

Fig. 2. Packing of the molecule in the unit cell (viewed down *a*).

$C(1^b)$ is longer than that of $C(4)-C(4^b)$ by 0.10 \AA . $C(1)$ and $C(1^b)$ are out of the mean plane formed by $C(4)$, $C(5)$, $C(6)$ and $C(4^b)$ by 8° in opposite directions. This bending is quite large, although it is smaller than that of the overcrowded compound 1,3,6,8-tetra-*tert*-butyl-naphthalene, 22° (Handal, White, Franck, Yuh & Allinger, 1977). These distortions in the naphthalene

ring are rationalized by the existence of the bulky triazole rings in *peri* position.

Fig. 2 (a projection along *a*) shows the packing of the molecules in the unit cell. The packing of the molecules in the crystal reveals normal intermolecular contacts equal to the sum of the van der Waals radii.

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Acta Cryst. (1986). C42, 480-482

The Structure of Carbazole at 168 K

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(Received 1 July 1985; accepted 19 November 1985)

Abstract. $C_{12}H_9N$, $M_r = 167.21$, orthorhombic, *Pnma*, $a = 7.628(1)$, $b = 18.935(2)$, $c = 5.657(1) \text{ \AA}$, $V = 817.0(2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.36 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.744 \text{ cm}^{-1}$, $F(000) = 352$, $T = 168 \text{ K}$, $R = 0.10$, $wR = 0.045$ for 1047 unique reflections ($R = 0.050$ for reflections having $I > 3\sigma$). The carbazole molecule has mirror symmetry, and is slightly non-planar, the dihedral angle between the two planes in the molecule being 2.5° . The space group is identical to that found for the room-temperature structure. The

H atom on nitrogen does not show the deviation from the mean molecular plane reported for the room-temperature structure.

Introduction. There has been a continuing interest in our laboratory in studying by low-field EPR methods the host-composition dependence of the zero-field splittings of dilute triplet guest molecules in a binary host crystal of mutually soluble components (Lundstedt, 1984). Three molecules that satisfy the conditions formulated by Kitaigorodsky (1973) for the formation of a continuous series of solid solutions and that are otherwise acceptable as potential host systems

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for our studies are carbazole, dibenzofuran and fluorene. Experimental results confirm that the solid-liquid phase diagrams for dibenzofuran/carbazole and dibenzofuran/fluorene (Kravchenko & Pastukhova, 1957) as well as for carbazole/fluorene (Kravchenko & Eremenko, 1952) show formation of neither eutectics nor peritectics. However, the presence of disorder in the crystal structure of dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984) severely compromises the usefulness of this compound as one member of a two-component host. Therefore, the crystal structure of carbazole at 168 K has been investigated in anticipation of the use of the fluorene/carbazole host system in low-temperature EPR studies. The crystal structure of fluorene at 159 K has been recently determined (Gerkin, Lundstedt & Reppart, 1984).

The room-temperature structure of carbazole has been studied by Lahiri (1968, 1969), Kurahashi, Fukuyo, Shimada, Furusaki & Nitta (1969) and by Robinson & Scott (1969).

