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The Crystal Structures of the 1:1 Complexes of Skatole and Indole with *s*-Trinitrobenzene

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Crystals of complexes of both skatole and indole with *s*-trinitrobenzene are monoclinic, $P2_1/a$, with $Z = 4$. Unit-cell constants at −140 °C are, for the skatole complex:

$$a = 16{\cdot}76,\ b = 6{\cdot}61,\ c = 13{\cdot}45\ \text{Å};\ \beta = 95{\cdot}6°,$$

and for the indole complex:

$$a = 15{\cdot}87,\ b = 6{\cdot}58,\ c = 13{\cdot}47\ \text{Å};\ \beta = 94{\cdot}8°.$$

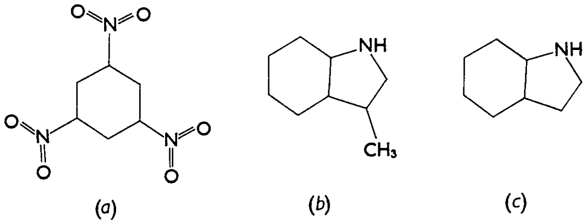
The crystal structure of the skatole complex was determined by inspection of certain sections of the three-dimensional Patterson synthesis, and refined with the aid of three-dimensional Fourier and differential syntheses. The crystal structure of the indole complex was solved by analogy with that of the skatole complex, but was found to be disordered, with the indole molecule capable of assuming two alternative orientations. It was refined with the aid of three-dimensional Fourier syntheses and bounded projections.

Both skatole and indole molecules are planar, to the accuracy of the analyses, but the *s*-trinitrobenzene molecule is not. The NO_2 groups are twisted out of the plane of the benzene nucleus by amounts which vary, and which are probably governed by molecular packing.

The constituent molecules overlap each other with an average interplanar spacing of 3·30 Å. The relative orientations in all cases suggest a decisive attraction between a non-substituted (2, 4, 6) carbon position of the *s*-trinitrobenzene molecule, and the nitrogen atom of the skatole or indole molecule.

Introduction

The crystal structure analyses of the 1:1 complexes of these molecules (Fig. 1) were undertaken in order to discover any salient features which might aid in the understanding of the intermolecular binding forces. A secondary object (realized only in part) was to establish with reasonable accuracy the stereochemistry of the constituent molecules.



(*a*) (*b*) (*c*)

Fig. 1. (*a*) *s*-Trinitrobenzene. (*b*) Skatole. (*c*) Indole.

Experimental

Weissenberg and precession photographs were used to establish that both materials crystallize in the monoclinic system, with space group $P2_1/a$ (C_{2h}^5). Photographs taken at room temperature suggested that there was intense thermal motion in the specimens; moreover, the indole complex was found to decompose in the X-ray beam. All essential measurements for the analyses were therefore obtained from photographs taken at about −140 °C. Crystal data for both materials at room temperature and at −140 °C are summarized in Table 1. The unit-cell constants were obtained from precession photographs.

Both complexes crystallize as needles, with the long axes parallel to **b**. Intensity data were therefore collected on *y*-axis Weissenberg photographs. Copper radiation was used throughout, and values of *k* ranged from zero to six. The equi-inclination setting was used for upper levels, and the correlation of the data was accomplished by means of a double-slit technique. The Nonius integrating Weissenberg goniometer was used, and errors due to distortion of spots on upper-level photographs were minimized by the use of some integration in the horizontal direction. A few reflexions on or near the y^* axis were not accessible, but some of these were obtained on precession photographs. Some of the very intense reflexions were also measured on the G. E. XRD5 spectrogoniometer and goniostat, together with enough moderately intense reflexions for correlation. Copper radiation and a scintillation counter were used, in the 'moving crystal-moving counter' technique described by Furnas (1953).

In spite of fairly rapid decomposition, a set of intensity data was obtained for the indole complex at room temperature, several specimens being destroyed in the process. Full data for both complexes

Table 1. *Crystal data*

Quantity	Estimated error	Skatole, *s*-trinitrobenzene		Indole, *s*-trinitrobenzene	
		20 °C	−140 °C	20 °C	−140 °C
a	0·04 Å	16·91 Å	16·76 Å	15·96 Å	15·87 Å
b	0·02	6·75	6·61	6·77	6·58
c	0·04	13·50	13·45	13·57	13·47
β	0·2°	95·8°	95·6°	94·5°	94·8°
V	12 Å^3	1533 Å^3	1482 Å^3	1462 Å^3	1402 Å^3
Formula weight	—	344·28		330·25	
D_m (measured density)	0·02 g.cm^{-3}	1·49 g.cm^{-3}	—	1·52 g.cm^{-3}	—
D_x (calculated density)	0·01 g.cm^{-3}	1·49 g.cm^{-3}	1·54 g.cm^{-3}	1·50 g.cm^{-3}	1·56 g.cm^{-3}
Z	—	4		4	
μ (Cu $K\alpha$)	—	—	12·0 cm^{-1}	—	12·4 cm^{-1}
Colour	—	Orange-red		Yellow-orange	

were also collected at about −140 °C. The cooling technique for precession photographs and for goniostat procedures was essentially that described by Burbank & Bensey (1952), in which the specimen is maintained in a stream of cold gaseous nitrogen which is itself surrounded by an envelope of warm, dry air. For Weissenberg photographs the warm-air envelope was not used, but the layer-line screen was heated, and partially sealed. In order to prevent dislodgement by the flow of nitrogen, the specimens were enclosed in thin-walled Lindemann-glass tubes. The working temperature was measured by substituting a thermocouple for the specimen.

