BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2174—2179 (1969)

The Crystal and Molecular Structure of Carbazole

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(Received December 27, 1968)

The crystal structure of carbazole has been refined with three-dimensional X-ray data. Single crystals obtained from the melt are orthorhombic with four molecules in a unit cell of the dimensions $a=7.77_2$, $b=19.18_2$ and $c=5.72_5$ Å; space group is *Pnma*. Positional and thermal parameters were obtained by the least-squares method. The final discrepancy index R is 10.9% excluding zero intensity data. The e.s.d.'s in bond lengths not involving hydrogen atoms are 0.006—0.010 Å, and the corresponding errors in bond angles are about 0.5°. The molecule is planar within the deviation of 0.03 Å. A crystallographic mirror plane normal to the b-axis passes through the nitrogen atom and is perpendicular to the molecular plane. Comparison of the observed and theoretical bond lengths is made with discussion thereof. Some physical properties related to the crystal structure are also discussed by comparing its structure with that of fluorene. With the help of thermodynamical data, it has been argued that the hydrogen bond of N-H···N between molecules is not formed not only in the crystalline state but also in the liquid state.

A preliminary note on the crystal structure analysis of carbazole[1] was reported in 1966 by the authors. However, as the analysis was not sufficiently precise, a three-dimensional refinement has been undertaken. The main purpose of this investigation is to elucidate the molecular structure in detail, so as to obtain some information about the behavior of the hydrogen atom attached to the nitrogen. It will also be of significance to compare the experimental result with the theoretical one calculated by the MO method. It is further hoped that discussions may be given on some physical properties such as sublimation, cleavage, density and melting point in relation to the crystal structure.

Experimental

The crystals in colorless plates obtained from the melt belong to the orthorhombic system. The cell dimensions were determined from $hk0$ and $0kl$ Weissenberg photographs calibrated with silicon powder lines. The crystal data are summarized in Table 1. From systematic absences ($0kl$ with $k+l$ odd and $hk0$ with h odd) and intensity statistics, the space group of this crystal is determined to be *Pnma*. There are four molecules in the unit cell, and the molecule should have a mirror in it. The integrated intensities of 698 reflections were estimated visually from multiple-film equi-inclination Weissenberg photographs of the layers $hk0$ to $hk5$ and $0kl$ to $4kl$. Lorentz and polarization corrections were applied together with a spot-shape correction for upper layers, and all the intensities were placed on a common scale. Since the cross section of the crystals used was small enough(0.2×0.5 mm^2 for the a- and 0.3×0.5 mm^2 for the c-axis), no correction was made for the absorption effect.

TABLE 1. CRYSTAL DATA

Compound: Carbazole
$C_{12}H_9N$
MW = 167.2
mp = 245°C
Unit cell: (Cu$K\alpha$ radiation)
Orthorhombic
$a = 7.772\pm0.005$ Å
$b = 19.182\pm0.010$ Å
$c = 5.725\pm0.005$ Å
$V = 853.5$ Å^3
$D_m = 1.29$ g/cm^3
$D_x = 1.301$ g/cm^3
$Z = 4$
$\mu = 6.06$ cm^{-1}
Space group; *Pnma*

Determination and Refinement of the Structure

The approximate coordinates of nitrogen and carbon atoms had already been found in the preliminary investigation. A least-squares refinement was started with the final parameters in that study. At first, hydrogen atoms were omitted from the calculations. After

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[1] M. Kurahashi, M. Fukuyo, A. Shimada, A. Furusaki and I. Nitta, This Bulletin, **39**, 2564 (1966).

four cycles of the refinement, R dropped from the initial value 22.0 to 17.6%. The positional parameters were further refined by the block-diagonal matrix least-squares method with the anisotropic temperature factors of the form $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)\}$, and R fell to 13.6% after four cycles. At this stage of refinement a three dimensional difference synthesis shown in Fig. 1 was calculated. In the map, the five of the eight highest peaks between 0.3 and 0.5 e.Å^{-3} corresponded to the hydrogen atoms. Including these, further four cycles of the refinement reduced R to 10.9%. Individual isotoropic temperature factors of 5.0 Å^2 had been assigned to these hydrogen atoms, and after the refinement those of the four hydrogen atoms attached to the benzene ring turned into 4.0—6.0 Å^2 and that of the hydrogen atom attached to the nitrogen increased to 7.3 Å^2.

