

## Structure of Triboluminescent 9-Isopropylcarbazole, C<sub>15</sub>H<sub>15</sub>N

BY ONUSA SARAVARI, NOBORU KITAMURA AND SHIGEO TAZUKE\*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

AND AKIO TAKENAKA AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

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**Abstract.**  $M_r = 209.29$ , orthorhombic,  $Iba2$ ,  $a = 16.8334$  (6),  $b = 17.9780$  (7),  $c = 7.9871$  (3) Å,  $V = 2417.1$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.15$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 5.17$  cm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 298$  K. Final  $R = 0.069$  for 890 independent observed reflections. The four molecules around the twofold rotation axis are packed closely by an approximate  $4_2$  symmetry to form a polar arrow along the  $c$  axis. Direct contacts are made with the terminal methyl groups and no stacking between the planar aromatic moieties of the carbazole is observed. These arrows are arranged rather loosely in a body-centered fashion.

**Introduction.** Recently, we have reported the triboluminescence (TL) and tribopolymerization of 9-ethyl-3-vinylcarbazole (Inoue & Tazuke, 1981; Tazuke, Supakorn & Inoue, 1982). To extend the studies of the TL property of carbazole derivatives, we synthesized several compounds and found that 9-isopropylcarbazole, hereafter NIPCZ, shows high TL activity. Meanwhile, Nowak, Krajewska & Samoć (1983) have shown that the TL and photoluminescence spectra of NIPCZ are essentially identical. The TL activity of organic compounds is correlated with the polarity of the crystals (Hardy, Kaska, Chandra & Zink, 1981), but there are only two reports on the crystal structures relevant to organic TL phenomena. In order to reveal the molecular arrangement of NIPCZ, we have performed an X-ray structure analysis. Although a preliminary note on the crystal data of NIPCZ was reported in connection with its charge-transfer complex with picryl chloride (Cherin & Burack, 1966), the structure determination has not been undertaken.

**Experimental.** NIPCZ synthesized from carbazole, according to the general method for the preparation of *N*-alkylated carbazole derivatives (Stevens & Tucker, 1923); transparent needle-like single crystals (by multiple sublimation),  $0.5 \times 0.1 \times 0.1$  mm; Rigaku

automated four-circle diffractometer, graphite-monochromated Cu  $K\alpha$  radiation; unit-cell dimensions determined by least squares with the  $2\theta$  values of 54 high-angle reflections; intensity data in the range  $3 < 2\theta < 125^\circ$ , range of  $hkl$ :  $h$  0→19,  $k$  0→9,  $l$  0→20,  $\omega$ - $2\theta$  scans, scan speed  $4^\circ$  ( $2\theta$ ) min<sup>-1</sup>, scan width  $1.4^\circ$  ( $2\theta$ ); three reference reflections monitored periodically showed no significant intensity deterioration; no absorption correction; 1050 measured independent reflections, 131 with no net intensities; observation threshold value  $F_{\text{lim}} = 1.527$ , standard deviations estimated by  $\sigma^2(F_o) = \sigma_p^2(F_o) + qF_o^2$  with  $\sigma_p(F_o)$  evaluated by counting statistics and  $q (=6.95 \times 10^{-5})$  from variations of the monitored reflections (McCandlish & Stout, 1975); the distribution of  $E^2$ s showed the noncentrosymmetric space group  $Iba2$ ; structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares,  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 1/\sigma^2(F_o)$ ; all H atoms calculated geometrically, confirmed on a difference map, included in the further refinement but not varied; final  $R = 0.069$  for 890 measured reflections with  $F_o > 3\sigma(F_o)$ ,  $R_w = 0.056$ ,  $S = 2.98$ ; max. shift of parameters in the last cycle  $0.4\sigma$ ; final  $\Delta\rho$  excursions  $\pm 0.14$  e Å<sup>-3</sup>; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs *LSAP80* (Takenaka & Sasada, 1980, unpublished) for least-squares refinement of the structure, *DCMS82* (Takenaka & Sasada, 1982, unpublished) for structure drawings, *LISTUP* (Takenaka & Sasada, 1983, unpublished) for calculation of molecular geometries.