Spot intensities were measured visually by comparison with a standard wedge. The greatest dimension, normal to **b**, of any specimen did not exceed 0·2 mm; absorption corrections were therefore deemed to be unnecessary, and were not applied.

For the skatole complex, 2939 reflexions were accessible, and of these, 1428 were observed. For the indole complex, 2760 reflexions were accessible; 1261 were observed at −140 °C, and 588 at room temperature.

Structure determination

The analysis of the skatole complex was attempted first. Consideration of the very intense 040 reflexion and of the distribution of Harker peaks along the line $\frac{1}{2}$, V, 0 of the Patterson synthesis suggested that both molecules must lie in or close to the planes $y=(2n+1)/8$. It was therefore expected that the most useful information in the Patterson synthesis would appear in the planes $V=0$, $\frac{1}{4}$, and $\frac{1}{2}$, and these planes were computed. From the one at $V=0$ the orientation of the benzene nucleus of the *s*-trinitrobenzene molecule was deduced, and it was inferred that the orientation of the benzene nucleus of the skatole molecule must be almost the same. Benzene–benzene vectors (some of which were, of course, Harker peaks) were identified in all three sections. Possible structures were reduced to a small number, only one of which satisfied packing requirements. This one proved to be correct, and was refined by three-dimensional Fourier and differential syntheses. In the final stages, finite summation corrections were estimated by comparison of F_o and F_c syntheses.

It was apparent from the syntheses that, while most of the carbon and nitrogen atoms in the structure were reasonably spherical, the oxygen atoms were significantly ellipsoidal, indicating considerable anisotropy of thermal motion. This anisotropy was believed likely to interfere with the estimation of finite summation corrections, and it was therefore simulated in structure-factor calculations by substituting for each oxygen atom two or more fractional atoms, suitably disposed (Kartha & Ahmed, 1960). In the final calculation, contributions of the hydrogen atoms were included also. Most of these atoms were merely assumed to be in reasonable positions, but those of the methyl group of the skatole molecule were located (not very accurately) from a Fourier synthesis. The scattering-factor curves used throughout were those of Freeman (1959). The coordinates and temperature factors used in the calculation are given in Table 2. The quantities ΔB_1 and ΔB_2 do not appear explicitly in the calculation, however; they merely indicate the magnitude of the anisotropy represented by the corresponding distributions of fractional atoms. For all practical purposes, ΔB_1 and ΔB_2 represent the components of anisotropic motion normal to, and in, the molecular plane. The ΔB_1 components, which are the larger in each case, are consistent with librations of the NO$_2$ groups about the adjacent C–N bonds. However, the oxygen positions have not been corrected for libration. The final atomic positions, derived from a further differential synthesis, are given in Table 3. The largest coordinate shift indicated at this stage was 0·009 Å, or less than two subsequently estimated standard deviations. Peak heights and curvatures are

Table 2. *Details of final structure-factor calculation for skatole — s-trinitrobenzene*

Atom	x	y	z	B	ΔB_1	ΔB_2
			s-Trinitrobenzene			
C(1)	0·1226	0·1050	0·1742	2·60	—	—
C(2)	0·1848	0·1095	0·2492	2·56	—	—
C(3)	0·1654	0·1161	0·3463	2·70	—	—
C(4)	0·0868	0·1167	0·3705	2·78	—	—
C(5)	0·0275	0·1121	0·2920	2·75	—	—
C(6)	0·0420	0·1083	0·1924	2·54	—	—
N(7)	0·1422	0·1015	0·0693	2·78	—	—
N(8)	0·2291	0·1255	0·4285	3·06	—	—
N(9)	−0·0578	0·1114	0·3155	2·95	—	—
O(10)	0·0919 0·0815 0·0822 0·0912	0·0819 0·1133 0·0809 0·1143	0·0048 0·0028 0·0024 0·0052	2·53	0·98	0·56
O(11)	0·2161 0·2077 0·2077 0·2161	0·1175 0·0763 0·1175 0·0763	0·0590 0·0528 0·0528 0·0590	2·61	1·58	0·53
O(12)	0·3032 0·2920 0·2959 0·2993	0·0787 0·1011 0·0709 0·1089	0·4056 0·4120 0·4105 0·4071	3·45	0·97	0·50
O(13)	0·2077 0·2185 0·2185 0·2077	0·2112 0·1372 0·2112 0·1372	0·5136 0·5088 0·5088 0·5136	2·60	5·10	0·89
O(14)	−0·0621 −0·0775 −0·0652 −0·0744	0·0962 0·1156 0·1261 0·0857	0·4102 0·3976 0·4080 0·3998	3·20	1·30	0·92
O(15)	−0·1096 −0·1096	0·1321 0·1149	0·2463 0·2463	3·53	0·28	—
H(2)	0·2462	0·1105	0·2302	3·20	—	—
H(4)	0·0728	0·1228	0·4471	3·20	—	—
H(6)	−0·0057	0·1062	0·1330	3·20	—	—
			Skatole			
C(16)	0·2050	0·5971	0·1652	2·78	—	—
C(17)	0·1967	0·6013	0·2669	2·66	—	—
C(18)	0·1176	0·6086	0·2922	2·50	—	—
C(19)	0·0521	0·6124	0·2199	2·82	—	—
C(20)	0·0600	0·6108	0·1194	3·08	—	—
C(21)	0·1372	0·6032	0·0933	2·96	—	—
C(22)	0·0061	0·6214	0·3723	2·70	—	—
C(23)	−0·0208	0·6188	0·2754	2·96	—	—
C(24)	−0·1057	0·6275	0·2294	3·33	—	—
N(25)	0·0903	0·6132	0·3853	2·86	—	—
H(16)	0·2654	0·5918	0·1433	3·20	—	—
H(17)	0·2481	0·5997	0·3222	3·20	—	—
H(20)	0·0090	0·6143	0·0646	3·20	—	—
H(21)	0·1456	0·6016	0·0147	3·20	—	—
H(22)	−0·0343	0·6270	0·4290	3·20	—	—
H(24*a*)	−0·1300	0·6400	0·3034	3·20	—	—
H(24*b*)	−0·1133	0·7667	0·1794	3·20	—	—
H(24*c*)	−0·1167	0·4933	0·1883	3·20	—	—
H(25)	0·1282	0·6114	0·4554	3·20	—	—