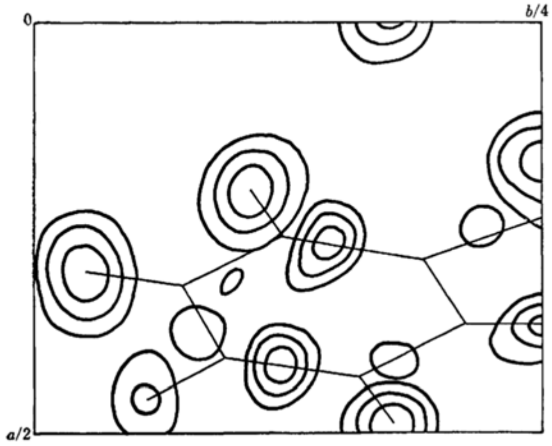

Fig. 1. Composite difference synthesis showing the hydrogen atoms. Contours at 0.1 e.Å^{-3} beginning at 0.2 e.A^{-3}.

Results and Discussion

Table 2 gives the final positional parameters of all the atoms with their e.s.d.'s evaluated in the least-squares calculations. The final temperature factors are listed in Table 3. The direction cosines and distances from the origin of the best planes through various sets of atoms in the molecule are presented in Table 4, together with the angles between these planes. The displacements of atoms from the various planes of Table 4 are given in Table 5. The electron density and difference syntheses in the molecular plane are shown in Fig. 2. The final calculated structure factors are compared in Table 6* with the observed values.

A crystallographic mirror plane normal to the b-axis passes through the nitrogen atom and is perpendicular to the molecular plane. Putting aside the positions of the hydrogen atoms, benzene rings and pyrrole ring in the carbazole molecule are respectively planar within the experimental error, less than 0.01 Å. Carbazole molecule itself is approximately planar within the deviations of 0.03 Å, though, strictly speaking, the two benzene rings in the molecule make an angle of 1.63°. The slightly bent structure might be due to the intermolecular interactions in the crystal field.

TABLE 2. POSITIONAL PARAMETERS AND THEIR e.s.d.'s

	x	σx	y	σy	z	σz
N	0.2373	(8)	0.2500	(*)	0.2346	(11)
C_1	0.2866	(6)	0.1911	(3)	0.3604	(8)
C_2	0.2596	(7)	0.1207	(3)	0.3047	(9)
C_3	0.3223	(8)	0.0734	(3)	0.4632	(11)
C_4	0.4075	(7)	0.0918	(3)	0.6682	(10)
C_5	0.4327	(6)	0.1618	(3)	0.7230	(9)
C_6	0.3698	(6)	0.2115	(3)	0.5679	(8)
H_N	0.1978	(128)	0.2500	(*)	0.0651	(175)
H_1	0.2160	(72)	0.1084	(27)	0.1505	(97)
H_2	0.3067	(75)	0.0293	(28)	0.4089	(104)
H_3	0.4297	(69)	0.0632	(29)	0.8130	(109)
H_4	0.4799	(72)	0.1743	(27)	0.9002	(94)

* Parameter constrained by symmetry requirements.

