

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

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(Received 10 February 1978; accepted 9 March 1978)

Abstract. (C₁₃H₁₄NO₂)_{*n*}, monoclinic, *P*2₁/*a*, *a* = 6.229 (5), *b* = 39.027 (10), *c* = 4.909 (4) Å, β = 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.

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 γ-ray 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 $\left(\begin{array}{c} R \\ \diagup \\ \text{C} \\ \diagdown \\ R \end{array} \right) \text{C} \equiv \text{C} - \text{C} = \text{C} \left(\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R \end{array} \right)$. The title compound was investigated because recent studies (Baughman, Witt & Yee, 1974; Iqbal, Chance & Baughman, 1978) show evidence for significant resonance contribution from the butatriene structure $\left(\begin{array}{c} R \\ \diagup \\ \text{C} \\ \diagdown \\ R \end{array} \right) \text{C} = \text{C} = \text{C} = \text{C} \left(\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R \end{array} \right)$ 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 0*k*0 for *k* odd and *h*0*l* for *h* odd. Intensities were collected on a computer-controlled Picker FACS-I system with Ni-filtered Cu Kα radiation. Of the 1140 independent, not systematically absent, reflections (2θ < 110°) significant counts were recorded for 728. The θ–2θ scan mode was used.

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

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Table 1. Final atomic coordinates (× 10⁴)

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

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|-------------|----------|-----------|
| 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 $\left(\begin{array}{c} R \\ \diagup \\ \text{C} \\ \diagdown \\ R \end{array} \right) \text{C} \equiv \text{C} - \text{C} = \text{C} \left(\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R \end{array} \right)$ | 1.21 | 1.43 | 1.34 |
| calculated | | | |
| Butatriene structure $\left(\begin{array}{c} R \\ \diagup \\ \text{C} \\ \diagdown \\ R \end{array} \right) \text{C} = \text{C} = \text{C} = \text{C} \left(\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R \end{array} \right)$ | 1.28 | 1.32 | 1.46 |
| calculated | | | |
| Kobelt & Paulus (1974) | 1.191 (4) | 1.356 (4) | 1.428 (4) |
| Hädicke <i>et al.</i> (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.