given in Table 4; reasonable agreement between observed and calculated quantities seems to justify the treatment of the anisotropy of thermal motion.

The Patterson synthesis for the indole complex was generally similar to that of the skatole complex, but its features were less well resolved, and seemed to indicate two possible orientations of the indole molecule. Neither orientation could be ruled out by packing considerations; both were therefore assumed for trial structures, but neither was consistent with the observed intensity data. Both orientations were then combined, as in a disorder structure. Prospects

Table 3. *Final atomic positions for skatole–s-trinitrobenzene*

$\pm(x, y, z;\ \frac{1}{2}+x, \frac{1}{2}-y, z)$

s-Trinitrobenzene

Atom	x	y	z
C(1)	0·1227	0·1046	0·1743
C(2)	0·1848	0·1091	0·2493
C(3)	0·1653	0·1164	0·3462
C(4)	0·0868	0·1162	0·3706
C(5)	0·0275	0·1118	0·2919
C(6)	0·0420	0·1073	0·1925
N(7)	0·1422	0·1007	0·0693
N(8)	0·2290	0·1267	0·4284
N(9)	−0·0578	0·1101	0·3154
O(10)	0·0867	0·0976	0·0039
O(11)	0·2119	0·0963	0·0560
O(12)	0·2976	0·0907	0·4088
O(13)	0·2131	0·1730	0·5110
O(14)	−0·0699	0·1048	0·4037
O(15)	−0·1096	0·1224	0·2464
Skatole			
C(16)	0·2049	0·5966	0·1652
C(17)	0·1966	0·6008	0·2667
C(18)	0·1176	0·6083	0·2921
C(19)	0·0520	0·6114	0·2199
C(20)	0·0600	0·6098	0·1194
C(21)	0·1371	0·6022	0·0932
C(22)	0·0062	0·6206	0·3724
C(23)	−0·0208	0·6174	0·2754
C(24)	−0·1057	0·6264	0·2293
N(25)	0·0902	0·6130	0·3852

for refinement seemed poor, however, and a more direct approach was attempted.

The near-equality of the unit-cell constants of the two complexes suggests a structural similarity. In order to confirm this similarity, some mixed crystals were grown. Approximately equal quantities of both materials were dissolved in methanol, which was then allowed to evaporate. The resulting crystals were found to be intermediate in colour, stench, and unit-cell constants to those of the constituent complexes. It was therefore assumed that the relative phases of most of the reflexions would be the same for both complexes, and a three-dimensional Fourier synthesis was computed, with the structure amplitudes of the indole complex and the relative phases of the skatole complex. The essential features of the synthesis are shown in Fig. 2. (The map shown is not, however, a section of the original synthesis; it is a bounded projection, computed at a late stage in the refinement. It shows the scattering matter contained between the planes $y=0$ and $y=\frac{1}{4}$, except that in the neighbourhood of one oxygen atom, indicated in Fig. 2(*a*) by a small arrow, the bounding planes were taken as $y=-\frac{1}{4}$ and $y=\frac{1}{4}$, in order to avoid truncating this atom.) It is obvious that the indole position is indeed disordered. The two orientations of the molecule do not seem to be equally probable, however, and relative weights of 0·63 and 0·37 were ultimately assigned to them.

