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Poly{1,2-bis[4-(phenylcarbamoyloxy)-*n*-butyl]-1-buten-3-ynylene}

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Abstract. $(C_{13}H_{14}NO_2)_n$, monoclinic, $P2_1/a$, a = 6.229 (5), b = 39.027 (10), c = 4.909 (4) Å, $\beta = 106.85$ (5)°, $D_x = 1.26$ g cm⁻³, Z = 4. The bond lengths of the polymer backbone indicate a strong contribution of electron delocalization.

Table 1. Final atomic coordinates $(\times 10^4)$

The e.s.d.'s are given in parentheses. The coordinates of the H atoms have been calculated.

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Introduction. Substituted diacetylenes have been found to be highly reactive in the solid state. Topochemical polymerization by 1:4 addition of neighboring molecules is initiated by exposure to UV, X-ray or yray irradiation or by thermal treatment. In this way large, nearly defect-free polymer single crystals can be obtained (Wegner, 1972; Baughman, 1974). These materials are of special interest as model substances for quasi-one-dimensional organic solids with interesting electronic properties (Wilson, 1975). From X-ray diffraction (Hädicke, Mez, Krauch, Wegner & Kaiser, 1971; Kobelt & Paulus, 1974; Enkelmann, 1977) and from spectroscopic studies (Baughman, Witt & Yee, 1974) the polymer backbone is best represented by the acetylene structure $\begin{pmatrix} R \ge C - C \equiv C - C \leq R \end{pmatrix}$. The title compound was investigated because recent studies (Baughman, Witt & Yee, 1974; Iqbal, Chance & Baughman, 1978) show evidence for significant reso-

nance contribution from the butatriene structure $\binom{R}{=}C=C=C=C=C\leq_R$ corresponding to considerable

 π -electron delocalization.

Polymerization of the crystals was effected by γ -ray irradiation with a dose of 100 Mrad. The specimen used for intensity collection was leached to remove residual monomer. It was mounted along **a**. The systematic absences were 0k0 for k odd and h0l for h odd. Intensities were collected on a computercontrolled Picker FACS-I system with Ni-filtered Cu $K\alpha$ radiation. Of the 1140 independent, not systematically absent, reflections ($2\theta < 110^{\circ}$) significant counts were recorded for 728. The θ -2 θ scan mode was used.

The raw data were corrected for Lorentz and polarization effects. Absorption corrections were ap-

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C(1)	4799 (17)	5039 (2)	6048 (13)
C(2)	4558 (19)	5101 (2)	8709 (20)
C(3)	3059 (27)	5408 (3)	9033 (22)
C(4)	1099 (25)	5497 (3)	6783 (20)
C(5)	-500 (23)	5768 (3)	7617 (22)
C(6)	-2248 (26)	5893 (3)	5271 (21)
C(7)	-5278 (26)	6297 (3)	4881 (26)
C(8)	-8110 (29)	6697 (4)	5386 (29)
C(9)	-8209 (27)	6974 (4)	6986 (26)
C(10)	-9953 (29)	7205 (4)	6190 (31)
C(11)	-11542 (27)	7163 (4)	3501 (34)
C(12)	-11337 (31)	6891 (4)	1921 (30
C(13)	-9648 (27)	6659 (3)	2741 (25)
O(1)	-3588 (16)	6109 (2)	6580 (13)
O(2)	-5652 (17)	6287 (2)	2284 (14
N	-6296 (21)	6465 (3)	6414 (18
H(1)	2135	5350	666
H(2)	4011	5655	9192
H(3)	1875	5641	5333
H(4)	125	5299	5667
H(5)	-937	5556	8667
H(6)	938	5940	8200
H(7)	-1250	6068	4333
H(8)	-3125	5709	4000
H(9)	-6096	6399	8459
H(10)	-7014	7006	8866
H(11)	-10050	7403	7451
H(12)	-12805	7332	2859
H(13)	-12549	6857	68
H(14)	-9512	6461	1483

 Table 2. Calculated and observed bond lengths (Å) in polydiacetylenes

	C(1)–C(1)	C(1)–C(2)	C(2)–C(2)
Acetylene structure	1.21	1.43	1.34
$\begin{pmatrix} R \ge C - C = C - C \leqslant_R \end{pmatrix}$ calculated			
Butatriene structure	1.28	1.32	1.46
$\binom{R > C = C = C = C < R}{calculated}$			
Kobelt & Paulus (1974)	1.191 (4)	1.356 (4)	1-428 (4)
Hädicke et al. (1971)	1.21	1.36	1.41
This study *	1.17 (1)	1.38 (1)	1.46 (1)

* An earlier refinement gave bond lengths of 1.24 (1), 1.37 (1) and 1.44 (1)Å.

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plied (Knox, 1967). The structure was solved with MULTAN (Declercq, Germain, Main & Woolfson, 1973). Refinement was by full-matrix least squares, minimizing $\sum w(F_o - F_c)$. The final R_w was 0.081, with R = 0.093. The weights were $1/[\sigma(F)]^2$, where $\sigma(F)$ was derived from counting statistics. The H atoms were assigned reasonable parameters and their contributions included in structure factor calculations. The programs used were those of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965). The final atomic coordinates are given in Table 1.*

Discussion. The observed bond lengths and angles are shown in Fig. 1. The bond lengths in the polymer backbone indicate indeed a contribution of the butatriene structure. In particular, the double and single bonds seem to be interchanged whereas the triple bond has the expected value. The bond lengths of the two model structures and of the known polydiacetylene structures

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33465 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



Fig. 1. Observed bond lengths (Å) and angles (°). The thermal ellipsoids represent 50% probability (Johnson, 1965). E.s.d.'s for C-C, 0.02; C-O, 0.01; C-N, 0.01 Å; the e.s.d. of the angles is 1.1°.

are listed in Table 2. The conjugation of the polymer backbone seems to be continued in the side chain. Here every second C-C bond is significantly shortened. Further investigations are necessary to elucidate the nature of this effect. The geometry of the hydrogen bonding is also shown in Fig. 1. The side chains are linked together by intramolecular hydrogen bonds parallel to the main chain forming sheets stacked along **a.** The urethane group and the phenyl ring are planar, forming an angle of 31.3° . The aliphatic side chain is an almost planar zigzag.

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