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The Crystal Structure of Indole

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Indole crystallizes in the orthorhombic space group $Pna2_1$ with unit-cell parameters $a=7{\cdot}86$, $b=5{\cdot}66$, $c=14{\cdot}89$ Å with four molecules per unit cell. The crystal structure was found to be disordered with the indole molecule capable of assuming two alternative orientations. The gross structure (R 0·23) was confidently predicted from the crystalline properties, weighted reciprocal lattice plot and by analogy with the structures of carbazole and the 1:1 complex of indole with *s*-trinitrobenzene, although it could not be carried to its logical stage of refinement because of very high interactions between the overlapping atoms.

Introduction

The investigation of the crystal structure of indole, C_8H_7N (Fig. 1), forms part of a general programme of study undertaken in our laboratory on heterocyclic compounds which have important uses in the manufacture of drugs and dyes. It was undertaken to explain the physical properties of indole, such as cleavage, melting point *etc.*, and to discover any salient features which might aid in the understanding of the intermolecular binding forces in the structure.

Experimental

Successive recrystallization by slowing down the rate of evaporation of the solvent at room temperature (27 °C) from a solution of the compound in cyclohexane yielded colourless transparent platy crystals – platy on the {001} face with length parallel to the shortest crystallographic axis b. The crystal exhibited a pronounced cleavage parallel to (001) and also displayed cleaving tendencies parallel to (100). The single crystals chosen for the collection of X-ray diffraction data were sealed inside Lindemann glass capillary tubes as the compound was highly volatile. A preliminary photographic investigation showed that large numbers of potential reflexions were practically absent. Therefore no attempt was made to reduce the platy crystal to a minute cylindrical or spherical shape in order to minimize absorption error, in case of loss of intensity. A fairly large crystal $0{\cdot}7\times0{\cdot}5\times0{\cdot}28$ mm was used and Weissenberg multiple photographs were taken at room temperature (27 °C) of all the measurable layer lines for rotation about the a and b axes with Cu K radiation. The non-zero layer lines were recorded in the equi-inclination setting for Cu $K\alpha$ (1·5418 Å). The photographs revealed considerable intensity damping – most of the high-order reflexions were weak and a large number of possible reflexions were not observed experimentally. Intensities fell off very rapidly with increasing Bragg angle, suggesting unusual thermal activity. Also the diffraction pattern includes diffuse regions associated with some very intense reflexions which may also be interpreted as a result of thermal effects. Moreover indole was found to decompose on long exposures to the X-ray beam. The unit-cell constants were obtained from single-crystal oscillation and Weissenberg photographs about the a and b axes. The crystal density, measured by flotation, gave $Z=4$. Systematic extinctions $0kl$ with $k+l$ odd and $h0l$ with h odd were observed, indicating possible space groups $Pnam$ and $Pna2_1$.

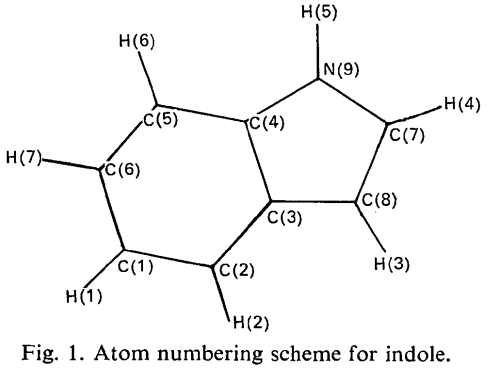


Fig. 1. Atom numbering scheme for indole.