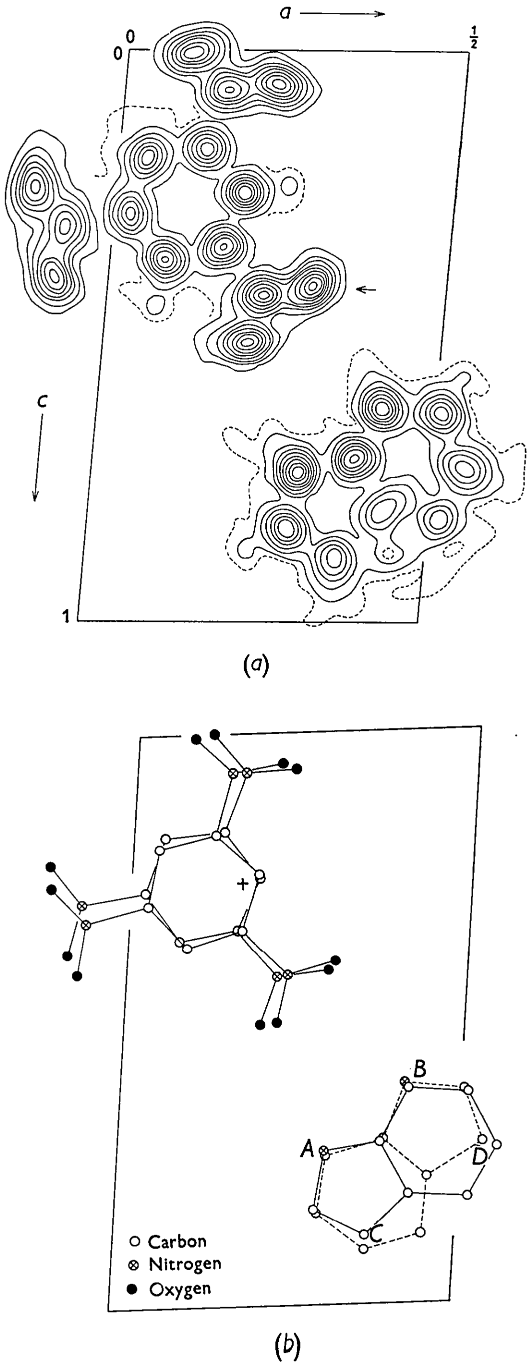


Fig. 2. (*a*) Bounded projection for indole — *s*-trinitrobenzene complex. Bounding planes are $y=0$ and $y=\frac{1}{4}$, except that in the neighbourhood of the atom indicated by the small arrow, the bounding planes are $y=-\frac{1}{4}$ and $y=\frac{1}{4}$. Solid contours are drawn at intervals of 1 e.Å^{-2}, the lowest being at 1 e.Å^{-2}. Broken contours at $\frac{1}{2}$ and $\frac{3}{4}$ e.Å^{-2} have been added where necessary to emphasize certain details. (*b*) Interpretation of (*a*). The libration of the *s*-trinitrobenzene molecule is indicated by the doubling of the atoms, and the assumed centre of libration is shown as a small cross. The indole molecule with the solid outline is assumed to have weight 0·63; that with the broken outline, 0·37.

Table 4. *Peak heights and curvatures for skatole — s-trinitrobenzene*

Values in italics are from F_c differential synthesis

Atom	(e.Å^{-3})	ϱ_{xx} (e.Å^{-5})	ϱ_{yy} (e.Å^{-5})	ϱ_{zz} (e.Å^{-5})	ϱ_{xy} (e.Å^{-5})	ϱ_{yz} (e.Å^{-5})	ϱ_{xz} (e.Å^{-5})
C(1)	9·4	−76·9	−83·3	−84·8	−0·3	−1·7	5·9
	9·2	*−77·5*	*−81·6*	*−80·7*	*0·3*	*−1·7*	*5·3*
C(2)	9·5	−82·5	−82·6	−90·7	4·3	1·5	6·3
	9·2	*−81·7*	*−79·3*	*−83·8*	*4·6*	*0·2*	*6·8*
C(3)	9·2	−73·1	−77·2	−88·8	0·3	−2·1	7·5
	9·2	*−77·0*	*−75·3*	*−82·9*	*1·6*	*−2·8*	*8·9*
C(4)	9·1	−73·7	−78·2	−89·7	−2·3	3·0	11·3
	9·1	*−78·9*	*−77·6*	*−83·3*	*−1·8*	*2·1*	*9·9*
C(5)	9·5	−82·5	−82·7	−88·5	1·5	−0·4	9·6
	9·3	*−82·1*	*−80·7*	*−84·2*	*1·5*	*−0·9*	*7·3*
C(6)	9·8	−92·2	−84·4	−95·2	0·7	2·2	11·3
	9·5	*−92·3*	*−82·0*	*−88·6*	*1·5*	*2·3*	*11·6*
N(7)	11·2	−99·7	−88·9	−106·0	0·8	4·8	4·9
	11·1	*−98·0*	*−86·2*	*−98·1*	*0·8*	*4·6*	*4·4*
N(8)	9·7	−75·6	−69·8	−93·9	−0·9	0·2	5·3
	10·1	*−81·4*	*−72·6*	*−87·2*	*0·9*	*−1·5*	*6·8*
N(9)	10·1	−86·5	−77·6	−92·1	−2·0	0·1	11·2
	10·3	*−85·7*	*−77·4*	*−89·6*	*−1·4*	*−0·2*	*6·6*
O(10)	12·1	−94·5	−83·5	−118·8	4·6	2·2	3·3
	12·1	*−96·3*	*−83·9*	*−110·0*	*4·8*	*1·6*	*2·7*
O(11)	11·6	−101·5	−73·2	−109·3	−1·3	0·1	17·4
	11·7	*−102·0*	*−75·5*	*−105·2*	*−1·4*	*−0·6*	*13·6*
O(12)	10·2	−80·4	−56·1	−89·9	−2·1	1·4	0·8
	10·5	*−82·9*	*−61·4*	*−85·9*	*0·3*	*0·8*	*3·7*
O(13)	9·0	−56·2	−41·4	−87·2	1·9	−4·8	−0·9
	9·2	*−63·2*	*−39·4*	*−81·1*	*2·0*	*−4·1*	*2·8*
O(14)	10·9	−86·6	−75·3	−101·5	4·0	4·3	24·6
	11·1	*−88·5*	*−76·9*	*−97·4*	*2·5*	*2·8*	*18·9*
O(15)	11·5	−96·9	−82·9	−95·5	0·4	−5·1	11·0
	11·5	*−95·1*	*−85·4*	*−94·3*	*0·8*	*−4·2*	*8·8*
C(16)	8·8	−79·7	−70·7	−77·4	−2·6	0·5	11·1
	8·8	*−80·4*	*−70·2*	*−76·1*	*−3·4*	*2·5*	*9·3*
C(17)	9·3	−85·1	−82·1	−77·8	0·5	3·7	6·3
	9·2	*−83·5*	*−81·5*	*−77·2*	*0·9*	*5·0*	*7·8*
C(18)	9·7	−81·7	−84·0	−96·3	−0·1	−2·2	6·0
	9·5	*−82·0*	*−80·4*	*−85·6*	*−0·6*	*−1·8*	*5·0*
C(19)	9·1	−70·4	−82·4	−83·0	−0·4	3·7	3·4
	9·1	*−72·4*	*−80·0*	*−79·9*	*0·1*	*3·1*	*4·6*
C(20)	8·2	−74·2	−69·0	−79·2	0·8	−2·7	3·2
	8·6	*−76·7*	*−68·3*	*−77·1*	*1·0*	*−2·8*	*5·4*
C(21)	8·4	−69·1	−71·3	−75·3	−1·7	2·0	5·7
	8·5	*−70·3*	*−71·3*	*−74·8*	*−0·9*	*1·3*	*3·8*
C(22)	8·6	−68·2	−67·2	−83·6	−1·0	2·0	9·2
	8·5	*−72·4*	*−65·2*	*−76·7*	*−0·3*	*2·5*	*6·8*
C(23)	7·9	−58·6	−60·8	−74·4	−0·3	−0·7	13·4
	8·1	*−63·6*	*−60·5*	*−70·5*	*−0·2*	*−0·4*	*12·0*
C(24)	7·5	−68·2	−56·9	−69·0	−0·4	−2·7	8·3
	8·0	*−70·4*	*−62·1*	*−68·0*	*−0·5*	*−2·3*	*7·5*
N(25)	10·6	−82·8	−88·8	−103·5	3·1	1·3	13·7
	10·7	*−87·3*	*−88·0*	*−95·6*	*2·8*	*2·1*	*13·8*