TABLE 3. THERMAL VIBRATION PARAMETERS FOR THE EXPRESSION $T=\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)\}$ AND THEIR e.s.d.'s

	B_{11}	σ	B_{22}	σ	B_{33}	σ	B_{12}	σ	B_{23}	σ	B_{31}	σ
N	0.0179	(12)	0.0047	(2)	0.0231	(18)	0.0000	(*)	0.0000	(*)	−0.0116	(27)
C_1	0.0134	(7)	0.0039	(2)	0.0232	(15)	0.0004	(7)	0.0010	(9)	0.0029	(19)
C_2	0.0191	(10)	0.0045	(2)	0.0290	(18)	−0.0029	(8)	−0.0058	(10)	0.0012	(24)
C_3	0.0217	(12)	0.0034	(2)	0.0455	(23)	−0.0026	(8)	−0.0022	(12)	0.0113	(29)
C_4	0.0208	(11)	0.0038	(2)	0.0373	(20)	0.0013	(8)	0.0047	(11)	0.0037	(27)
C_5	0.0149	(9)	0.0045	(2)	0.0242	(15)	−0.0009	(7)	0.0010	(10)	0.0004	(20)
C_6	0.0105	(7)	0.0038	(2)	0.0229	(14)	−0.0009	(6)	−0.0012	(8)	−0.0008	(17)

* Parameter constrained by symmetry requirements.

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* The complete data of the F_o-F_c table are kept as Document No. 6903 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥250 for photoprints. Payment may be made by check or money order payable to: Chemical Society of Japan.

TABLE 4. EQUATIONS OF THE PLANES AND ANGLES BETWEEN DIFFERENT PLANES

1 Carbazole ring plane
2 Benzene ring plane (1)
3 Benzene ring plane (2)
4 Pyrrole ring plane

Equations of planes

1 $-0.8765X \qquad -0.4815Z-1.0841=0$
2 $-0.8746X+0.0142Y-0.4847Z-1.1229=0$
3 $-0.8746X-0.0142Y-0.4847Z-0.9867=0$
4 $-0.8795X \qquad -0.4760Z-1.0757=0$

Angles between different planes

	2	3	4
1	0.84°	0.84°	0.37°
2		1.63°	1.00°
3			1.00°

TABLE 5. DEVIATIONS OF ATOMS FROM VARIOUS PLANES

	1	2	3	4
N	−0.026*	−0.005	−0.005	−0.003*
C_1	−0.015*	−0.008*	0.024	0.003*
C_2	0.015*	0.002*	0.073	0.035
C_3	0.025*	0.003*	0.099	0.039
C_4	0.010*	−0.002*	0.084	0.015
C_5	−0.011*	−0.003*	0.045	−0.008
C_6	−0.010*	0.008*	0.029	−0.001*
C_6'	−0.010*	0.029	0.008*	−0.001*
C_5'	−0.011*	0.045	−0.003*	−0 008
C_4'	0.010*	0.084	−0.002*	0.015
C_3'	0.025*	0.099	0.003*	0.039
C_2'	0.015*	0.073	0.002*	0.035
C_1'	−0.015*	0.024	−0.008*	0.003*
H_N	−0.22*	−0.21	−0.21	−0.20
H_1	−0.11	−0.13	−0.06	−0.09
H_2	−0.02	−0.05	0.07	−0.00
H_3	0.26	0.24	0.34	0.26
H_4	0.16	0.17	0.21	0.15
H_4'	0.16	0.21	0.17	0.15
H_3'	0.26	0.34	0.24	0.26
H_2'	−0.02	0.07	−0.05	−0.00
H_1'	−0.11	−0.06	−0.13	−0.09

Least-squares plane is determined by the atoms with *.

Figure 3 shows the projection of the molecule upon its mirror plane. There the nitrogen atom and the hydrogen attached to it are given by the electron density contours, of which those for the hydrogen are drawn on the basis of a difference synthesis. As seen in the figure, electron density contours of the hydrogen atom are elongated in the direction normal to the molecular plane, where the peak is located. In view of the contour lines and anisotropic thermal parameters for the nitrogen clearly showing its oscillation in the direction normal to the molecular plane, the elongation mentioned above will imply that the hydrogen oscillates apparently more intensely than the nitrogen in the same direction.