Although the space group could not be fixed unambiguously from the extinctions, $Pnam$ could be ruled out from the following considerations: The centrosymmetric space group $Pnam$ with $Z=4$ is possible only when the molecules have the same point symmetries as the special positions in this space group or when the molecular planes coincide with the crystallographic mirror plane m. The possibility of a molecular centre of symmetry or a molecular mirror plane is ruled out by chemical considerations. Thus $Pnam$ with $Z=4$ would only be possible if the molecular plane coincided with the crystallographic mirror planes m parallel to (001) located at $z=\frac{1}{4}$ and $\frac{3}{4}$. Thus each plane would have to contain two completely flat molecules. The possibility of an almost perfect layer structure parallel to (001) with layers of molecules at $z=\frac{1}{4}$ and $\frac{3}{4}$ is not compatible with the packing requirements since

the two mirror planes are separated by 7·443 Å, *i.e.* one half the *c* translation. In addition, a layer structure parallel to (001) is not compatible with the higher refractive index along the *c* axis. Again the observed structure factors of the 00*l* reflexions do not agree with those calculated for a molecule at $Z=\frac{1}{4}$. The ambiguity in space group was finally resolved in favour of $Pna2_1$ by the statistical test proposed by Wilson (1949, 1950) and Howells, Phillips & Rogers (1950).

The crystal data are given in Table 1. The integrated intensities of 262 reflexions were visually estimated. They were corrected for the Lorentz and polarization effects and for upper-level spot-shape irregularities and then converted to structure factors. Scaling was by cross-layer comparison. The correction for absorption was neglected because of the relatively small absorption path, 0·5 mm, and the low absorption coefficient ($\mu=5{\cdot}487$ cm^{-1}) for Cu $K\alpha$.

Analysis of the structure

A trial model of indole was adopted based on related compounds. The model was assumed to be planar with standard C–C and C–N bond distances which conform with the steric considerations of the chemical structure. The orientation and position of this molecular frame in the unit cell were determined as follows. The much longer *c* axis and the relatively higher refractive index when the vibrations are parallel to **c** suggest that the molecular length is along **c**. Furthermore the principal

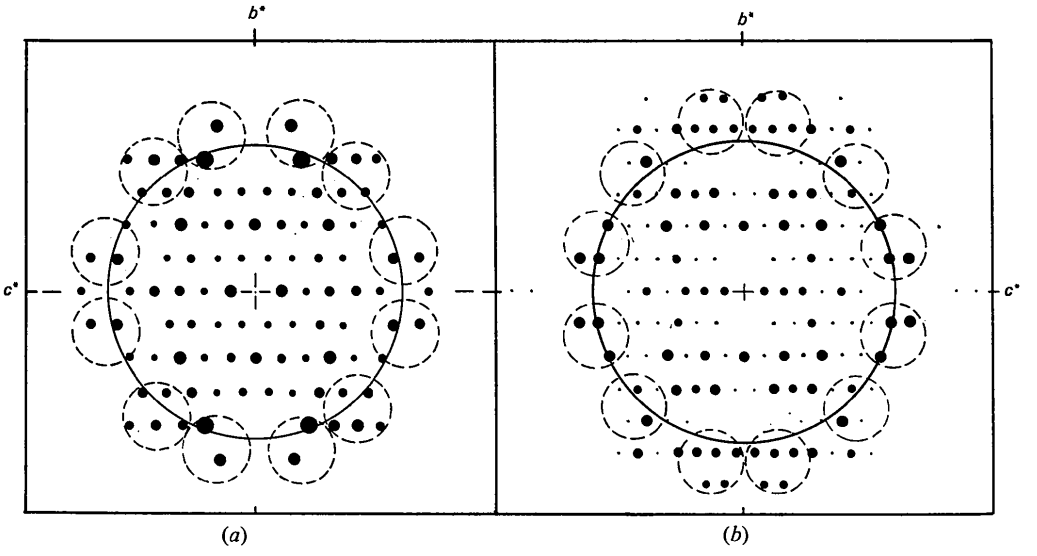


Fig. 2. 0*kl* weighted reciprocal lattices of indole (*a*) and carbazole (*b*) (weights proportional to the unitary structure factors).