Experimental. Commercial carbazole (Eastman, No. 600) purified by vertical zone refining, 70 passes; clear, colorless crystal from ethanol (crystals grown from acetone were twinned), parallelepiped, $0.09 \times 0.22 \times 0.29$ mm. Syntex $P\bar{1}$ diffractometer, with LT-1 low-temperature attachment. Setting angles for 20 reflections ($21 < 2\theta < 23^\circ$) used to determine unit-cell constants and crystal orientation. Temperature measured at cold-stream exit nozzle during data collection and at crystal site after data collection with Fluke 2100A digital thermometer (type K thermocouple). Temperature measured at site of crystal 168 K, estimated uncertainty ± 2 K. Data collected for 1528 reflections with $+h, +k, +l$, ω - 2θ scan, $4 < 2\theta < 60^\circ$, $h_{\max} = 10$, $k_{\max} = 26$, $l_{\max} = 7$, scan range $2\theta \text{ Mo } K\alpha_1 - 1.0^\circ$ to $2\theta \text{ Mo } K\alpha_2 + 1.0^\circ$, background/scan time ratio 0.5. Uncertainties assigned using $\sigma_I^2 = R^2(C+4B) + (0.02I)^2$, C is total counts, R is scan rate, B is total background counts, I is intensity. Only multiply measured reflections were six standards (031, 060, 082, 101, 131, 201) for which $R_{\text{int}} = 0.01$, max. intensity variation 6%. 1047 unique reflections after systematic absences removed. Absorption correction using program of Alcock (1970). Transmission factors 0.97–0.99. Systematic absences indicated space group $Pna2_1$ or $Pnma$. 1042 reflections with $I > 0$ used in least-squares refinement using *SHELX76* (Sheldrick, 1976), function minimized $\sum w(|F_o| - |F_c|)^2$, $w = \sigma_F^{-2}$. Initial nitrogen and carbon positions taken from Lahiri (1968). Attempts at refinement in $Pna2_1$ unsuccessful ($R > 0.5$), so space group assigned as $Pnma$, identical to that at room temperature. Non-hydrogen atoms refined anisotropically, hydrogen atoms, positions determined from $F_o - F_c$ map, refined isotropically. Final refinement cycle, $R = 0.10$, $wR = 0.045$, $S = 1.4$, max. shift/e.s.d. ratio = 0.06. Structure factor calculation for

all reflections with $I > 3\sigma_I$ gave $R = 0.050$. Max. peak on the final $F_o - F_c$ map, $0.43 \text{ e}\text{\AA}^{-3}$, located between N and C(1) atoms. Min. peak, $-0.41 \text{ e}\text{\AA}^{-3}$, located at center of five-membered ring. Scattering factors for C and N from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).*

Discussion. The final positional parameters and equivalent isotropic temperature factors are given in Table 1. Interatomic distances and angles are shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42651 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$), calculated using the equation $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{150}
N	0.7580 (3)	0.2500	0.7678 (5)	29 (1)
C(1)	0.7099 (3)	0.3095 (1)	0.6405 (4)	26 (1)
C(2)	0.7369 (3)	0.3803 (1)	0.6962 (4)	30 (1)
C(3)	0.6765 (3)	0.4291 (1)	0.5363 (4)	33 (1)
C(4)	0.5911 (3)	0.4092 (1)	0.3287 (4)	30 (1)
C(5)	0.5652 (3)	0.3390 (1)	0.2745 (4)	26 (1)
C(6)	0.6258 (3)	0.2883 (1)	0.4320 (4)	22 (1)
H(1)	0.819 (4)	0.250	0.920 (6)	49 (11)
H(2)	0.797 (3)	0.394 (1)	0.846 (3)	19 (6)
H(3)	0.690 (3)	0.478 (1)	0.571 (4)	29 (7)
H(4)	0.553 (3)	0.448 (1)	0.215 (4)	43 (7)
H(5)	0.511 (3)	0.322 (1)	0.123 (4)	27 (7)

Standard deviations are given within parentheses.

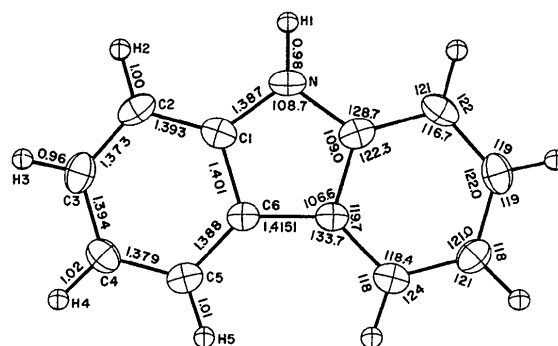


Fig. 1. Bond lengths and angles for carbazole. Uncertainties for bonds and angles not involving hydrogen atoms are less than 0.003 Å and 0.2°, respectively; for those involving hydrogen atoms, the uncertainties are less than 0.03 Å and 1°.

