108·5°	109·8°
N(1)—C(2)—C(3)	110·8	109·9
C(2)—C(3)—C(9)	105·7	106·2
C(2)—C(3)—C(10)	127·5	126·4
C(9)—C(3)—C(10)	126·8	127·3
C(9)—C(4)—C(5)	119·0	119·9
C(4)—C(5)—C(6)	121·1	120·9
C(5)—C(6)—C(7)	121·8	121·4
C(6)—C(7)—C(8)	117·1	118·0
C(7)—C(8)—C(9)	122·3	121·2
C(7)—C(8)—N(1)	130·3	132·0
N(1)—C(8)—C(9)	107·4	106·8
C(8)—C(9)—C(3)	107·5	107·2
C(8)—C(9)—C(4)	118·7	118·6
C(3)—C(9)—C(4)	133·8	134·1
C(3)—C(10)–C(11)	116·6	113·7
C(10)–C(11)–N(11)	110·9	110·9
C(10)–C(11)–C(12)	–	111·1
N(11)–C(11)–C(12)	–	108·0
C(11)–C(12)–O(12)	–	112·4
C(11)–C(12)–O′(12)	–	122·4
O(12)–C(12)–O′(12)	–	125·2

complex agrees with that in the crystal structure of methanol (1·42 Å; Tauer & Lipscomb, 1952).

A table of atomic deviations from least-squares planes through the indole and picrate rings has been deposited.* The nine atoms of each indole ring are nearly coplanar; the maximum deviation from the least-squares plane through the indole ring is 0·017 Å for tryptamine and 0·013 Å for tryptophan. However, C(10) is displaced from the indole plane by 0·127 Å in the tryptamine complex and by 0·070 Å in the tryptophan complex. The six atoms in the benzene rings of the picrate ions are coplanar within 0·01–0·02 Å, but the immediate nonhydrogen-atom substituents deviate from the benzene planes by amounts ranging up to 0·09 Å. As found for picrate ions in other crystal structures, the nitro groups are twisted out of the benzene plane. The *ortho* nitro groups [O(2)–N(2)–O′(2) and O(6)–N(6)–O′(6)] are twisted 16° and 29°, respectively, in the tryptamine complex and 11° and 15°, respectively, in the tryptophan complex. The *para* nitro groups are more nearly parallel to the benzene plane, with tilts of 7° in the tryptamine complex and 2° in the tryptophan complex. The picrate ions assume similar conformations in the crystal structures of ammonium and potassium picrate (Maartmann-Moe, 1969), where the *ortho* nitro groups are tilted 26° from the benzene plane, and the *para* nitro groups are nearly coplanar with the benzene rings.

The crystal packing schemes for the tryptamine and tryptophan complexes are depicted in Figs. 3 and 4, respectively. The hydrogen bonds are shown in Figs. 3 and 4, and hydrogen-bond dimensions are compiled in Table 7. All hydrogen atoms that are covalently bonded to oxygen or nitrogen atoms participate in hydrogen bonding. The hydrogen-bonding patterns in the two crystal structures have several features in common. In both structures, the H(N11) and H′(N11) hydrogen atoms of the protonated amino groups form bifurcated hydrogen bonds in which one N–H···O contact is much shorter than the other. Atom N(1) of the indole ring also appears to form a bifurcated hydrogen bond to the two oxygen atoms of a nitro group, but, again, one N–H···O contact is appreciably shorter than the other. The *para* nitro groups of the picrate ions accept no hydrogen bonds. In the tryptophan picrate complex, the methanol molecules hydrogen bond exclusively with tryptophan carboxyl groups, and *vice versa*.

* See footnote p. 1845.

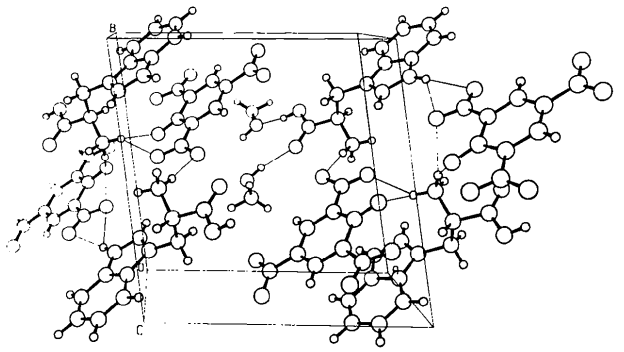

Fig. 4. A perspective view of the crystal structure of D,L-tryptophan picrate–methanol. Covalent and hydrogen bonds are represented by heavy and light lines, respectively.

