

Poly[1,2-bis(diphenylaminomethyl)-1-buten-3-ynylene]

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Abstract. $(C_{30}H_{24}N_2)_n$, triclinic, $P\bar{1}$, $a = 9.052(3)$, $b = 9.737(9)$, $c = 13.645(7)$ Å, $\alpha = 109.67(6)$, $\beta = 109.08(3)$, $\gamma = 85.51(7)^\circ$, $Z = 2$, $M_r = 412n$, $D_x = 1.28$ Mg m $^{-3}$. The polymer backbone is best described by a poly-en-yne system where triple bonds are conjugated with double bonds.

Introduction. Single crystals of the monomer were obtained from $CHCl_3$ solution by evaporation at room temperature. The initially colourless monomer crystals quickly turn red on exposure to normal laboratory light. Solid-state polymerization was carried out by thermal annealing at 343 K for 24 h. The polymer crystals are deep red with a metallic green lustre. A crystal $0.8 \times 0.5 \times 0.1$ mm was used for the intensity collection which was carried out on a Nonius four-circle diffractometer with graphite-monochromated $Mo K\alpha$ radiation and the θ - 2θ scan mode. Of the 5903 accessible reflections, significant counts were recorded for 3794 ($2\theta < 60^\circ$). The others were given zero weight in the refinement. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolson, 1973). Refinement was by full-matrix least squares. Unit weights were used throughout. The coordinates of the H atoms were found in a difference map. All positional parameters were refined with anisotropic thermal motion assumed for the non-hydrogen and isotropic for the H atoms. On termination R was 0.068. No absorption correction was applied. The programs used were those of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors for C and N were from *International Tables for X-ray Crystallography* (1968), and for H from Stewart, Davidson & Simpson (1965). The final atomic coordinates and isotropic thermal parameters are listed in Table 1.*

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35214 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Suitably substituted diacetylenes are known to polymerize in the solid state. The polymerization is initiated by thermal annealing or high-energy radiation. Each monomer joins with two neighbouring molecules in a 1,4-addition reaction forming a planar, fully conjugated polymer chain which is oriented in a well defined crystallographic direction. Owing to the special reaction mechanism this topochemical polymerization is the only method presently known which leads to macroscopic, nearly defect-free polymer single crystals (Wegner, 1972, 1979). The title compound is of special interest because it is one of the few examples where complete conversion to polymer can be reached under very mild conditions by thermal annealing at temperatures substantially lower than the monomer melting point. This is important since polymerization by high-energy radiation introduces radiation defects which make the polymer crystals obtained in this way less suited for physical measurements and, in particular, for spectroscopic studies. This investigation was undertaken to assist further in-

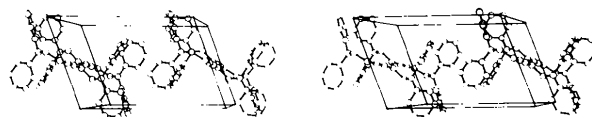


Fig. 1. Stereoscopic diagram of the packing (Johnson, 1965). The c axis is horizontal and a vertical.

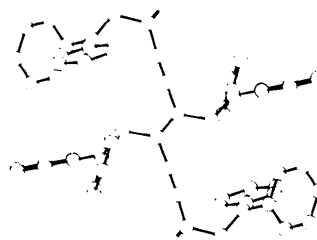


Fig. 2. Projection of the structure on the plane of the polymer backbone.