The carbazole molecule at 168 K has mirror symmetry, with the mirror plane bisecting the C(6)—C(6')* bond and containing the N—H(1) bond. As was found analogously in our earlier study of fluorene, only the asymmetric unit is planar, giving the molecule a 'V' shape. The dihedral angle between the two least-squares planes in the molecule is 2.5°, an increase from the value of 1.6° found for this angle at room temperature (Kurahashi *et al.*, 1969). The C(6)—C(6') bond length of 1.451 Å is larger than that found for the corresponding bonds in dibenzofuran, 1.438 Å, and in fluorene, 1.422 Å, indicating the increasing aromatic character of this bond for the latter two compounds.

Kurahashi *et al.* found that the hydrogen atom attached to the nitrogen atom deviated from the mean molecular plane by 0.2 (1) Å in the room-temperature structure. They speculated that, although this deviation may not be significant, it could be an indication that the hydrogen atom oscillates back and forth across the molecular plane under the influence of a double-well potential. We find that at 168 K the same hydrogen atom has a deviation from the mean molecular plane of only 0.03 (3) Å, which is comparable to the deviations found for the rest of the atoms in the molecule. While this does not disprove that the hydrogen atom oscillates between two positions at room temperature, we feel that the large deviation found at room temperature is perhaps only an artifact of their data.

The thermal ellipsoids derived from the present structure analysis were subjected to both a 'rigid-bond' analysis (Hirshfeld, 1976) and a 'rigid-body' analysis

(Rosenfield, Trueblood & Dunitz, 1978). The average difference between the mean-square vibrational amplitudes was 0.004 (2) Å for bonded atoms and 0.003 (2) Å for all atoms, indicating that the experimental thermal parameters approximate the true vibrational ellipsoids, and that the carbazole molecule as a whole behaves as a rigid body.

A stereoview of the unit cell is shown in Fig. 2. The closest contact distance between molecules occurs between H(3) and H(4) atoms and is 2.55 Å. The H(1) atom also has a short contact distance of 2.59 Å with two C(6) atoms. The angle that the mean molecular plane makes with the *a* axis decreases slightly from 28.8° at room temperature to 28.2° at 168 K.

The major difference between the crystal structures of carbazole, dibenzofuran and fluorene is the presence of disorder in the dibenzofuran structure. A disorder in carbazole similar to that found in dibenzofuran would lead to very short contact distances (<2 Å) between C(1) atoms in the disordered molecule and four atoms in neighboring ordered molecules, which is probably the reason such a disorder is not seen.

WJR gratefully acknowledges support from a Procter and Gamble Company fellowship. The authors wish to thank Dr Judith C. Gallucci and Alan P. Lundstedt for their assistance during this investigation. Computational facilities were provided by the Ohio State University IRCC.

* Primed atoms are related to the corresponding unprimed atoms by the mirror plane.

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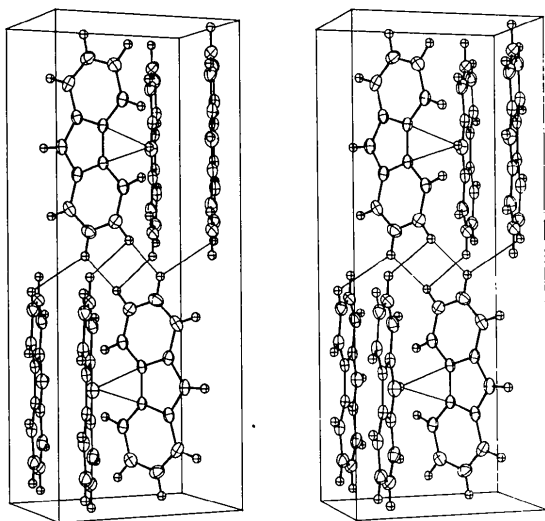


Fig. 2. Stereoview of the carbazole unit cell drawn using ORTEPII (Johnson, 1971). The closest intermolecular contact distances are shown.