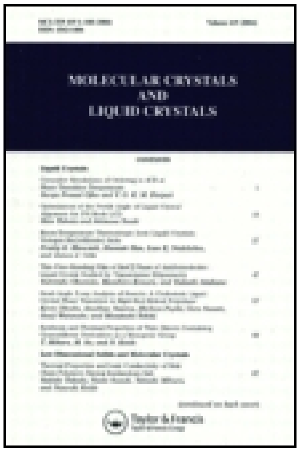

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The Crystal Structure of Carbazole: a Partical Determination

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The Crystal Structure of Carbazole: a Partial Determination

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Abstract—A partial determination of the crystal structure of carbazole $(C_6H_4)_2NH$ has been made. The symmetry is orthorhombic, space group Pnam, and the lattice parameters are $a = 7.779$ Å, $b = 5.722$ Å, $c = 19.15$ Å. The structure has four molecules in the unit cell arranged in two close packed layers parallel to the (001) plane. The molecular packing is very similar to that in anthracene; however the unit cell of anthracene contains only two molecules in a single close packed layer.

1. Introduction

Our interest in the crystal structure of carbazole arose from the problem of purifying anthracene which, when obtained from natural sources, invariably contains carbazole as a major impurity, and one which is not effectively removed by zone-refining. Since the theoretical efficiency of zone-refining depends, inter alia, on the liquid–solid phase equilibrium, and published phase diagrams of the anthracene–carbazole system were contradictory, we made a detailed study of this system by calorimetric and X-ray diffraction methods. Five distinct solid phases occur, the crystal structures of which are closely related to those of the pure components.[1] Since only the crystal structure of anthracene had previously been published[2,3] we undertook a partial determination of that of carbazole $(C_6H_4)_2NH$.

The space group and approximate lattice parameters were determined from the crystal morphology and single crystal oscillation photographs, powder photographs being used to refine the lattice parameters. A hypothetical crystal structure was derived by considering the possible molecular packings within the unit cell which satisfied the symmetry requirements. Calculated intensities of the X-ray powder lines for this structure were in fairly good agreement with the observed intensities. A complete structure determination was outside the scope of this investigation.

2. Experimental

Single crystals of carbazole about 2 mm × 1 mm × 0.25 mm were grown by sublimation under vacuum in a sealed pyrex tube at about 120 °C. These crystals were orthorhombic, class mmm. The habit was tabular with a pair of prominent faces bounded by small faces of six different forms which could be provisionally indexed in the manner shown in Fig. 1. This set of indices was chosen to facilitate comparison with anthracene which also crystallizes with prominent (001) faces.

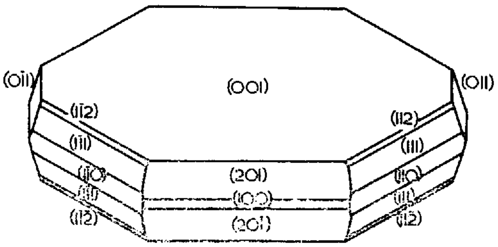

Figure 1. Projection of an idealized carbazole crystal grown from the vapour.

Single crystal photographs were taken with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) for oscillations about the three principal axes. Systematic absences for $h0l$ reflexions if h was odd, and for $0kl$ reflexions if $k + l$ was odd, together with the external morphology, place carbazole in the space group Pnam ($= D_{2h}^{16}$).

Approximate lattice parameters derived from the oscillation photographs were refined using powder photographs taken with filtered Cu Kα radiation in a 19 cm camera. The standard deviation in d calculated from 17 strong lines was about 1 in 10,000. Since sharp lines were obtained only for Bragg angles from about 10° to 25° extrapolation procedures were not possible, so that specimen eccentricity may have limited the accuracy to about 1 in 1000. The final lattice parameters were $a = 7.779$ Å, $b = 5.722$ Å, $c = 19.15$ Å at 22 °C. Visual estimates of the line intensities were made, averaging the results of different exposures to include both strong and weak lines.