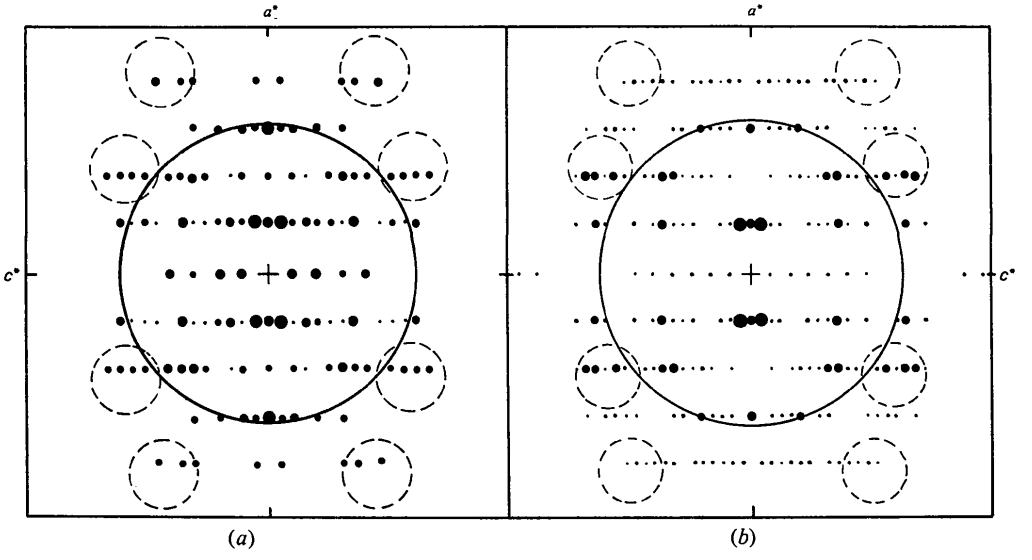


Fig. 3. *h*0*l* weighted reciprocal lattices of indole (*a*) and carbazole (*b*) (weights proportional to the unitary structure factors).

Table 1. *Crystal data*

Compound	Indole (C_8H_7N)	Carbazole ($C_{12}H_9N$)
Unit-cell		
a	$7{\cdot}86 \pm 0{\cdot}02$ Å	7·82 Å
b	$5{\cdot}66 \pm 0{\cdot}01$	5·73
c	$14{\cdot}89 \pm 0{\cdot}02$	19·17
V	662·4 Å^3	871·1 Å^3
M.W.	117·15	167·21
m.p.	52 °C	245°C
b.p.	253	355
d_{calc}	1·19 g cm^{-3}	1·27 g cm^{-3}
d_{obs}	1·186	1·24
Z	4	4
μ(Cu $K\alpha$)	5·487 cm^{-1}	5·8 cm^{-1}
Crystal characteristics	Both are soluble in common organic solvents and form colourless transparent platy crystals – platy on {001} with lengths parallel to the b axis, exhibiting cleavage parallel to (001) and (100)	
Refractive indices		
r.i.$_a$ (vibration parallel to a axis)	1·5	1·56
r.i.$_b$ (vibration parallel to b axis)	1·69	1·72
Absent spectra	$h0l$ $h=2n+1$	$h0l$ $h=2n+1$
	$0kl$ $k+l=2n+1$	$0kl$ $k+l=2n+1$
Space group	$Pna2_1$	$Pnam$*

* But the alternative space group $Pna2_1$ would give an identical molecular distribution in the unit-cell.

indices of refraction (1·5 when the vibrations are parallel to **a** and 1·69 along **b**) measured on the {001} face with white light suggested that the nearly flat indole molecule has a definite tendency to arrange itself more or less in planes which must lie closer to (100) than to (010). This conclusion conformed with the very intense 200 reflexion and the weaker 020 reflexion. The orientation of the molecule was more conclusively determined from the $0kl$ weighted reciprocal lattice plot [Fig. 2(*a*)]. This orientation, obtained