Another unusual feature of the map is the elongation of the peripheral atoms of the *s*-trinitrobenzene molecule, suggesting that this molecule is undergoing a strong libration in its own plane, about the point indicated. It seemed prudent to consider, however, whether this seeming libration might not in fact be a disorder phenomenon; the molecule might adopt one of two nearly identical orientations, depending

Table 5. *Final atomic positions, including details of final structure-factor calculation, for indole — s-trinitrobenzene*

Coordinates in braces are those of the fractional atoms used in calculations

s-Trinitrobenzene

Atom	*x*	*y*	*z*	*B*	ΔB_1	ΔB_2
C(1)	0·1266	0·1083	0·1725	2·10	—	0·92
	0·1200	0·1083	0·1750			
	0·1333	0·1083	0·1700			
C(2)	0·1891	0·1100	0·2500	2·10	—	0·12
	0·1883	0·1100	0·2475			
	0·1900	0·1100	0·2525			
C(3)	0·1638	0·1067	0·3450	2·10	—	0·31
	0·1600	0·1067	0·3442			
	0·1675	0·1067	0·3458			
C(4)	0·0808	0·1117	0·3662	2·10	—	1·29
	0·0750	0·1117	0·3600			
	0·0867	0·1117	0·3725			
C(5)	0·0242	0·1100	0·2858	2·10	—	2·80
	0·0217	0·1100	0·2733			
	0·0267	0·1100	0·2983			
C(6)	0·0434	0·1133	0·1887	2·10	—	2·00
	0·0467	0·1133	0·1783			
	0·0400	0·1133	0·1992			
N(7)	0·1521	0·1033	0·0683	2·30	—	2·10
	0·1417	0·1033	0·0683			
	0·1625	0·1033	0·0683			
N(8)	0·2308	0·1033	0·4275	2·30	—	1·29
	0·2233	0·1033	0·4283			
	0·2383	0·1033	0·4267			
N(9)	−0·0688	0·1142	0·3084	2·30	0·23	4·24
	−0·0650	0·1083	0·3250			
	−0·0725	0·1200	0·2917			
O(10)	0·0975	0·1058	0·0034	2·50	0·15	4·64
	0·0833	0·1083	0·0067			
	0·1117	0·1033	0·0000			
O(11)	0·2242	0·0967	0·0583	2·50	—	2·26
	0·2150	0·0967	0·0533			
	0·2333	0·0967	0·0633			
O(12)	0·3012	0·0633	0·4112	2·50	1·49	1·50
	0·3058	0·0433	0·4042			
	0·3058	0·0833	0·4042			
	0·2967	0·0433	0·4183			
	0·2967	0·0833	0·4183			
O(13)	0·2134	0·1492	0·5104	2·50	1·61	3·01
	0·2250	0·1283	0·5092			
	0·2250	0·1700	0·5092			
	0·2017	0·1283	0·5117			
	0·2017	0·1700	0·5117			
O(14)	−0·0812	0·1108	0·4058	2·50	0·20	6·42
	−0·0733	0·1150	0·4167			
	−0·0892	0·1067	0·3950			
O(15)	−0·1184	0·1300	0·2408	2·50	0·25	5·97
	−0·1167	0·1233	0·2600			
	−0·1200	0·1367	0·2217			
H(2)	0·2550	0·1100	0·2333	2·50	—	—
H(4)	0·0650	0·1151	0·4467	2·50	—	—
H(6)	−0·0100	0·1159	0·1250	2·50	—	—

on the particular orientation of an adjacent indole molecule. One might then expect these two orientations also to have unequal probabilities of occurrence. However, no reasonable packing consideration could be found to account for such interdependence of the orientations of the two molecules. Finally, three sets of structure factors for the *h*0*l* zone were computed, for structures in which the two appropriate orienta-

Table 5 (*cont.*)

Indole *a* (weight 0·63)

