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Poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne]

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Abstract. $(C_{30}H_{20}N_2)_n$, monoclinic, $P2_1/c$, a = 12·865 (5), b = 4·907 (4), c = 17·403 (5) Å, β = 108·3 (4)°, $Z = 2/n$, $M_r = n(408·5)$, D_{obs} = 1·30, D_{calc} = 1·301 g cm^{-3}. Intensity data collected on a two-circle diffractometer using graphite-monochromated Cu $K\alpha$ radiation were refined by full-matrix least squares to an R factor of 0·086. Single-crystal structure analyses show that the polymer backbone has the alternating double–single–triple–single bonding pattern and is a planar conjugated system. The carbazolyl groups are planar and make angles of 43·3 and 81° with the b axis and the plane of the polymer backbone, respectively.

Introduction. Intensity data were collected on a Hewlett–Packard–Canberra controlled Supper diffractometer of Weissenberg geometry, using graphite-monochromated Cu $K\alpha$ (λ = 1·54178 Å) radiation and a pulse-height analyser. A fixed-counter moving-crystal technique with variable step scans was used (Hanson & Nordman, 1975) (scan range = 9 to 12°; rate = 2 to 8° min^{-1}; sin $2\theta_{max}$ = 1·0). 880 reflections were measured; 426 were considered to be observed [*i.e.* $I > 0$ (Hanson, 1969)]. Each scan range was divided into ten equal parts, and counts were accumulated during each moving part and stored in the computer. With scan ranges of 9 to 12°, several of the partial scans represent readings of the background on each side of the peak. The intensities of four standard reflections on the $h0l$ level were measured every 50 reflections on the $h0l$ level, and also between levels. These intensities did not change during the course of data collection. Evaluation of the integrated intensities and reduction to structure factor counts was done by a data-reduction program of Hanson (1969). No absorption corrections were made.

The locations of the atoms in the carbazolyl group were determined by application of *MULTAN* (Germain, Main & Woolfson, 1971). The XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used to calculate difference Fourier maps to locate the remaining non-hydrogen atoms and to refine the structure by full-matrix least-squares methods. The quantity $\Sigma w(|F_{obs}| - |F_{calc}|)^2$ was minimized in least-squares refinement with $w = 1$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). No attempt was made to locate the H atoms. The final R factor was 0·0858 for observed reflections only; for observed and non-observed reflections it was 0·381. The fractional coordinates are listed in Table 1.*

Table 1. *Fractional coordinates*

Figures in parentheses are standard deviations.

	x	y	z
N	0·697 (1)	0·262 (3)	0·638 (1)
C(1)	0·507 (2)	0·121 (3)	0·506 (1)
C(2)	0·534 (1)	0·404 (2)	0·521 (1)
C(3)	0·646 (1)	0·492 (3)	0·585 (1)
C(4)	0·775 (2)	0·109 (4)	0·614 (1)
C(5)	0·811 (2)	0·094 (5)	0·544 (1)
C(6)	0·897 (2)	−0·098 (6)	0·548 (2)
C(7)	0·943 (2)	−0·277 (5)	0·615 (2)
C(8)	0·908 (2)	−0·268 (4)	0·683 (1)
C(9)	0·827 (2)	−0·076 (4)	0·682 (1)
C(10)	0·770 (2)	−0·027 (4)	0·740 (1)
C(11)	0·782 (2)	−0·143 (5)	0·818 (2)
C(12)	0·713 (2)	−0·055 (5)	0·859 (2)
C(13)	0·634 (2)	0·162 (5)	0·832 (1)
C(14)	0·617 (2)	0·294 (5)	0·756 (2)
C(15)	0·687 (2)	0·188 (4)	0·714 (1)

Discussion. Wegner (1969, 1972) has shown that large and almost defect-free monocrystalline polymers can be obtained *via* solid-state polymerization of diacetylenes ($RC{\equiv}C{-}C{\equiv}CR$). The resulting polymer has a fully conjugated backbone and can be represented by the mesomeric forms: (I) poly(en-yne) or (II) poly(butatriene) structures. Poly[2,4-hexadiyne-1,6-diol