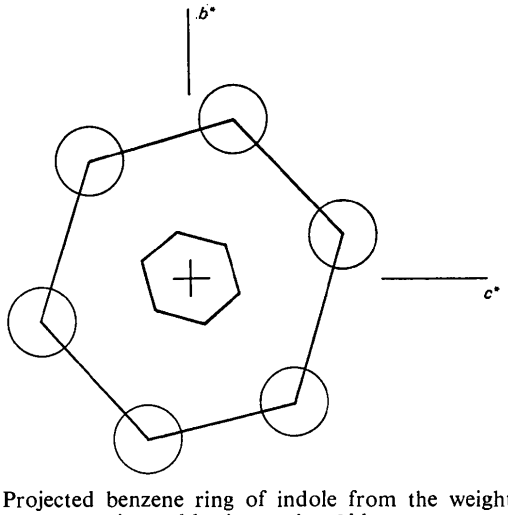


Fig. 4. Projected benzene ring of indole from the weighted reciprocal-lattice section $0kl$.

from the projected benzene ring traced from the transform (Fig. 4), was compatible with the optical data and cell structure.

A comparative study of indole and carbazole (Lahiri, 1968; Kurahashi, Fukuyo, Shimada, Furasaka & Nitta, 1968) indicated a strong structural similarity (Table 1). The similar space-group symmetry in both compounds, the near equality of their a and b axial lengths and the difference of 4·28 Å in the lengths of the c axes, sufficient to incorporate the additional benzenoid ring of the molecule of carbazole (*cf.* the axial lengthening of anthracene with respect to naphthalene), all point to this structural similarity. Furthermore the nearly identical crystalline characters of both compounds also confirm that they are similarly accommodated in the unit cells, and the pronounced cleavage along (001) and (100) for both suggests a close resemblance in the van der Waals distances and molecular packing. Finally, the values of the refractive indices and the strong resemblance in the distribution of points of high weights and the very similar benzene transforms developed in the weighted reciprocal lattice plot for the two compounds (Figs. 2 and 3) confirm that they should have nearly identical orientations. Thus it was concluded that the indole part of the carbazole molecule has virtually retained the orientation of the actual indole compound.

A geometrical trial model constructed from the $0kl$ weighted reciprocal lattice plot (whose orientation resembles very closely that of the indole group in carbazole) was translated in the unit cell to a position of closest fit with the indole part of the carbazole. The usual trial and error method of fitting the calculated structure factors to those observed was adopted for different positions of the molecule near this expected region until a relatively satisfactory fit was obtained. The correctness of the trial structure was tested by comparing the observed and calculated structure amplitudes of all the 262 observed reflexions using the structure-factor program written by F. R. Ahmed for the IBM 1620 computer. The value of the isotropic thermal parameter B was taken as 4 Å^2 for all the atoms. The R value was 0·33 for this ideal geometrical structure. The atomic coordinates of the trial structure are recorded in Table 2. No intermolecular distance calculated on the basis of these atomic positions is less than the sum of the van der Waals radii of the atoms involved. Moreover the pronounced cleavage parallel to (001) and the cleaving tendency parallel to (100) can be well explained by this molecular disposition [Fig. 5(*a*), (*b*)]. The residual 0·33 was significantly lower than the most probable value (0·59) of the residual suggested by Wilson for a completely wrong structure in the non-centrosymmetric case and hence refinement of the structure was attempted using the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) adapted for the CDC 3600 computer. However, subsequent least-squares refinement proved disappointing and the R value could not be reduced

below 0·28. Moreover the refinement distorted the structural model to highly improbable ones and the thermal parameters of the atoms after refinement were observed to be abnormally high, ranging from 5·64 to 10·2. This failure is attributed to the presence of disorder in the structure. It is believed that two alternative orientations of the molecule exist, though they may not be present with equal probability. No decisive information on the disordered state could be inferred from the Fourier and difference syntheses. A trial model of the disordered state of indole was established by analogy with the crystal structure of the 1:1 complex of indole with *s*-trinitrobenzene in which Hanson (1964) has also observed the presence of disorder involving indole. Such a disordered structure in which the alternative orientations exhibit maximum overlap ensured a less drastic deviation from the original ordered trial model and the crystal characteristics, weighted reciprocal plot and resemblance with carbazole can equally well be interpreted on the basis of the disordered structure.