Atom	x	y	z	B	ΔB_1	ΔB_2
C(16)	−0·0117	0·6200	0·3633	2·10	—	—
C(17)	0·0767	0·6167	0·3725	2·10	—	—
C(18)	0·1150	0·6083	0·2833	2·10	—	—
C(19)	0·0692	0·6133	0·1900	2·10	—	—
C(20)	−0·0183	0·6150	0·1817	2·10	—	—
C(21)	−0·0583	0·6150	0·2683	2·10	—	—
C(22)	0·2100	0·6067	0·1667	2·10	—	—
C(23)	0·1317	0·6067	0·1183	2·10	—	—
N(24)	0·1983	0·6100	0·2667	2·10	—	—
H(16)	−0·0483	0·6229	0·4317	2·50	—	—
H(17)	0·1167	0·6150	0·4483	2·50	—	—
H(20)	−0·0550	0·6143	0·1083	2·50	—	—
H(21)	−0·1267	0·6176	0·2650	2·50	—	—
H(22)	0·2650	0·6047	0·1300	2·50	—	—
H(23)	0·1183	0·6057	0·0383	2·50	—	—
H(24)	0·2467	0·6096	0·3200	2·50	—	—
Indole *b* (weight 0·37)						
C(25)	0·2041	0·6067	0·1600	2·10	—	—
C(26)	0·1933	0·6100	0·2583	2·10	—	—
C(27)	0·1100	0·6100	0·2867	2·10	—	—
C(28)	0·0433	0·6133	0·2183	2·10	—	—
C(29)	0·0483	0·6133	0·1183	2·10	—	—
C(30)	0·1317	0·6083	0·0933	2·10	—	—
C(31)	−0·0067	0·6200	0·3667	2·10	—	—
C(32)	−0·0358	0·6167	0·2767	2·10	—	—
N(33)	0·0817	0·6133	0·3817	2·10	—	—
H(25)	0·2650	0·6047	0·1300	2·50	—	—
H(26)	0·2467	0·6096	0·3200	2·50	—	—
H(29)	−0·0067	0·6146	0·0600	2·50	—	—
H(30)	0·1383	0·6076	0·0067	2·50	—	—
H(31)	−0·0483	0·6229	0·4317	2·50	—	—
H(32)	−0·1000	0·6187	0·2433	2·50	—	—
H(33)	0·1167	0·6150	0·4483	2·50	—	—

tions of the *s*-trinitrobenzene molecule were assigned weights: 0·63 to 0·37; 0·37 to 0·63; 0·50 to 0·50. The agreement residual for the first set was 0·23, for the second, 0·23, and for the third, 0·19. It was therefore concluded that the phenomenon was a result of thermal libration, or that it could at least be treated as such.

The structure was refined somewhat with the aid of three-dimensional Fourier syntheses and bounded projections. The final atomic positions, and the details of the last structure-factor calculation are given in Table 5. The libration of the *s*-trinitrobenzene molecule has been represented by separating the atoms into pairs, as indicated in Fig. 2(*b*). In addition, some of the oxygen atoms appeared to vibrate anisotropically with respect to the molecular axes, in the manner observed for the skatole complex. For two of these atoms, therefore, it has been necessary to effect a further separation, as shown in the table. The quantities ΔB_1 and ΔB_2 indicate the magnitudes of the anisotropic components normal to, and in, the molecular plane, but do not appear explicitly in the calculations. The r.m.s. amplitude of libration represented by ΔB_2 is about 4°.

The indole configuration shown in Fig. 2(*b*), with the nitrogen atoms occupying positions *A* and *B*, was chosen because it seemed to give the best interpretation of the observed electron-density distribution. However, the molecules would fill the space just as well if they were so oriented that the nitrogen atoms lay in the regions *C* and *D*, and this configuration would display a similar electron-density distribution. Indeed, all four positions could be occupied by nitrogen atoms, corresponding to a fourfold disorder of the indole position. Quantitative confirmation of the assumed configuration was therefore sought by making careful electron counts, on both F_o and F_c syntheses, of the regions *A*, *B*, *C* and *D*. The results are summarized in Table 6. Actual counts fall short of the nominal values because it was necessary to limit the region of counting somewhat, in order

Table 6. *Comparison of electron counts from* F_o *and* F_c *syntheses*

Region	Nominal count	F_o count	F_c count	F_o/F_c count ratio
A	6·63 e	4·97 e	4·97 e	1·00
B	6·37	4·69	4·59	1·02
C	6·00	4·44	4·46	1·00
D	6·00	4·64	4·73	0·98

Table 7. *Agreement summary*

$\Delta F = |F_o| - |F_c|$

F_T = estimated minimum observable structure amplitude for reflexion considered

	Number of reflexions			
	Skatole — *s*-trinitrobenzene		Indole — *s*-trinitrobenzene	
Category	Observed	Unobserved	Observed	Unobserved
1. ($|\Delta F| \leq F_T$ or $|\Delta F| \leq 0{\cdot}2\,F_o$)	1347	1324	1047	1229
2. ($F_T < |\Delta F| \leq 2\,F_T$ or $0{\cdot}2\,F_o < |\Delta F| \leq 0{\cdot}4\,F_o$)	73	183	188	261
3. ($2\,F_T < |\Delta F| \leq 3\,F_T$ or $0{\cdot}4\,F_o < |\Delta F| \leq 0{\cdot}6\,F_o$)	6	4	23	9
4. ($3\,F_T < |\Delta F| \leq 4\,F_T$)	2	—	3	—

to exclude contributions from neighbouring atoms. Observed and calculated values agree well, and it is clear that the transfer of any part of the nitrogen atoms to alternative positions would worsen the agreement.