Table 1. Final positional and thermal parameters

(a) Final atomic coordinates ($\times 10^4$) for C and N and Debye-Waller factors equivalent to the anisotropic temperature factors. E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
N(1)	6586 (3)	3066 (2)	8386 (2)	2.1 (1)
N(2)	3689 (3)	1885 (3)	11866 (2)	2.3 (1)
C(1)	5397 (3)	4391 (3)	9833 (2)	1.7 (1)
C(2)	5115 (4)	3084 (3)	10008 (2)	1.9 (1)
C(3)	4905 (3)	1965 (3)	10146 (2)	1.8 (1)
C(4)	4701 (3)	610 (3)	10280 (2)	1.6 (1)
C(5)	6655 (4)	4369 (3)	9335 (3)	2.1 (1)
C(6)	5199 (4)	2798 (3)	7479 (3)	2.3 (1)
C(7)	4223 (4)	3917 (4)	7254 (3)	3.3 (2)
C(8)	2882 (5)	3607 (5)	6351 (4)	4.7 (2)
C(9)	2480 (5)	2189 (6)	5650 (4)	5.4 (3)
C(10)	3423 (5)	1066 (5)	5878 (4)	4.3 (2)
C(11)	4743 (5)	1365 (4)	6780 (3)	3.3 (1)
C(12)	8023 (4)	2573 (3)	8212 (3)	2.0 (1)
C(13)	9379 (4)	2660 (3)	9100 (3)	2.7 (1)
C(14)	10784 (4)	2234 (4)	8928 (3)	3.3 (2)
C(15)	10912 (4)	1678 (4)	7898 (4)	3.4 (2)
C(16)	9577 (4)	1546 (4)	7014 (3)	3.4 (2)
C(17)	8157 (5)	1992 (3)	7161 (3)	2.7 (1)
C(18)	3760 (4)	533 (3)	10998 (3)	2.2 (1)
C(19)	4966 (4)	2272 (3)	12849 (3)	2.3 (1)
C(20)	6471 (5)	1950 (4)	12822 (3)	3.7 (2)
C(21)	7739 (5)	2347 (5)	13775 (4)	4.5 (2)
C(22)	7535 (6)	3064 (5)	14767 (3)	4.4 (2)
C(23)	6047 (6)	3345 (5)	14812 (3)	4.5 (3)
C(24)	4767 (5)	2957 (4)	13864 (3)	3.6 (2)
C(25)	2180 (4)	2358 (3)	11902 (3)	2.2 (1)
C(26)	1870 (4)	3847 (3)	12170 (3)	2.4 (1)
C(27)	416 (4)	4325 (3)	12191 (3)	3.0 (1)
C(28)	-801 (4)	3345 (4)	11928 (3)	3.4 (2)
C(29)	-499 (4)	1862 (4)	11660 (4)	3.5 (2)
C(30)	961 (4)	1377 (3)	11654 (3)	2.9 (1)

(b) Final atomic parameters ($\times 10^3$) for H. E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(1)	773 (4)	440 (4)	993 (3)	2.3 (7)
H(2)	657 (5)	524 (5)	914 (4)	5.2 (11)
H(3)	442 (5)	491 (4)	782 (3)	4.0 (9)
H(4)	198 (7)	436 (6)	624 (5)	8.7 (16)
H(5)	145 (5)	200 (5)	497 (4)	5.7 (11)
H(6)	318 (6)	9 (5)	526 (4)	7.9 (14)
H(7)	554 (5)	69 (4)	684 (3)	5.1 (9)
H(8)	932 (4)	306 (4)	985 (3)	2.3 (7)
H(9)	1167 (4)	237 (4)	957 (3)	2.9 (8)
H(10)	1191 (4)	145 (4)	777 (3)	2.3 (7)
H(11)	966 (4)	114 (4)	626 (3)	2.1 (7)
H(12)	721 (4)	187 (4)	652 (3)	2.1 (7)
H(13)	260 (4)	29 (4)	1049 (3)	2.9 (8)
H(14)	430 (5)	-14 (4)	1131 (3)	4.5 (10)
H(15)	664 (4)	149 (4)	1212 (3)	3.0 (8)
H(16)	880 (5)	218 (4)	1373 (3)	4.1 (9)
H(17)	840 (5)	340 (4)	1546 (3)	4.3 (10)
H(18)	584 (4)	376 (4)	1552 (3)	3.9 (8)
H(19)	369 (4)	314 (4)	1394 (3)	3.6 (9)
H(20)	280 (5)	451 (4)	1243 (3)	3.8 (9)
H(21)	13 (5)	535 (5)	1251 (4)	5.4 (10)
H(22)	-193 (5)	374 (5)	1198 (3)	3.4 (10)
H(23)	-152 (5)	121 (5)	1142 (4)	5.4 (11)
H(24)	117 (5)	41 (5)	1133 (3)	5.6 (11)

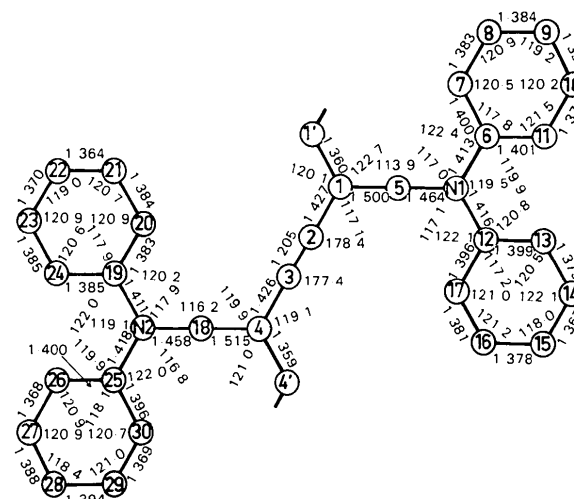


Fig. 3. Observed bond lengths (Å) and angles (°) between C and N. E.s.d.'s of bond lengths range from 0.002 to 0.004 Å, of bond angles from 0.2 to 0.4°.