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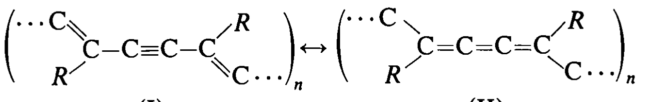
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33094 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

bis(*p*-toluenesulfonate)] (PTS, *R* = $CH_2SO_3C_6H_4$-CH_3) (Kobelt & Paulus, 1974) and poly[2,4-hexadiyne-1,6-diol bis(phenylurethane)] (HDU, *R* = $CH_2OCONHC_6H_5$) (Hädicke, Mez, Krauch, Wegner & Kaiser, 1971) have a poly(en-yne) structure (I), while poly[5,7-dodecadiyne-1,12-diol bis(phenylurethane)] [TCDU, *R* = $(CH_2)_4OCONHC_6H_5$] (Enkelmann & Lando, 1977) has been shown to have a poly(butatriene) structure (II).



(I) (II)

Recently we have noted that a new diacetylene, poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (DCHD, *R* = *N*-carbazolylmethyl), can be polymerized quantitatively by heat or by γ irradiation with large changes in the lattice parameters between monomer and polymer (Yee & Chance, 1977). The aim of this three-dimensional structure analysis is to provide a basis for interpreting the highly anisotropic optical properties (Hood, Müller, Eckhardt, Chance & Yee, 1977) of the DCHD polymer, as well as its interesting mechanical, thermomechanical and photoconductive properties (Yee & Chance, 1977).

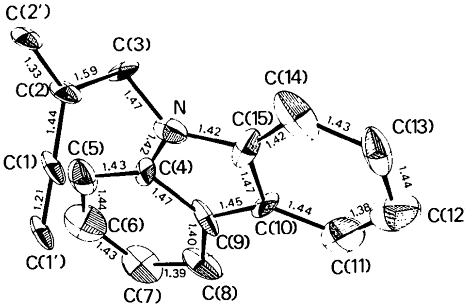


Fig. 1. Bond lengths (Å) in $(C_{30}H_{20}N_2)_n$. The average error is about 0·02 Å. The primed atomic positions are generated by symmetry relationships.

Table 3. *Deviations* (Å) *from the least-squares plane of the carbazolyl ring*

The plane equation is 7·545*x* + 3·361*y* + 3·932*z* = 8·619, where *x*, *y*, and *z* are the fractional coordinates of the defining atoms in the direct cell.

C(4)	0·014	C(8)	0·018	C(12)	−0·045
C(5)	−0·036	C(9)	0·041	C(13)	−0·018
C(6)	−0·024	C(10)	0·014	C(14)	−0·003
C(7)	−0·017	C(11)	0·021	C(15)	0·007
				N	0·029

Examination of bond lengths (Fig. 1) and bond angles (Table 2) shows that the DCHD polymer has the bonding pattern of the poly(en-yne) structure (I). This appears to be consistent with the results of the optical studies of the DCHD polymer (Hood *et al.*, 1977).

The carbazolyl group makes an angle of 43·3° with the *b* axis. Consequently, there is no significant overlap or π-electron interaction between carbazolyl groups (see Fig. 2). Since large changes in the relative positions of the substituent groups are not expected to occur on polymerization, as observed in the PTS system (Enkelmann & Wegner, 1977), this observation explains the absence of any significant excimer emission in the monomer crystals of DCHD (Yee & Chance, 1977). The atoms of the carbazolyl group lie in a plane within experimental error [the maximum distance of any atom from the plane is 0·045 Å for C(12), see Table 3]. Important torsional angles are C(1′)–C(1)–C(2)–C(3) −116·7°, C(1′)–C(1)–C(2)–C(2′) +123·8°, C(1)–C(2)–C(3)–N −53·7°, and C(2)–C(3)–N–C(4) +102·8°. The *ORTEP* (Johnson, 1965) drawing (Fig. 2) shows the orientation of the carbazolyl groups in the unit cell. The plane of the polymer's fully conjugated backbone makes an angle of 81° with the plane of the carbazolyl group. The closest distance between the stacks of carbazolyl groups is 3·36 Å.

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Table 2. *Bond angles* (°)

The average error is about 2·0°.