It had originally been observed for the indole complex that the intensity data collected at room temperature differed from those collected at −140 °C in a manner suggestive of more than a mere increase in isotropic thermal motion. In the hope of discovering any temperature-dependent structural changes, therefore, a three-dimensional Fourier synthesis was computed with the room-temperature structure amplitudes and the low-temperature phases. The only new feature revealed was a considerable increase in the apparent libration of the *s*-trinitrobenzene molecule. The libration was so great that few of the atoms of this molecule were resolved. The effect of temperature on the phenomenon seems conclusive evidence that it is a true thermal libration. Refinement of the room-temperature structure was considered unnecessary, and was not attempted.

Assessment of results

The proposed structures for both complexes are stereochemically plausible, and the Fourier syntheses are reasonable. For the skatole complex, the agreement between observed and calculated peak heights and curvatures is fairly good. The decisive proof of the correctness of both structures, however, is the reasonable agreement between observed and calculated structure amplitudes. A summary of the agreement is given in Table 7. For the skatole complex, $F_c(000) = 712$, and the agreement residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}13$ for observed reflexions only. For the indole complex, $F_c(000) = 680$ and $R = 0{\cdot}19$; the comparatively high value for this agreement residual results from incomplete refinement due to disorder, and from the difficulty of adequately representing the extraordinary thermal motion of the *s*-trinitrobenzene molecule. Lists of F_o and F_c for both structures are available from the author, on request.

For the skatole complex the mean standard deviations of coordinates, estimated by Cruickshank's method (Lipson & Cochran, 1953) are, for carbon, 0·005 Å, and for nitrogen and oxygen atoms, 0·004 Å. Individual values vary somewhat, particularly for the anisotropically vibrating oxygen atoms. It is unlikely that the analysis is as accurate as these figures would suggest, however. Because of the low yield of observed reflexions (less than half of those accessible), the finite summation correction is as great as 0·05 Å, or 10 standard deviations, in an extreme case. Errors in the estimated corrections may well be appreciable, particularly for the oxygen atoms. It does not seem profitable to consider the standard deviations for the incompletely refined indole complex.

Discussion

The skatole molecule may be considered planar, as no atom lies more than about twice its estimated standard deviation of coordinates from the molecular plane $0{\cdot}5706x + 6{\cdot}6052y - 0{\cdot}1582z = 4{\cdot}0420$. Moreover, application of the χ^2 test (*International Tables for X-ray Crystallography*, 1959) shows that deviations from planarity are not significant ($\chi^2 = 10{\cdot}4$, $n = 7$, $P > 5\%$). The *s*-trinitrobenzene molecule in the skatole complex is obviously not planar, as some of the oxygen atoms lie well out of the plane of the benzene nucleus. Neither are the carbon and nitrogen atoms of the molecule coplanar; three of these atoms lie more than three times their estimated standard deviation from the mean plane, and the χ^2 test indicates a highly significant departure from planarity ($\chi^2 = 43{\cdot}6$, $n = 6$, $P \ll 0{\cdot}1\%$). Only the benzene nucleus proves to be planar; no atom lies more than 1·4 times its estimated standard deviation from the mean plane $0{\cdot}0055x + 6{\cdot}6072y - 0{\cdot}3909z = 0{\cdot}6275$, and for this plane $\chi^2 = 5{\cdot}85$, $n = 3$, $P > 5\%$. Both this and the skatole plane are nearly normal to **b**, and the average interplanar distance, in the region of molecular overlap, is 3·30 Å.

The non-planarity of the *s*-trinitrobenzene molecule results from the behaviour of the NO_2 groups. One group is inclined to the plane of the benzene nucleus by 14°, another by 4°, and the third is virtually coplanar with the benzene nucleus. Non-planarity thus appears to be a property not of the molecule but of

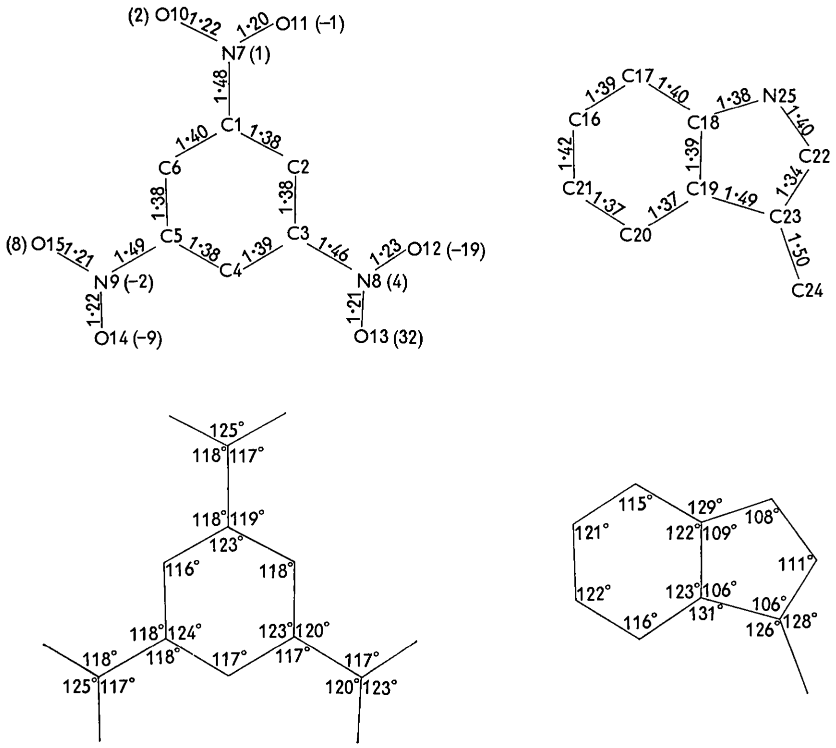


Fig. 3. Bond lengths and angles in the skatole — *s*-trinitrobenzene complex. The quantities in parentheses are the distances of the atoms of the NO_2 groups (in Å × 100) from the mean plane of the benzene nucleus.

the manner of packing. However, it would seem that the molecule offers little resistance to distorting forces.