It may be noted that such elongation can be interpreted as one of the two following possibilities. The first is to assume that the valence state of the nitrogen atom is mainly the sp² state and the equilibrium position of the hydrogen atom lies in the molecular plane, its out-of-plane oscillation being quite violent. The second is that the state is more or less sp³ and the equilibrium position of

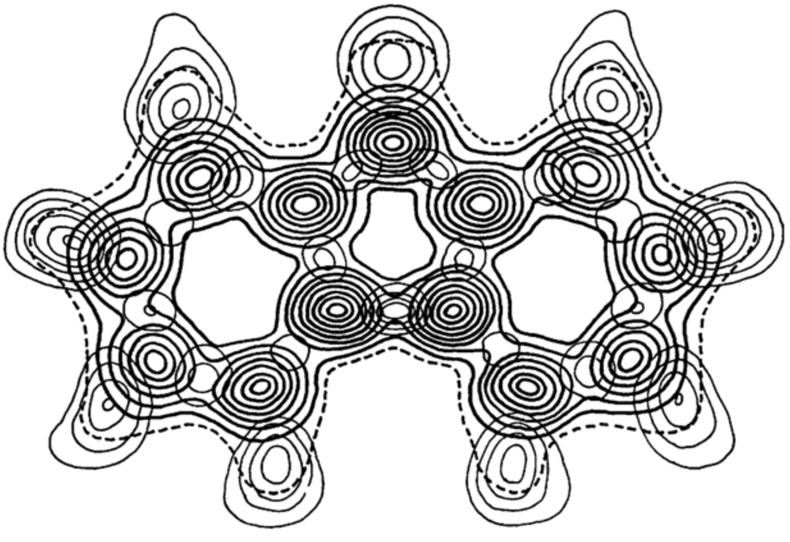

Fig. 2. Electron density and difference syntheses on the molecular plane. The contour lines, starting from 1.0 e.Å^{-3} are at intervals of 1.0 e.Å^{-3}. The broken line is 0.5 e.Å^{-3}. The fine lines, starting from 0.1 e.Å^{-3} are at intervals of 0.1 e.Å^{-3}.

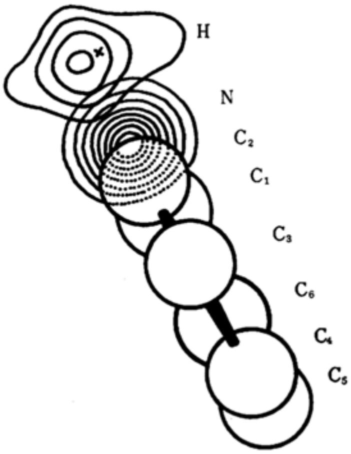

Fig. 3. Electron density for the nitrogen and difference synthesis for the attached hydrogen atom. The contour lines for the nitrogen, starting from 1.0 e.Å^{-3} are at intervals of 1.0 e.Å^{-3}, and for the hydrogen starting from 0.15 e.Å^{-3} at intervals of 0.1 e.Å^{-3}. The cross shows the position of the hydrogen atom determined by the least-squares method. The circles show the carbon atoms.

the hydrogen atom is on either side of the molecular plane and moves back and forth between these two positions somewhat like the umbrella inversion of ammonia molecule.

The cross in Fig. 3 indicates the position of the hydrogen determined by the least-squares method. It is deviated by 0.22 Å from the mean molecular plane (Table 5, 1), the e.s.d.'s of its positional parameters being of the order of 0.10 Å (Table 2). The temperature factor obtained by the least-squares method for this hydrogen atom is 7.33 Å^2, which is the largest of the hydrogen atoms in the molecule. Although it is not certain that the N–H bond is bent as the cross shows, there remains a possibility that this bending might be really due to the crystal field or some other reason. Anyhow, evidence that the hybridization state of the nitrogen is purely sp^3, can be excluded, for in such a case the deviation of the hydrogen from the molecular plane should be as large as 0.6 Å.