**Discussion.** Atomic parameters are listed in Table 1.† The molecular structure, along with the bond lengths

† Lists of anisotropic thermal parameters of C and N atoms, H-atom coordinates, structure factors and deviations of atoms from the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39500 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* To whom correspondence should be addressed.

Table 1. Fractional coordinates and equivalent isotropic temperature factors

The  $B$  values are the equivalent isotropic temperature factors calculated from anisotropic thermal parameters using the equation  $B = 8\pi^2(U_1 + U_2 + U_3)/3$ , where  $U_1$ ,  $U_2$  and  $U_3$  are principal components of the mean-square displacement matrix  $U$ . Values in square brackets are anisotropy defined by  $[(B - 8\pi^2U_i)^2/3]^{1/2}$ , and those in parentheses are e.s.d.'s; they refer to last decimal places.

	$x$	$y$	$z$	$B(\text{\AA}^2)$
C(1)	0.0736 (3)	0.1902 (3)	0.1456	7.1 [9]
C(2)	0.0465 (3)	0.2457 (4)	0.038 (1)	8.8 [14]
C(3)	0.0920 (5)	0.2697 (3)	-0.094 (1)	8.3 [28]
C(4)	0.1661 (4)	0.2403 (3)	-0.1251 (9)	7.3 [34]
C(5)	0.3381 (4)	0.1447 (3)	-0.108 (1)	8.7 [44]
C(6)	0.4015 (6)	0.0985 (6)	-0.060 (2)	12.3 [84]
C(7)	0.3912 (6)	0.0522 (5)	0.075 (2)	13.3 [76]
C(8)	0.3264 (5)	0.0504 (3)	0.171 (1)	9.5 [37]
N(9)	0.1906 (3)	0.1061 (3)	0.2037 (8)	6.7 [22]
C(10)	0.1485 (3)	0.1602 (3)	0.1161 (9)	5.8 [12]
C(11)	0.1950 (3)	0.1843 (3)	-0.0191 (9)	5.5 [14]
C(12)	0.2688 (4)	0.1439 (3)	-0.012 (1)	6.2 [17]
C(13)	0.2645 (4)	0.0969 (3)	0.129 (1)	6.5 [14]
C(14)	0.1689 (5)	0.0731 (3)	0.365 (1)	10.0 [65]
C(15)	0.1017 (4)	0.0237 (3)	0.364 (1)	11.4 [75]
C(16)	0.1800 (4)	0.1244 (4)	0.508 (9)	10.9 [71]

Table 2. Intermolecular distances less than 4.0 Å

Standard deviations are given in parentheses.

C(1)...C(2 <sup>b</sup> )	3.864 (9)	C(13)...C(4 <sup>a</sup> )	3.716 (9)
C(2)...C(3 <sup>b</sup> )	3.78 (1)	C(2)...C(6 <sup>a</sup> )	3.80 (1)
C(3)...C(1 <sup>b</sup> )	3.761 (9)	C(4)...C(16 <sup>a</sup> )	3.60 (1)
C(6)...C(8 <sup>b</sup> )	3.66 (1)	C(4)...C(12 <sup>a</sup> )	3.884 (9)
N(9)...C(15 <sup>b</sup> )	3.882 (9)	C(4)...C(16 <sup>a</sup> )	3.71 (1)
C(8)...C(7 <sup>b</sup> )	3.88 (2)	C(15)...C(15 <sup>b</sup> )	3.53 (2)
C(1)...C(5 <sup>a</sup> )	3.857 (9)		

Symmetry code: (i)  $-x, y, \frac{1}{2} + z$ ; (ii)  $-x, y, \frac{1}{2} + z$ ; (iii)  $x, -y, -\frac{1}{2} + z$ ; (iv)  $x, -y, \frac{1}{2} + z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (vi)  $-\frac{1}{2} + x, \frac{1}{2} - y, z$ ; (vii)  $x, y, -1 + z$ ; (viii)  $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ix)  $-x, -y, z$ .

