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Bis(1-carbazolyl)butadiyne

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Abstract. $C_{28}H_{16}N_2$, $M_r = 380.43$. Orthorhombic, $P2_12_12$, $a = 15.306$ (3), $b = 13.742$ (3), $c = 4.656$ (1) Å, $Z = 2$, $D_c = 1.29$, $D_o = 1.28$ (1) g cm⁻³. The carbazolyl groups on opposite ends of the butadiyne rod are rotated with respect to each other by 85.2°. The resulting propeller-shaped molecules stack in columns along c . The arrangement of the molecules within the stacks is not amenable to the topochemical polymerization that such diacetylene monomers are often observed to undergo.

Introduction. The topochemical polymerization of organic molecules to yield large single-crystal polymers has received considerable attention in recent years (Wegner, 1977). A mechanism for one such class of polymerizations, that of the diacetylenes, has been proposed by Wegner (1969) and elaborated upon by Baughman (1974). The title compound seemed to be an interesting candidate for such a reaction since the strongly electron-donating carbazolyl groups would be conjugated into the polyene backbone of the resulting material. The photochemically stable compound, prepared by the oxidative coupling of *N*-ethynylcarbazole, slowly turns black and undergoes an exothermic reaction (Barrall, 1977) when heated to 240°C in an inert atmosphere, yielding a noncrystalline substance that retains the habit of the original monomer crystal. Since destructive polymerization was a possible explanation for this phenomenon, we undertook this study to determine those factors responsible for the rather extreme conditions.

A crystal of approximate dimensions 0.1 × 0.18 × 0.3 mm perpendicular to the faces (110), (1 $\bar{1}$ 0) and (001), respectively, and obtained by recrystallization

from ethyl acetate, was used for data collection. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer using θ – 2θ scans and graphite-monochromatized Cu $K\alpha$ radiation to $\theta = 76^\circ$. The scan range was $\Delta\theta = (0.8 + 0.2 \tan \theta)^\circ$ and was extended by 25% at each end for background. The variable scan rate was computed such that 5000 counts were to be

Table 1. *Final atomic positional parameters* ($\times 10^4$)

Standard deviations are in parentheses.

	x	y	z
N	3663 (1)	8196 (1)	7875 (4)
C(1)	4708 (1)	9621 (2)	7690 (7)
C(2)	4199 (1)	8968 (2)	7715 (6)
C(3)	3798 (1)	7374 (1)	9606 (5)
C(4)	4481 (1)	7192 (2)	1493 (6)
C(5)	4467 (2)	6315 (2)	2934 (6)
C(6)	3794 (2)	5648 (2)	2528 (7)
C(7)	3114 (1)	5843 (2)	664 (6)
C(8)	3115 (1)	6720 (1)	9156 (5)
C(9)	2885 (1)	8056 (1)	6309 (5)
C(10)	2532 (1)	7152 (1)	7067 (5)
C(11)	1754 (1)	6859 (2)	5796 (6)
C(12)	1366 (1)	7456 (2)	3798 (6)
C(13)	1732 (2)	8345 (2)	3047 (6)
C(14)	2501 (1)	8664 (2)	4298 (6)
H(4)	4938*	7634	1761
H(5)	4935	6149	4273
H(6)	3791	5031	3576
H(7)	2651	5397	366
H(11)	1511	6248	6325
H(12)	820	7239	2890
H(13)	1437	8746	1618
H(14)	2745	9262	3781

* Hydrogen atoms were placed in fixed, calculated positions.

obtained, if possible, in a maximum time of 90 s. An aperture with a height of 4 mm and width of $(4.0 + 0.87 \tan \theta)$ mm was placed in front of the counter 173 mm from the crystal. The intensities of three standard reflections, measured every 50 reflections, showed no variation over the course of data collection. 1105 reflections were collected, of which 1053 were judged to be observed by the criterion $F^2 \geq 2\sigma(F^2)$. The 52 reflections not satisfying this criterion were not used in the least-squares refinement.