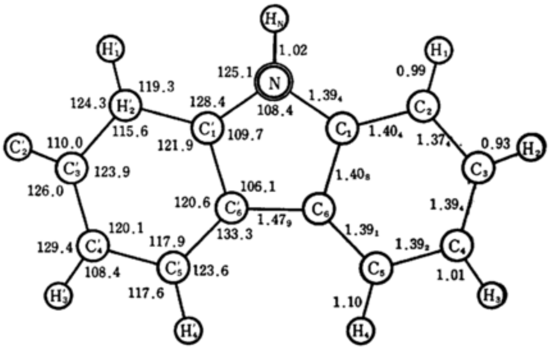

Fig. 4. Bond lengths and angles of carbazole.

Table 7. Comparison with theoretical investigation

	Bond order	Bond length		
		Theoretical*1	Observed*2	(e.s.d.)
N-C_1	0.420	1.375	1.394 (1.399)	0.006
C_1-C_2	0.572	1.414	1.404 (1.405)	0.008
C_2-C_3	0.722	1.387	1.374 (1.377)	0.008
C_3-C_4	0.607	1.408	1.394 (1.398)	0.008
C_4-C_5	0.719	1.388	1.392 (1.395)	0.008
C_5-C_6	0.584	1.412	1.391 (1.394)	0.007
C_6-C_1	0.593	1.410	1.408 (1.414)	0.006
C_6-C_6'	0.404	1.444	1.479 (1.484)	0.010

*1 Theoretical bond lengths were calculated by

$$r(\text{C-C}) = 1.517 - 0.18p$$
$$r(\text{C-N}) = 1.451 - 0.18p$$

r: bond length p: bond order

*2 Bond lengths corrected for thermal motion are in parentheses. The thermal parameters of the molecule were reasonably well explained on the basis of rigid-body motion.

Bond lengths and angles are shown in Fig. 4. The e.s.d.'s of the bond distances are about 0.007 Å, except for 0.010 Å for the central C–C bond related to the mirror symmetry. The average C–C bond distance in the six-membered ring is 1.39_4 Å which is very close to the value found in crystalline benzene. Several theoretical treatments2-4) have been made on carbazole. The observed bond lengths are compared with theoretical values calculated by SCFMO,4) which is shown in Table 7. Observed C_5–C_6 is shorter by 0.02_1 Å, and C_6–C_6' and N–C_1 are longer by 0.03_5 and 0.01_9 Å respectively than theoretical values. It is suggestive that these are related to either C_6 or N, of which the hybridization state may be somewhat deviated from the standard sp^2 as seen in the bond angle distribution.

The bond angles in the five-membered ring ranges from 106.1° to 109.7° and that in the phenyl ring ranges from 115.6° to 123.8°. The e.s.d.'s are about 0.5°. Using the observed bond lengths and sp^2 orbital skeletons for nitrogen and carbon atoms, the observed distribution of the bond angles may be qualitatively explained by the molecular model based on the assumption that all the bonds

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2) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

3) R. W. Schmid, *Helv. Chim. Acta*, **45**, 1982 (1962).

4) K. Nishimoto, private communication.

in the molecule share the strain force uniformly.

The crystal structure is shown in Fig. 5. The nearest approach between two nitrogen atoms of the neighboring molecules is 3.89 Å, and this shows that the hydrogen bond such as N-H···N is not formed in the crystal. This supports Aihara's conclusion from the measurement of the vapor pressure.⁵⁾ The position of the hydrogen atom attached to the nitrogen also shows this fact. In addition, it is sterically impossible to form hydrogen bond if the nitrogen is trigonally hybridized. Molecular packing seems to be uniform in *a*- and *c*-directions, and close contacts of 3.42—3.68 Å between molecules are found for any pair of neighboring molecules. On the other side there is considerably large space around $y=0$ and $y=1/2$, and the nearest approach between carbon atoms C_3 and C_4' of the neighboring molecules in the *b*-direction is as large as 3.87 Å. This is the reason why the crystal cannot elongate along the *b*-axis and shows excellent cleavage parallel to the (010) plane.