Table 2. *The positional parameters of the non-hydrogen atoms of the indole molecule (ordered structure) derived by consideration of the intensities of the h0l and 0kl reflexions*

The isotropic temperature factor was taken as 4·0 Å² for all the atoms.

	x	*y*	*z*
C(1)	0·593	0·343	0·038
C(2)	0·570	0·288	0·129
C(3)	0·633	0·439	0·195
C(4)	0·719	0·646	0·171
C(5)	0·742	0·702	0·080
C(6)	0·679	0·550	0·014
C(7)	0·711	0·628	0·323
C(8)	0·628	0·428	0·289
N(9)	0·767	0·763	0·250

The disposition of the disordered trial structure in $Pna2_1$ is such that of the two possible overlapping molecular orientations one is more or less in the original position (which is assumed to be essentially correct) and the other in the same plane as the original orientation. Since the two orientations of the molecule may or may not be equally probable, structure-factor calculations were first made with equal weights assigned to both orientations and subsequently a number of sets of structure-factor calculations were made with different relative weights to obtain better agreement between the observed and calculated structure factors. Significantly better agreement was obtained when weights of $\frac{2}{3}$ and $\frac{1}{3}$ were assigned to the original and alternative orientations. The *R* value decreased abruptly from 0·33 for the ordered structure to 0·23 for the disordered one – an appreciable improvement considering that in both cases the ideal geometrical model was retained [the disordered structure viewed along the *a* and *b* axes is shown in Fig. 6(*a*) and (*b*)]. The final atomic coordinates are given in Table 3.

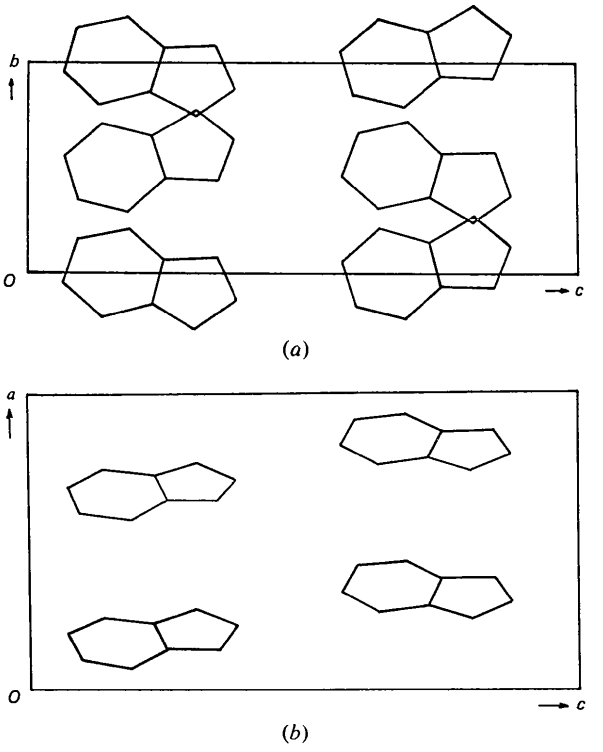


Fig. 5. Projections of the unit-cell of indole (ordered structure). (*a*) *a* axis. (*b*) *b* axis.