The remarks concerning the planarity of the molecules apply in general to the indole complex also, although the analysis is somewhat less accurate. The equations of the indole molecules, and of the benzene nucleus of the *s*-trinitrobenzene molecule are

$$0{\cdot}230x + 6{\cdot}580y - 0{\cdot}122z = 4{\cdot}141$$

and

$$0{\cdot}139x + 6{\cdot}580y + 0{\cdot}030z = 0{\cdot}746$$

respectively. The average interplanar spacing in the region of overlap is 3·29 Å. This distance, and the corresponding one for the skatole complex, are considerably less than the van der Waals separation for aromatic molecules (3·40 Å), and indicate the operation of other intermolecular binding forces.

Shortest intermolecular distances in the skatole complex (other than those between overlapping molecules) are 2·97 Å for O–O, 3·20 Å for N–O, 3·25 Å for C–O, and 3·69 Å for C–C. Corresponding distances in the indole complex are 2·84 Å for O–O, 3·22 Å for N–O, 3·20 Å for C–O, and 3·73 Å for C–C. None of these distances is less than the expected van der Waals separation for the atoms involved.

Bond lengths and angles for the two molecules of the skatole complex are given in Fig. 3. The standard deviation of bond lengths, estimated by Cruickshank's method, is 0·007 Å. Values obtained by direct comparison of chemically equivalent bonds, however, are 0·008 Å for C–C, and 0·011 Å for N–O. The latter values probably afford a more realistic appraisal of the accuracy of the analysis. The state of refinement of the structure of the indole complex is such that a discussion of bond lengths would be inappropriate.

The overlapping of the constituent molecules in the three structures considered (one for the skatole, and two for the indole, complex) is shown in Fig. 4. It can be seen that in each case a non-substituted (2,4,6) carbon position of the *s*-trinitrobenzene molecule is almost completely overlapped by the nitrogen atom of the skatole or indole molecule. The remaining non-substituted carbon positions are overlapped by carbon atoms, but no substituted (1,3,5) carbon position is so overlapped. It seems significant that this should be so for all three structures. It might be argued that the configuration for the skatole complex is fortuitous, resulting from packing considerations, but this could hardly be so for the indole complex as well. It is concluded that the nitrogen atoms of the indole and skatole molecules, and the carbon atoms at the non-substituted positions of the *s*-trinitrobenzene molecule, play a decisive role in the intermolecular binding.

It is easy to see why the indole position is disordered. Molecules with different orientations fill the available space equally well, and are practically equivalent in

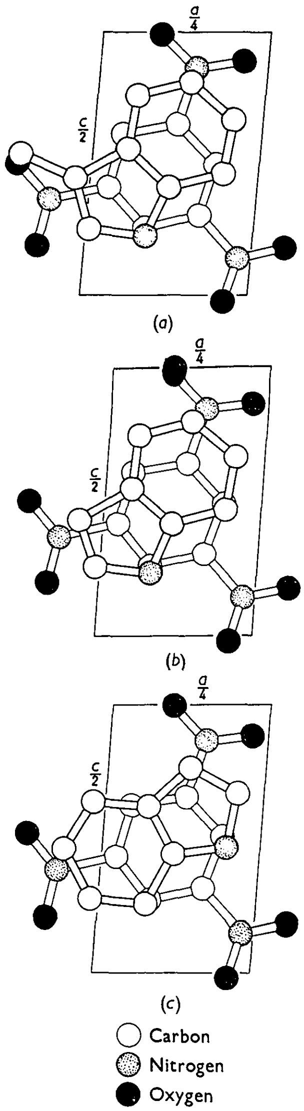


Fig. 4. Projections along **b** of the asymmetric units of the several structures, showing overlap. (*a*) Skatole — s-trinitrobenzene. (*b*) and (*c*) The two contributing structures of indole — *s*-trinitrobenzene.

the way in which they overlap the *s*-trinitrobenzene molecule. It is less easy to see why the two orientations do not have equal probabilities of occurrence, but a tentative answer is suggested by a study of the indole–indole intermolecular distances. The shortest distances occur between pairs of molecules lying on opposite sides of (average) centres of symmetry. Each molecule can have the orientation *a* or *b* (Table 5), and a pair of neighbouring molecules can have the configurations *a*–*a*, *a*–*b*, *b*–*a*, or *b*–*b*. The shortest intermolecular distances (considering only carbon and nitrogen atoms) for these configurations are: for *a*–*a*, 4·00 Å; for *a*–*b* (and *b*–*a*), 3·94 Å; for *b*–*b*, 3·73 Å. While the last distance is not unduly short, it is much shorter than the others; moreover it requires a hydrogen–hydrogen distance of 2·2 Å. It seems possible that, with alternatives available, the configuration *b*–*b* is forbidden. This restriction would lead to the relative probabilities of occurrence of *a* and *b* of 2 or 1, or 0·67 to 0·33, which is close to the observed ratio of 0·63 to 0·37.

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