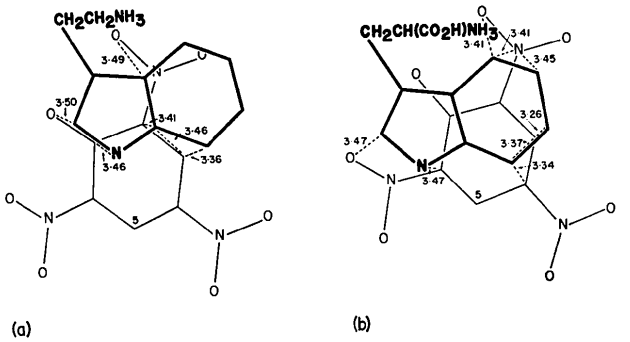

Fig. 5. Geometries of the stacked indole–picrate pairs in (*a*) tryptamine picrate and (*b*) D,L-tryptophan picrate–methanol. The views are normal to the least-squares planes through the indole rings. All indole–picrate interatomic distances within 3·5 Å are shown. The picrate ring carbon atom C(5) is indicated, thereby fixing the labels of all remaining picrate atoms.

Table 7. *Hydrogen-bond dimensions*

The coordinates of atoms denoted by superscripts may be obtained from the corresponding values in Table 3 by applying the following symmetry operations:

(*a*)	$1+x$,	y,	z	(*e*)	$-x$,	$1-y$,	$1-z$
(*b*)	x,	$-1+y$,	z	(*f*)	$1-x$,	$1-y$,	$1-z$
(*c*)	x,	y,	$1+z$	(*g*)	$1-x$,	$2-y$,	$1-z$
(*d*)	$-x$,	$1-y$,	$-z$				

Tryptamine picrate

Donor	Acceptor	Distance $D\cdots A$	Distance H$\cdots A$	Angle D–H$\cdots A$
N(1)—H(1)	O(2)[b]	3·069 Å	2·33 Å	151°
N(1)—H(1)	O′(2)[b]	3·306	2·54	157
N(11)–H(N11)	O(1)	2·812	1·87	160
N(11)–H(N11)	O(2)	2·984	2·42	117
N(11)–H′(N11)	O(1)[g]	2·786	1·94	144
N(11)–H′(N11)	O′(6)[g]	3·185	2·38	139
N(11)–H″(N11)	O(6)[f]	3·103	2·23	158

D,L-Tryptophan picrate–methanol

N(1)–H(1)	O(2)[c]	3·147 Å	2·49 Å	132°
N(1)–H(1)	O′(2)[c]	3·180	2·31	170
N(11)–H(N11)	O(1)	2·736	2·04	129
N(11)–H(N11)	O′(6)	3·130	2·32	144
N(11)–H′(N11)	O(1)[d]	2·734	1·89	150
N(11)–H′(N11)	O(2)[d]	3·066	2·35	134
N(11)–H″(N11)	O(6)[e]	2·969	2·01	171
O(12)–H(O12)	O[d]	2·570	1·69	166
O—H(O)	O′(12)[a]	2·795	1·93	163

Both crystal structures display distinct indole–picrate pairs that are stacked approximately plane-to-plane. These stacked pairs are stabilized by a bifurcated hydrogen bond between the terminal amino group of

the indole derivative and two adjacent oxygen atoms of the picrate anion. Fig. 5 shows the stacking patterns of the indole–picrate rings as viewed perpendicular to planes through the indoles. In both structures, the indole and picrate moieties are nearly parallel and are separated by an interplanar spacing of 3·3–3·5 Å. The angle of tilt between the stacked rings is about 4° in the tryptamine complex, and about 6° in the tryptophan complex. All indole–picrate contacts shorter than 3·5 Å are given in Fig. 5; of these, only the indole carbon–picrate carbon aromatic contacts C(7)–C(3) for tryptamine picrate and C(6)–C(3), C(7)–C(3), C(7)–C(4) for tryptophan picrate are shorter than normal van der Waals separation (Pauling, 1960).