A measurement of the density of carbazole was made by water displacement. Apart from out-gassing at reduced pressure to remove air bubbles no special precautions were taken. The value of $\rho = 1.308 \text{ gm cm}^{-3}$ corresponds to 4.03 molecules in the unit cell.

3. The Structure

The carbazole molecule is known, from spectroscopic evidence, to be planar.[4] The exact bond lengths and interbond angles are not known, but our assumed structure, (Fig. 2(a)), which is based on the data of Allen and Sutton[5] for pyrrole and benzene, agrees well with a theoretical calculation by Dewar and Gleicher[6] and is unlikely to be seriously in error.

Since the unit cell of carbazole contains only four molecules while the space group Pnam has, in general, eight equivalent positions it follows that the centres of the molecules, and also the four nitrogen atoms must lie in special positions. The only physically reasonable arrangement which satisfies this is one in which pairs of molecules related by the a-glide plane have their centres at $(x, y, \frac{1}{4})$ and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4})$ and at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4})$ and $(x, y, \frac{3}{4})$ relative to an origin at a centre of symmetry (i.e. on the mirror planes of the unit cell) and the long axes of the molecules are parallel to the c crystallographic axis. This structure, a projection of which is shown in Fig. 3, can be described as two parallel

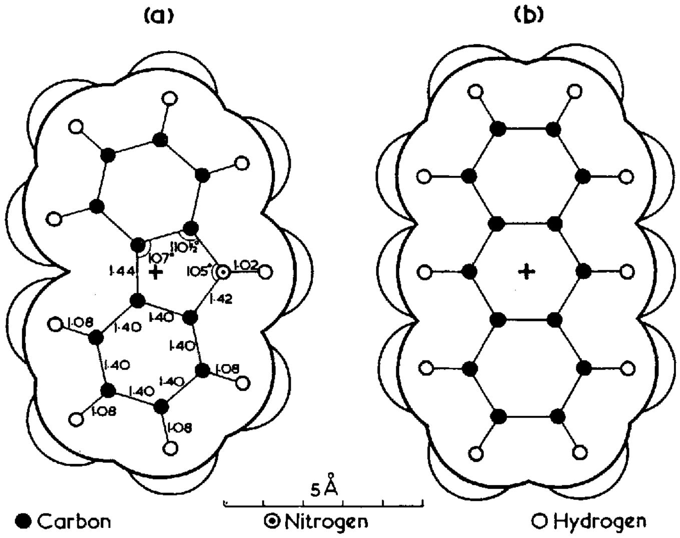

Figure 2. Molecular configurations of (*a*) carbazole and (*b*) anthracene. The centres of the molecules (+) are the centres of gravity. Outlines are the intermolecular radii after Kitaigorodskii.

layers of molecules, each layer being closely packed in a herringbone array.

For the assumed molecular structure of Fig. 2(a) the crystal structure is completely determined by the x and y coordinates of the centre of a molecule and the angle (ϕ) between the plane of the molecule and the (100) plane. The intensities of the X-ray powder lines were calculated, taking account of multiplicity, Lorentz and polarization factors, for different values of these parameters and fitted qualitatively to the observed intensities, with particular emphasis being placed on relative intensities within groups of closely spaced strong lines. The best fit was obtained with $x = 0.146$, $y = -0.026$ and $\phi = 28°$ which gives the physically satisfactory packing shown in Fig. 3. Table I compares the observed and calculated intensities, and the residual of these intensities, $R = \sum | I_0 - I_c | / \sum I_0$, is 0.20.