The systematic absences ($h00, h \neq 2n; 0k0, k \neq 2n$) indicated the space group to be $P2_12_12$ (D_2^3 , No. 18) (*International Tables for X-ray Crystallography*, 1969). The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) with 105 reflections with $E > 1.50$, the resulting E map revealing all the non-H atoms. The structure was refined by full-matrix least squares, with anisotropic temperature factors assigned to all the non-H atoms. The H atoms were placed in fixed, calculated positions and assigned isotropic temperature factors of 5.0 \AA^2 . The refinement converged at $R = 0.043$ and $R_w = 0.050$, based on 1051 observations and 136 variables. The 200 and 020 reflections appeared to suffer from severe extinction and were excluded from the data set. The error in an observation of unit weight was 1.49. The weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. The maximum shift in any parameter at convergence was 0.001 that of its standard deviation. The neutral scattering factors of C and N were taken from *International Tables for X-ray Crystallography* (1974), while those of H were taken from Stewart, Davidson & Simpson (1965). All computations were done with an IBM 360/195 computer using programs previously described (Mayerle, 1977). Final atomic positional parameters are listed in Table 1.*

Discussion. The atom labelling scheme and the anisotropic thermal ellipsoids of bis(1-carbazolyl)butadiyne are shown in Fig. 1. Bond distances and angles are listed in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33237 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

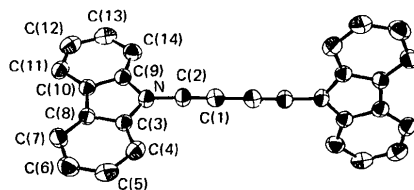


Fig. 1. The bis(1-carbazolyl)butadiyne molecule. The 50% probability ellipsoids are shown.

The two molecules in the unit cell possess crystallographic twofold symmetry. There is nothing unusual about their internal geometry. The C(1)–C(2) triple bond length of 1.188 (3) Å and the C(1)–C(1') length of 1.373 (4) Å are typical for diacetylenes (Mayerle & Clarke, 1978, and references therein; Hanson, 1975; Morosin & Harrah, 1977). The carbazolyl moiety is planar to within 0.02 Å, the formula of its mean plane being given by $0.519X - 0.434Y - 0.737Z + 4.666 = 0$ where X, Y and Z (in Å) are along a, b and c respectively. Examination of Table 2 shows that the bond lengths are not significantly different from those in carbazole itself (Kurahashi, Fukuyo, Shimada,

Table 2. Bond distances (Å) and angles (°)

N–C(2)	1.344 (3)	C(1')–C(1)–C(2)	179.4 (3)
N–C(3)	1.402 (3)	C(1)–C(2)–N	175.8 (3)
N–C(9)	1.410 (3)	N–C(3)–C(4)	128.3 (2)
C(1)–C(1')	1.373 (4)	N–C(3)–C(8)	108.7 (2)
C(1)–C(2)	1.188 (3)	C(4)–C(3)–C(8)	122.9 (2)
C(3)–C(4)	1.387 (3)	C(3)–C(4)–C(5)	117.0 (2)
C(3)–C(8)	1.395 (3)	C(4)–C(5)–C(6)	121.4 (2)
C(4)–C(5)	1.379 (3)	C(5)–C(6)–C(7)	121.0 (2)
C(5)–C(6)	1.392 (3)	C(6)–C(7)–C(8)	118.9 (2)
C(6)–C(7)	1.382 (4)	C(3)–C(8)–C(7)	118.8 (2)
C(7)–C(8)	1.395 (3)	C(3)–C(8)–C(10)	107.4 (2)
C(8)–C(10)	1.447 (3)	C(7)–C(8)–C(10)	133.8 (2)
C(9)–C(10)	1.399 (3)	N–C(9)–C(10)	108.4 (2)
C(9)–C(14)	1.385 (3)	N–C(9)–C(14)	128.7 (2)
C(10)–C(11)	1.390 (3)	C(10)–C(9)–C(14)	122.9 (2)
C(11)–C(12)	1.375 (4)	C(8)–C(10)–C(9)	107.2 (2)
C(12)–C(13)	1.389 (4)	C(8)–C(10)–C(11)	134.1 (2)
C(13)–C(14)	1.385 (4)	C(9)–C(10)–C(11)	118.7 (2)
		C(10)–C(11)–C(12)	119.0 (2)
C(2)–N–C(3)	125.3 (2)	C(11)–C(12)–C(13)	121.4 (2)
C(2)–N–C(9)	126.5 (2)	C(12)–C(13)–C(14)	121.0 (3)
C(3)–N–C(9)	108.2 (2)	C(9)–C(14)–C(13)	117.0 (2)