and angles, is shown in Fig. 1. The bond lengths of the central ring are similar to those in carbazole (Kurahashi, Fukuyo, Shimada, Furusaki & Nitta, 1969), but the C(11)–C(12) bond is shortened. This shortening is a general trend of *N*-alkylated carbazole derivatives, as found in 9-methylcarbazole (Popova & Chetkina, 1979) and 9-vinylcarbazole (Tsutsui, Hirotsu, Umesaki, Kurahashi, Shimada & Higuchi, 1976). The length of the C(7)–C(8) bond is shorter than the usual value (1.398 Å), probably because of the large thermal motion. All the rings in the molecule are strictly planar, but the two benzene rings are slightly bent away from the central five-membered ring in the same direction, their dihedral angle being 1.8°, as a common feature of carbazole derivatives (Popova & Chetkina, 1979).

The C(10)–N(9)–C(14)–C(15), C(10)–N(9)–C(14)–C(16), C(13)–N(9)–C(14)–C(15), and C(13)–N(9)–C(14)–C(16) torsion angles are 70.9 (9), 287.5 (8), 239.2 (7), and 95.7 (8)°, respectively. The two terminal C–C bonds in the isopropyl group are short due to their large thermal motion. By assuming their lengths to be 1.54 Å, the intramolecular distances were examined; the C(15)–C(10), C(16)–C(10), C(15)–C(1), and C(16)–C(1) distances are 3.315 (6), 3.280 (6), 3.539 (5), and 3.635 (5) Å, respectively.

The crystal structure projected along the  $c$  axis is shown in Fig. 2(a). The four molecules around the twofold rotation axis are packed closely by an

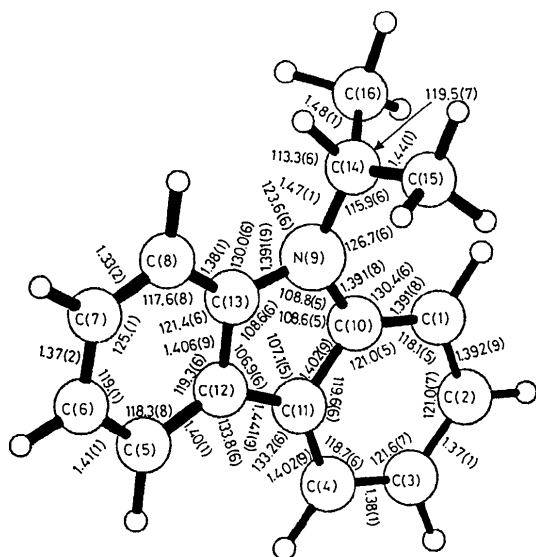


Fig. 1. Molecular structure of 9-isopropylcarbazole. Bond lengths (Å) and angles (°) are shown together with atomic numbering.

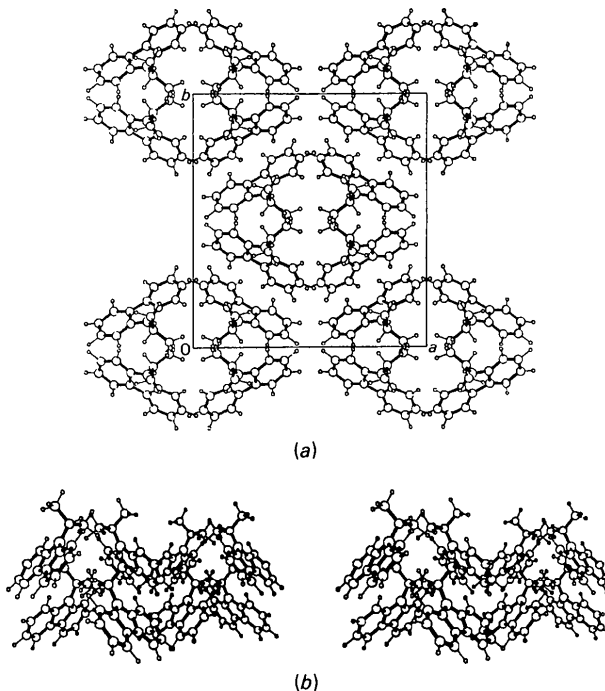


Fig. 2. Crystal structure of 9-isopropylcarbazole: (a) projected along the  $c$  axis and (b) side-view of the polar arrows.

approximate  $4_2$  symmetry to form a polar arrow along the  $c$  axis; its side-view is shown in Fig. 2(b).