C(1′)–C(1)–C(2)	174·4	C(7)–C(8)–C(9)	116·4	C(9)–C(10)–C(11)	132·1
C(1)–C(2)–C(2′)	120·9	C(8)–C(9)–C(4)	125·1	C(10)–C(11)–C(12)	118·2
C(1)–C(2)–C(3)	120·1	C(9)–C(4)–C(5)	117·7	C(11)–C(12)–C(13)	124·3
C(2′)–C(2)–C(3)	119·0	C(9)–C(4)–N	106·0	C(12)–C(13)–C(14)	121·6
C(2)–C(3)–N	111·0	C(4)–C(9)–C(10)	105·2	C(13)–C(14)–C(15)	112·1
C(3)–N–C(4)	116·6	C(8)–C(9)–C(10)	129·6	C(14)–C(15)–C(10)	128·2
N–C(4)–C(5)	136·3	C(9)–C(10)–C(15)	112·5	C(14)–C(15)–N	130·3
C(4)–C(5)–C(6)	116·4	C(11)–C(10)–C(15)	115·4	C(15)–N–C(3)	128·3
C(5)–C(6)–C(7)	123·6	C(10)–C(15)–N	101·5	C(15)–N–C(4)	114·8
C(6)–C(7)–C(8)	120·9				

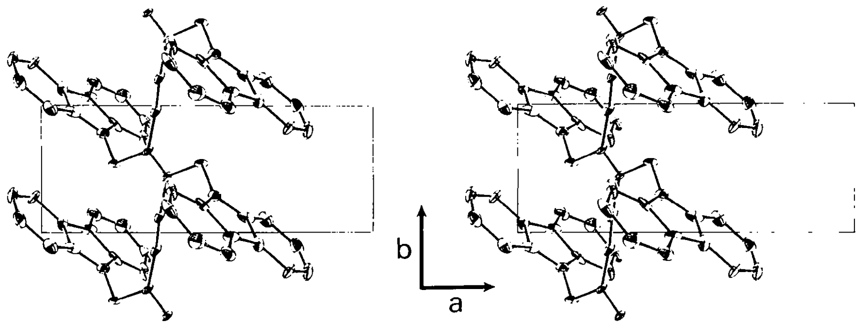

Fig. 2. Stereoview looking down the c^* axis to show the relation of units along the polymer chain axis.

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[2-Phenyl-4-(*p*-chlorophenyl)-5-thiazolyl]acetic Acid

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Abstract. $C_{17}H_{12}ClNO_2S$, $M_r = 329{\cdot}8$, triclinic, $P\bar{1}$, $a = 7{\cdot}423\ (1)$, $b = 9{\cdot}098\ (1)$, $c = 11{\cdot}549\ (1)$ Å, $\alpha = 79{\cdot}73\ (2)$, $\beta = 79{\cdot}49\ (1)$, $\gamma = 88{\cdot}47\ (2)°$, $Z = 2$, μ(Mo $K\alpha$) = $3{\cdot}95$ cm^{-1}, $D_x = 1{\cdot}453$, $D_m = 1{\cdot}45\ (1)$ g cm^{-3}, at 20 ± 2°C. For 2850 reflexions with $I > 0$, $R = 0{\cdot}039$ and $R_w = 0{\cdot}040$. The phenyl group bonded to the thiazolyl system in the 2 position is twisted by 15·6° with respect to the plane of the heterocyclic ring; the twist angle of the second phenyl ring is 35·9°. The plane of the carboxyl group is almost exactly perpendicular to the plane of the thiazolyl ring. The structure consists of centrosymmetric dimers formed by hydrogen bonds between carboxyl groups of adjacent molecules.

Introduction. It has been pointed out (Shen, 1972) that a major concern in the current search for new antiarthritic drugs is to minimize their side effects. In the field of aryl- and heteroarylalkanoic acids, a partial dissociation of activity and toxicity has been achieved by the fortuitous selection of some aryl moieties. The preferred geometry of the aryl groups has been indicated by Shen (1972) as a possible means to a rational approach to this problem. In line with this interest, the structure of the title compound, a nonsteroidal antiinflammatory agent (Brown, Cater, Cavalla, Green, Newberry & Wilson, 1974), has been investigated.

Crystals in the form of colourless prisms were