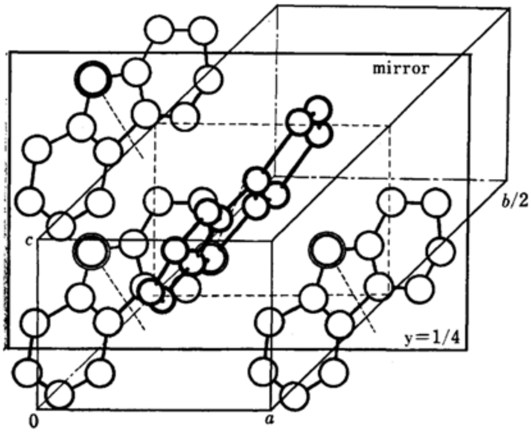

Fig. 5. Crystal structure of carbazole.

Carbazole crystal belongs to the same space group as fluorene⁶⁾ where N-H in carbazole is

TABLE 8. COMPARISON BETWEEN CARBAZOLE AND FLUORENE

Carbazole $C_{12}H_9N$	Fluorene $C_{13}H_{10}$
MW 167.2	MW 166.2
Crystal data	
$a = 7.77_2$ Å	$a = 8.49$ Å
$b = 19.18_2$ Å	$b = 18.97$ Å
$c = 5.72_5$ Å	$c = 5.72$ Å
$V = 853.5$ Å^3	$V = 921.4$ Å^3
$D_m = 1.29_0$ g/cm^3	$D_m = 1.20_6$ g/cm^3
$D_x = 1.30_1$ g/cm^3 $z = 4$	$D_x = 1.19_7$ g/cm^3 $z = 4$

Atomic parameters

	x	*y*	*z*		*x*	*y*	*z*
N	0.237	1/4	0.235	C_1	0.204	1/4	0.250
C_1	0.287	0.191	0.360	C_2	0.267	0.189	0.373
C_2	0.260	0.121	0.305	C_3	0.250	0.114	0.335
C_3	0.322	0.073	0.463	C_4	0.322	0.068	0.487
C_4	0.407	0.092	0.668	C_5	0.408	0.091	0.676
C_5	0.433	0.162	0.723	C_6	0.427	0.163	0.724
C_6	0.370	0.211	0.568	C_7	0.358	0.211	0.566

Thermodynamical data

Carbazole	Fluorene
mp = 245°C	mp = 115°C
bp = 355°C	bp = 293°C
ΔH_m*1 = 7.04 kcal/mol	ΔH_m*2 = 4.80 kcal/mol
ΔH_v*3 = 15.5 kcal/mol	ΔH_v*4 = 13.5 kcal/mol
$\Delta H_m + \Delta H_v$ = 22.5 kcal/mol	$\Delta H_m + \Delta H_v$ = 18.3 kcal/mol
ΔH_s*5 = 21.9 kcal/mol	
ΔH_s*6 = 20.2 kcal/mol	

*1 *International Critical Table*, **5**, 134, (1929).
*2 "Coal Tar Data Book," Vols. 1 and 2, D2, The Coal Tar Research Association, England.
*3 *International Critical Table*, **3**, 226 (1928).
*4 *Ibid.*, **3**, 227 (1928).
*5 F. S. Mortimer and D. V. Murphy, *Ind. Eng. Chem.*, **15**, 1140 (1923).
*6 A. Aihara, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 492 (1955).

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5) A. Aihara, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 492 (1955).