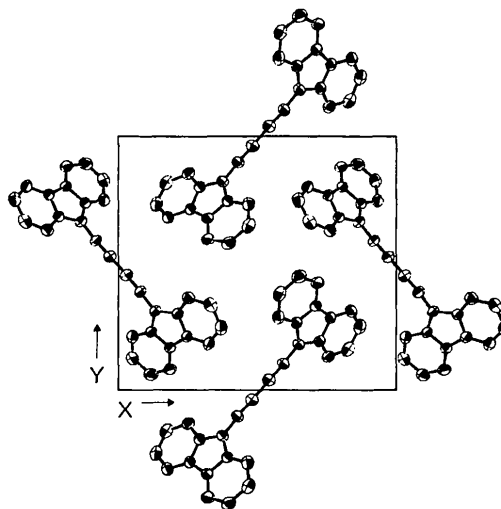


Fig. 2. The projection of the structure on the ab plane. The molecules situated at $x = \frac{1}{2}, y = 0$ are centered at $z \approx 0.8$. The molecules at $x = 0, y = \frac{1}{2}$ are at $z \approx 0.2$.

Furusaki & Nitta, 1969) and that the mirror plane perpendicular to the molecular plane in carbazole is approximately retained in this compound. The carbazolyl moieties on opposite ends of the diacetylenic rod are rotated with respect to each other, giving a propeller-like shape to the molecule. The dihedral angle between the carbazolyl planes is $85.2 (2)^\circ$.

The projection of the structure on the *ab* plane is shown in Fig. 2. The molecules pack in stacks along the short *c* axis. The carbazolyl rotation mentioned above has the effect of reducing the perpendicular distance between carbazolyl groups along the stack to 3.427 \AA and makes it unnecessary for the molecules to pack in the slipped manner associated with 1,4-addition polymerization. In Baughman's (1974) notation, γ_1 , the angle between the molecular and stacking axes, is 90° . As a direct consequence of this, the potentially reacting carbon atoms, C(2) and its twofold rotationally related counterpart in the next molecule along the stack, are $5.977 (3) \text{ \AA}$ apart. Since the two atoms must approach to within $\sim 4 \text{ \AA}$ of each other in order to react (Wegner, 1977) it is unlikely that, in the absence of a high-temperature phase transition, the process occurring at 240°C is a topochemical 1,4-addition polymerization

such as described by Wegner (1969) for other diacetylenes. Differential thermal analysis has shown no evidence for a phase transition between room temperature and 240°C (Barrall, 1977).

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Etude de la Forme Cristalline du Benzonitrile à 198 K

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Abstract. $\text{C}_6\text{H}_5\text{CN}$, tetragonal, space group $P4_12_12$ (or $P4_32_12$) $a = 6.361 (5)$, $c = 14.24 (1) \text{ \AA}$, $V = 576.04 \text{ \AA}^3$, $Z = 4$. Single crystals were grown in sealed Lindemann-glass capillaries directly on the goniometer by a zone-melting technique. Intensity data were measured on an automatic diffractometer with $\text{Mo K}\alpha$ radiation; $\mu = 0.73 \text{ cm}^{-1}$. The final *R* index is 0.061 for 233 observed reflexions.

Introduction. Un monocristal a été obtenu par la méthode de zone fondue décrite par Renaud & Fourme (1966) à l'aide de dispositifs permettant la croissance de monocristaux sur tête goniométrique à partir de corps organiques liquides à température ordinaire. Le liquide contenu dans un tube capillaire scellé (0,2 à 0,3 mm de diamètre) est refroidi par un jet d'azote. Une spire chauffante placée dans le gaz froid produit le

gradient de température convenable. La progression lente à vitesse constante du tube capillaire à travers cette spire conduit à l'obtention du monocristal. Des supports de spires adaptés à différents diffractomètres automatiques sont décrits dans une publication à paraître.

Le benzonitrile utilisé est présenté dans la qualité 'puriss' par la firme Fluka et exempt d'aniline. Ce composé fond à 260 K, il présente une surfusion de 30 K et, pour réduire le plus possible l'agitation thermique, les enregistrements ont été réalisés à 198 K, un point de transition ayant été décelé à 190 K environ.

Pour simplifier la résolution de la structure, nous avons supposé connue la forme de la molécule et adopté comme modèle celui de Casado, Nygaard & Sørensen (1971) qui résulte d'une étude de la phase liquide par microondes.