Intermolecular distances less than  $4.0 \text{ \AA}$  are listed in Table 2. Within the arrow, the shortest distance between the methyl groups related by twofold rotation is  $3.53(2) \text{ \AA}$ . The other methyl group makes contact with the N atom of the neighboring molecule by weak electrostatic interaction. There is no stacking between the planar aromatic moieties of the carbazole. Arrangement of these arrows in a body-centered fashion is rather loose.

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*Acta Cryst.* (1984). **C40**, 1619–1624

## Etude Structurale de la Solution Solide Monomère–Polymère du Bis[*p*-chlorophényl]carbamate] de Hexadiyne-2,4 Diyle-1,6, $C_{20}H_{14}Cl_2N_2O_4$

PAR CATHERINE BROUTY, PIERRE SPINAT ET ANNICK WHULER

Laboratoire de Minéralogie–Cristallographie des Universités Pierre et Marie Curie et Paris VII, associé au CNRS (LA 09), 4 place Jussieu, 75230 Paris CEDEX 05, France

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**Abstract.** 75% monomer–25% polymer,  $M_r = 417.2$ , triclinic,  $P\bar{1}$ ,  $a = 12.115(4)$ ,  $b = 8.217(4)$ ,  $c = 4.856(3) \text{ \AA}$ ,  $\alpha = 101.5(1)$ ,  $\beta = 83.4(1)$ ,  $\gamma = 96.0(1)^\circ$ ,  $V = 469.0(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 1.477 \text{ Mg m}^{-3}$ ,  $F(000) = 214$ ,  $\lambda(\text{Cu K}\alpha) = 1.54178 \text{ \AA}$ ,  $\mu = 3.45 \text{ mm}^{-1}$ ,  $T = 163 \text{ K}$ ,  $R = 0.09$  for 824  $hkl$  with  $F_o \geq 0.01 F_o(\text{max.})$ . This study of single-crystal polymerization under X-ray radiation shows that polymer molecules grow inside the monomer crystal structure with a solid-solution process. The variations in unit-cell parameters are established as a function of polymer ratio, which is determined from successive structure refinements (163 K) after different periods of X-ray exposure (293 K) of the single crystal. In these conditions, the crystal does not polymerize completely: 65% polymer (molecular %) is the upper limit which can be reached. Conformations of polymer and monomer molecules are described and the observed displacements occurring during polymerization are given for all the atoms. Intermolecular H-bond stretch is observed for monomer molecules.

**Introduction.** Le bis[*p*-chlorophényl]carbamate] de hexadiyne-2,4 diyle-1,6 (communément appelé HD<sub>p</sub>CPU) appartient à la famille des composés diacétyléniques  $R-C\equiv C-C\equiv C-R$  dont la caractéristique est d'être polymérisable à l'état cristallin.

Suivant la nature du solvant utilisé, HD<sub>p</sub>CPU présente trois phases cristallines monomères de polymérisabilité (ou activité) très différente (Patel, Duesler, Curtin & Paul, 1980; Patel & Miller 1981): une forme incolore inactive, une seconde rose modérément active et la troisième bleue très réactive; la coloration du monomère apparaît dès que le cristal contient quelques % de chaînes polymères.

Contrairement à un certain nombre d'autres composés diacétyléniques, en particulier les HD<sub>p</sub>TS ( $R = \text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$ ) (Bloor, Koski, Stevens, Preston & Ando, 1975; Chance & Patel, 1978; Robin, 1980), HD<sub>p</sub>MBS ( $R = \text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{OCH}_3$ ) (Williams, Ando, Bloor & Hursthouse, 1980), HDDNP [ $R = \text{CH}_2\text{C}_6\text{H}_3(\text{NO}_2)_2$ ] (Albouy, 1982), le HD<sub>p</sub>CPU ne se polymérise pas thermiquement, mais uniquement sous