By assuming that the average molecule in a crystal has the same structure as a single molecule we have implicitly assumed complete

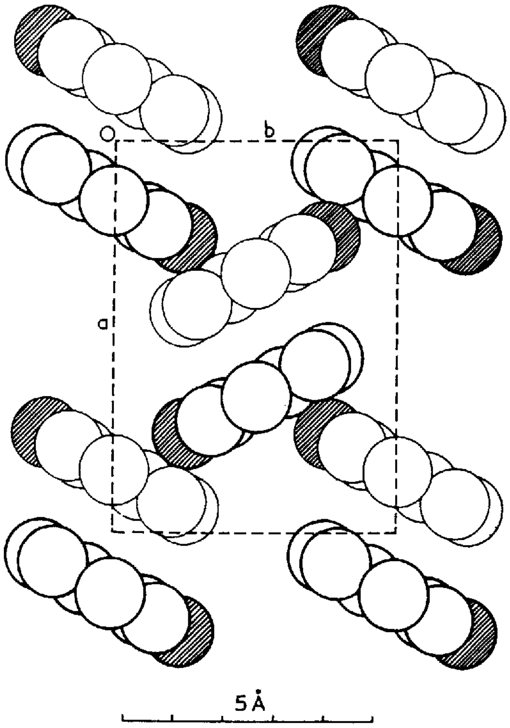

Figure 3. Projection of the crystal structure of carbazole on the (001) plane. Molecules with centres at $\frac{1}{4}c$ and $\frac{3}{4}c$ are distinguished by heavy and light lines respectively. Origin at a centre of symmetry.

orientational order in the crystal. This may not be the case but a complete electron density calculation would be needed to clarify the point; the evidence presented here is insufficient to justify or refute the hypothesis of complete order.

4. Discussion

The molecular structure assumed for carbazole is geometrically very similar to that of anthracene (Fig. 2(b)). The anthracene–carbazole system exhibits extensive solid solutions, indicating that the crystal structures of the pure components are not dissimilar.

The crystal structure of anthracene is well established (2, 3) and can be described as layers of molecules closely packed in a herringbone array parallel to the (001) plane with the long axes of the the molecules approximately parallel to the c-axis. The symmetry is monoclinic ($P2_1/a$), the lattice parameters are $a = 8.561$ Å, $b = 6.036$ Å, $c = 11.163$ Å, $\beta = 124° 42'$ and there are two molecules in the unit cell.

TABLE 1 Comparison of Observed and Calculated Intensities of the Powder Lines

Reflexion	Bragg angle (degrees)	Calculated intensity (Arbitrary units)	Observed intensity (Arbitrary units)
011	8.08	0.956	2
004	9.27	8.74	11
110	9.63	36.9	34
111	9.90	102.7	100
013	10.42	7.76	4
112	10.70	0.509	< 1
200	11.43	6.69	11
201	11.67	76.2	69
113	11.90	5.01	4
202	12.35	2.70	4
203	13.42	6.10	6
210	13.87	9.62	7
211	14.06	64.5	87
212	14.64	0.42	1
115	15.17	1.22	2
020	15.63	2.18	4
022	16.33	1.64	1
121	16.85	0.242	2
116	17.09	2.74	2
206	18.21	3.82	10
024	18.29		
008	18.79	0.968	< 1
310	19.05	11.28	10
222	20.12	1.06	1
225	22.98	2.12	1
320	23.66	2.96	10
209	24.39	1.98	2
410	24.75	6.45	11
411	24.87		

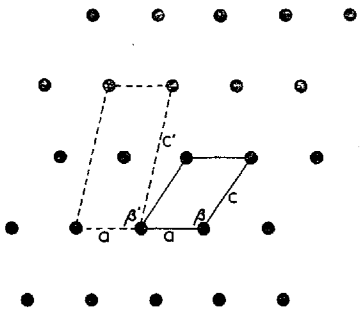

Figure 4. Projection of the crystal lattice of anthracene on the (010) plane. The primitive unit cell (solid lines) and a non-primitive cell based on two layers of the lattice (broken lines) are outlined.

The relationship between the two crystal structures may be seen by noting that it is possible to choose a non-primitive unit cell for anthracene with $a = 8.561$ Å, $b = 6.036$ Å, $c' = 18.818$ Å, $\beta' = 102° 44'$ (Fig. 4) which contains four molecules in two closely packed layers. This cell has a volume about 10% greater than that of carbazole and otherwise differs from it chiefly by small shears parallel to the (001) plane.

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