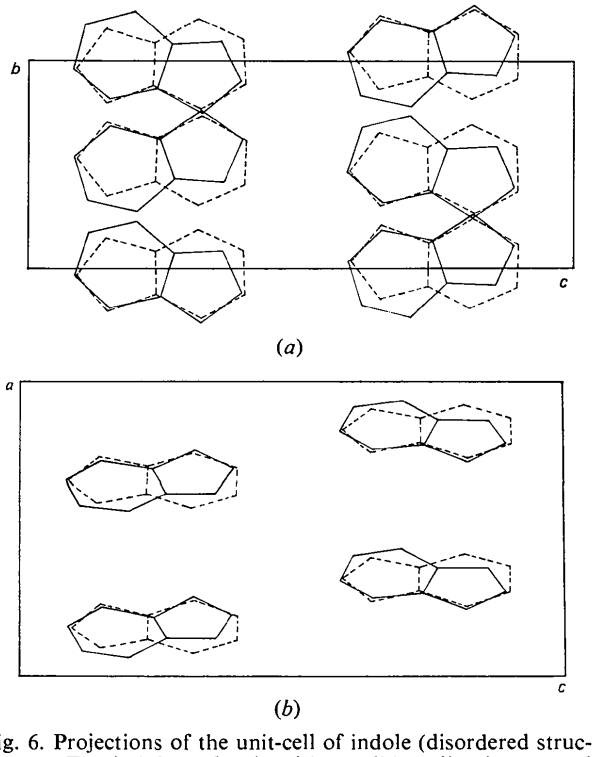


Fig. 6. Projections of the unit-cell of indole (disordered structure). The indole molecule with a solid outline is assumed to have weight 0·66, and that with a broken outline, 0·33. (*a*) *a* axis. (*b*) *b* axis.

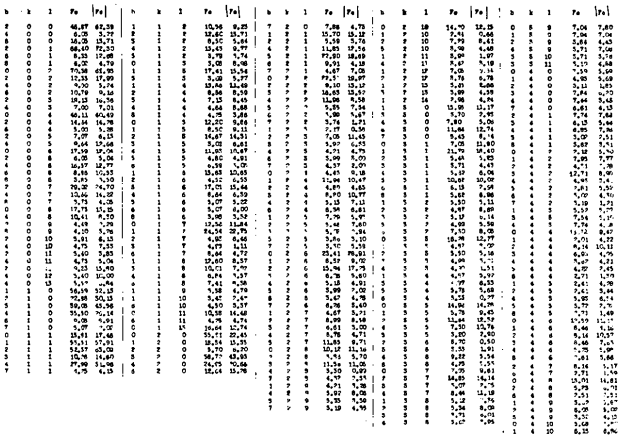
Table 3. *Positional parameters of the non-hydrogen atoms in the trial model of the disordered structure of indole*

$B = 4{\cdot}0$ Å^2 for all the atoms.

	x	y	z
Indole (*a*) (weight 0·66)			
C(1)	0·586	0·329	0·040
C(2)	0·565	0·274	0·130
C(3)	0·629	0·426	0·197
C(4)	0·715	0·634	0·172
C(5)	0·735	0·688	0·081
C(6)	0·671	0·535	0·015
C(7)	0·710	0·617	0·323
C(8)	0·626	0·416	0·291
N(9)	0·764	0·751	0·250
Indole (*b*) (weight 0·33)			
C(10)	0·622	0·405	0·326
C(11)	0·579	0·304	0·244
C(12)	0·623	0·414	0·164
C(13)	0·712	0·629	0·166
C(14)	0·756	0·731	0·249
C(15)	0·711	0·619	0·328
C(16)	0·668	0·529	0·020
C(17)	0·595	0·352	0·074
N(18)	0·740	0·700	0·077

Though it can be confidently asserted that the gross structure determination is correct, attempts to refine the structure by least-squares calculations proved to be futile on account of the interaction of overlapping atoms of the two probable orientations when simultaneously refined. Interaction could only be prevented by alternately refining the parameters of each of the possible orientations but since individually their contributions are high (the less predominant molecular orientation having a weight as high as as $\frac{1}{3}$) and their molecular dispositions and weights were determined only approximately, the error in the contribution of one would vitiate the course of refinement of the alternative orientation and therefore of the refinement in general. It is expected that better results would be obtained by taking low-temperature photographs.

Table 4. *Observed and calculated structure factors of the disordered structure of indole*



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