6) D. M. Burns and J. Iball, *Proc. Roy. Soc.*, **227A**, 200 (1955).

replaced by $\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{H}}$, and it resembles considerably that of fluorene in both cell dimensions and atomic parameters. Comparison of the crystal data, atomic parameters and thermodynamical data is shown in Table 8. Figure 6 shows the (010) projections of the crystal structure of both compounds. The plane of the fluorene molecules makes an angle of 55.2° to the *a*-axis, while the corresponding angle is 61.0° in carbazole. Intermolecular distances shown in Fig. 6 are generally shorter in carbazole than in fluorene.

As is easily expected from the crystal structure, subliming tendency of these compounds is related to the fact that strong intermolecular forces such as hydrogen bonds do not exist. However, effective partial volume around N-H will be smaller than that around $\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{H}}$, and carbazole, containing a nitrogen in a molecule, shows a dipole moment of 2.09 D.[7] Therefore the molecular arrangement would be influenced to some extent by such effects. Figure 6 shows such influence. In the crystal of carbazole, the dimension of *a*-axis is thus smaller, and this, in addition to the greater molecular weight by 1 than that of fluorene, leads to greater density.

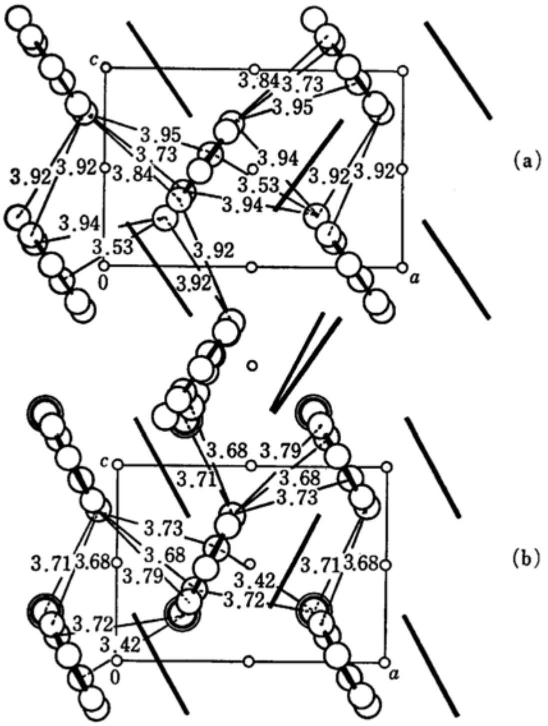

Fig. 6. Comparison of the crystal structure between fluorene (a) and carbazole (b).

The fact that the intermolecular distances are generally shorter in carbazole than in fluorene will imply stronger cohesive forces. In connection with this discussion, it is of interest to make comparison of thermodynamical data for these compounds. The lattice energy is directly related to ΔH_s (heat of sublimation). However, for lack of the datum on fluorene the sum of ΔH_m (heat of fusion) and ΔH_v (heat of vaporization) may be taken instead of ΔH_s and it comes out to be smaller by a few kcal/mol than the ΔH_s of carbazole.

Melting points of cabazole and fluorene are 245 and 115°C respectively. The large difference in melting points must depend on the difference either in ΔH_m or in ΔS_m (entropy change by fusion) because T_m (melting point) is given by $T_m = \Delta H_m / \Delta S_m$. ΔH_m's of carbazole and fluorene are reported to be 7.04 and 4.80 kcal/mol, so that ΔS_m's are calculated to be 13.6 and 12.4 e.u. respectively. It may be concluded that considerable difference in melting points is fairly due to the difference in ΔH_m connected to intermolecular interaction energy. On the other hand, comparison of the ΔS_m's will suggest that in the liquid state of carbazole there exists no perceptible hydrogen bond formation because in the latter case there would be some kind of ordering.

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[7] E. G. Cowlew and A. R. Parpington, *J. Chem. Soc.*, **1936**, 47.