Discussion

There has been considerable interest in the conformational properties of tryptamine, and a number of crystallographic studies of tryptamine derivatives have been reported. In a recent review, Baker, Chothia, Pauling & Weber (1973) show that the ethylamine side chains of tryptamines can assume several different conformations. The same general conformation is assumed by the ethylamine side chains in the crystal structures of tryptamine picrate, D,L-tryptophan picrate, tryptamine hydrochloride (Wakahara, Fujiwara & Tomita, 1970), 5-hydroxytryptamine (serotonin) picrate monohydrate (Thewalt & Bugg, 1972), and 5-methoxytryptamine (Quarles, 1971). However, considerably different side-chain conformations are found for a number of other tryptamine derivatives. The conformation of tryptamine and tryptophan in the presently reported complexes is in accord with that predicted for 5-hydroxytryptamine by theoretical calculations (Courrière, Coubeils & Pullman, 1971). However, the calculations suggest that other conformational states are only slightly less stable. It appears that, as long as staggered arrangements are maintained, the ethylamine moieties have considerable conformational freedom. Though the particular conformation found in any given crystal structure is probably largely influenced by crystal packing forces, it is noteworthy that the same conformation is found in the picrate donor–acceptor complexes of 5-hydroxytryptamine, tryptamine, and tryptophan despite rather large differences in their crystal-packing schemes.

The indole–picrate stacking interactions appear to be of the donor–acceptor (charge-transfer) kind. This interpretation is consistent with the observed color of the crystals: Whereas the indoles are colorless and picric acid is pale yellow, the tryptamine picrate and tryptophan picrate crystals are red, a color that is characteristic of the charge-transfer complexes which picric acid forms with a wide range of other aromatic donors (Kross & Fassel, 1957; Briegleb & Delle, 1960). Spectroscopic evidence for charge-transfer absorption bands in crystals of tryptophan picrate has been published (Matsunaga, 1973). However, it is not clear what role charge-transfer interactions play in determining the geometries of these indole–picrate π complexes. A number of studies have suggested that normal van der Waals interactions may be the principal determinants of the ground-state stabilities and geometries of aromatic donor–acceptor complexes (Briegleb, 1961; Dewar & Thompson, 1966; Mulliken & Person, 1969). In support of this possibility, the ring–ring spacings and stacking patterns in aromatic donor–acceptor complexes are similar to those in crystals of other polar aromatic compounds where charge-transfer forces are not important (Bugg, Thomas, Sundaralingam & Rao, 1971). Since the indole–picrate contacts in the tryptamine–picrate and tryptophan–picrate complexes are generally within the range of van der Waals separation, the interactions may be primarily attributable to normal van der Waals forces. It is noteworthy, however, that picric acid and the picrate ion have been found to form π complexes only with aromatic systems that are good electron donors. For example, in the crystal structures of guanine picrate monohydrate (Bugg & Thewalt, 1972), thioguanine picrate monohydrate (Bugg & Thewalt, 1972), and *N*-methylnicotinamide picrate (Freeman & Bugg, 1974), the picrate anion does not form stacked complexes with the aromatic cations, all of which are poor electron donors. Thus, it appears that the tendency to form π complexes may be greater when charge-transfer interactions are possible, even if the overall stabilities of the complexes are due principally to classical van der Waals interactions.

A prominent feature that distinguishes the tryptamine picrate and tryptophan picrate complexes from those of most other crystalline 1:1 aromatic donor–acceptor complexes (including that of serotonin picrate monohydrate) is the existence of discrete donor–acceptor pairs. Generally, aromatic complexes crystallize as infinite stacks of alternating donor and acceptor moieties, with each donor sandwiched between two acceptors and *vice versa*, thus forming continuous columns of overlapping π systems (Wallwork, 1961; Prout & Wright, 1968). In contrast, the donor–acceptor pairs in the tryptamine picrate and tryptophan picrate crystal structures are joined only by hydrogen bonds, with no π-π interactions occurring between neighboring pairs.

As shown in Fig. 5, the geometries of the stacked indole–picrate pairs are closely related in the tryptamine and tryptophan structures. The relative orientations of the indole and picrate moieties in the pairs differ mainly by a translation (about 1·5 Å) of the indole, relative to the picrate, along the line between atoms C(8) and C(5) of indole. In neither structure is there extensive overlap between the donor and acceptor moieties. The stacking patterns are such that a nitro group and the C(1)–O(1) group of the picrate ion interact with the indole ring. These interactions are similar to those found in the serotonin picrate complex (Thewalt & Bugg, 1972) and are consistent with the hypo-

thesis that donor–acceptor complexes of nitro-substituted aromatic compounds are stabilized by interactions of the polar nitro groups with the polarizable π-electron systems of adjacent molecules (Kross & Fassel, 1957; Briegleb & Delle, 1960; Briegleb, 1961).

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