Table 2. Least-squares planes

The values given are the angles between the calculated best planes which can be expressed as $P(xa) + Q(yb) + R(zc) = S$. The e.s.d.'s of the atoms defining the planes are 0.002 Å for the polymer chain and are in the range 0.01 to 0.02 Å for the benzene rings.

	Chain	<i>R</i> 1	<i>R</i> 2	<i>R</i> 3	<i>R</i> 4
Polymer chain	-	81.2	81.5	89.7	34.3
<i>R</i> 1	[C(6)-C(11)]	-	60.5	59.1	47.4
<i>R</i> 2	[C(12)-C(17)]	-	-	8.9	76.4
<i>R</i> 3	[C(19)-C(24)]	-	-	-	68.7
<i>R</i> 4	[C(25)-C(30)]	-	-	-	-
<i>P</i>	4.129	-6.940	2.498	1.820	-0.654
<i>Q</i>	0.286	-3.598	9.535	9.610	-2.548
<i>R</i>	8.824	11.583	-4.931	-6.293	13.147
<i>S</i>	2.207	4.052	0.415	-5.000	14.894

investigation of the complex polymerization mechanism and of the solid-state properties of polydiacetylenes.

Fig. 1 shows a stereoscopic packing diagram. The polymer backbone is oriented parallel to **b**. In order to obtain an effective side-chain packing the diphenylamino groups have different conformations. A projection of the crystal structure on the plane of the polymer chain is shown in Fig. 2. This is an unusual behaviour since in all other known structures of symmetrically substituted diacetylenes the molecules are located at centres of symmetry. Consequently, here the length of the polymer repeat unit is double the 4.9 Å normally observed in polydiacetylenes.

Bond lengths and angles are shown in Fig. 3. No unusual bond lengths or angles are observed. With few exceptions the values found in the two crystallo-

graphically different side groups are identical within experimental error. The bond lengths to the H atoms not shown range from 0.92 to 1.08 Å. Bond lengths in the polymer chain are consistent with a poly-en-yne structure where triple bonds are conjugated with double bonds. Within 0.01 to 0.02 Å the phenyl rings and the polymer backbone are planar. The equations of the calculated best planes and the angles between the different planes are listed in Table 2.

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Structure of 3,3-Di(*o*-tolyl)phthalide

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Abstract. $C_{22}H_{18}O_2$, $M_r = 314.18$, monoclinic, $P2_1/c$, $a = 8.614$ (2), $b = 7.210$ (2), $c = 27.620$ (6) Å, $\beta = 93.98$ (11)°, $Z = 4$, $\mu(\text{Cu } K\alpha) = 0.632 \text{ mm}^{-1}$, $D_c = 1.248$, $D_m = 1.245 \text{ Mg m}^{-3}$. The structure was refined to $R = 0.064$, $R_w = 0.065$, for 2252 independent reflections. The angle between the planes of the two tolyl groups is 81.7 (6)°, and the angles between the plane of the phthalide ring and the planes of each of the tolyl groups are 77.8 (3) and 65.1 (5)°. The two C–O bonds in the γ -lactone group differ significantly in length, 1.477 (4) and 1.368 (4) Å, the shorter being adjacent to the carbonyl group.

Introduction. 3,3-Di(*o*-tolyl)phthalide was synthesized according to the method of Bartlett & Jones (1942). It was recrystallized from nitromethane by slow evaporation at room temperature. Preliminary crystal data were determined by photographic methods. A transparent crystal 0.3 × 0.3 × 0.4 mm was used on a computer-controlled Picker diffractometer; 2252 independent reflections with $I > 3\sigma(I)$ were collected up to $2\theta = 120^\circ$ with Ni-filtered Cu $K\alpha$ radiation and the

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ω – 2θ scanning technique. The cell dimensions were obtained by a least-squares fit to the 2θ values of 20 reflections. Lorentz and polarization corrections were applied, but none were made for absorption.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The E map revealed all the nonhydrogen atoms. Full-matrix isotropic least-squares refinement gave $R = 0.108$. All H atoms were then located on a difference map. The final $R = 0.064$.*

Discussion. The final positional parameters are given in Table 1. Fig. 1 shows a perspective view of the molecule. The bond lengths and angles are given in Fig. 2.

The average C–C distances and the mean C–C–C angles of the phenyl rings in the two *o*-tolyl groups are 1.391 (13) Å, 120.0 (12)° and 1.392 (14) Å,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34986 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.