

the actual dimensionality of our system is almost certainly greater than 2.

Our choice of topology A is reinforced by the fact that the oscillations of Figure 10 connect directly to those observed in the neighborhood of the cross point *P* in Figure 8. From the cross-shaped diagram theory,⁵ such oscillations result from periodic transitions between two steady states, which cannot occur in case B where the oscillations are an intrinsic property only of the low iodide branch corresponding to the *S*₁ state. The theory predicts that oscillating systems resulting from the combination of bistability and a feedback can easily give rise to a subcritical bifurcation as in A and that as the time scale of the feedback decreases, resulting in a shorter oscillation period, the width of the hysteresis region will initially increase. The fact that the hysteresis phenomena shown in Figure 10 are most readily observed at lower pH, where the period of oscillation is shorter and where both process B and process C are more rapid, supports this view. Such behavior has also been observed in the Briggs-Rauscher⁵ and Belousov-Zhabotinskii^{18,19} systems.

With the exception of the above topological considerations, the results and discussion presented in this paper have been almost purely experimental. Although three overall processes (A), (B), and (C) have been suggested, no attempt has been made to construct a mechanism for this reaction. Before undertaking such

a task, we feel that it is essential to understand the component processes and any other competing reactions. The kinetics of the chlorite-iodide reaction A have been thoroughly studied in batch conditions.^{11,12} In contrast, almost nothing is known about the kinetics of the chlorite-iodine reaction B, which is apparently crucial in producing oscillations. Investigations of this system are now under way in this laboratory. Although much work has been done on the kinetics of the Dushman reaction (C), both its rate law¹⁵ and its mechanism^{15,20} remain subjects of some controversy. Finally, the role of chlorine dioxide, which is certainly present in significant amounts in the system at low pH, where oscillations are most prevalent, also remains to be established.

Given its central role in a new family of oscillatory reactions, the chlorite-iodide system is destined to be the subject of thorough study in the coming years. We emphasize here the importance of firmly establishing the kinetics of the component processes of this reaction, so that future mechanistic interpretations may have firm ground to rest upon.

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Diacetylene Monomers and Polymers with Chiral Substituents: Structure, Solid-State Polymerization, and Properties

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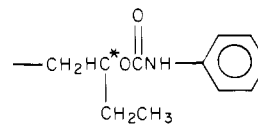
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Abstract: Two solid-state polymerizable monomer phases are obtained for the unresolved diacetylene having the chiral substituent group -CH₂HC*(CH₂CH₃)OCONHC₆H₅. The crystals of the first phase (phase I) are orthorhombic, space group *Pbca*, with *a* = 45.982 (7), *b* = 10.879 (1), *c* = 9.603 (1) Å; there are eight molecules in the cell. A three-dimensional structure determination for phase I indicates chiral molecules which react by 1,4-addition polymerization of glide-related neighbors having opposite handedness to provide a regular backbone structure in which nearest-neighbor substituent groups have different chirality, but next-nearest-neighbor groups have the same chirality. The crystals of phase II are monoclinic, space group *P2₁/c*, with *a* = 5.181 (2), *b* = 36.629 (10), *c* = 6.827 (2) Å, *β* = 113.17 (2)°, and there are two diacetylene monomer molecules in the cell. Centrosymmetric diacetylene molecules present in the racemic phase II react by 1,4-addition polymerization with translation-related neighbors. Phase I polymerizes by solid solution formation to provide a polymer crystal, while phase II polymer is ordered only in the chain-axis projection. The polymerization reactions are interpreted using least motion and symmetry arguments. The structural work on phase I suggests that backbone strain provides the blue-shifted absorption spectra and excludes excimer emission from overlapping phenyls as the origin of strong fluorescence.

I. Introduction

The bis(phenylurethane) of 5,7-dodecadiyne-3,10-diol (UDD) provides reactive phases which polymerize in the solid state by 1,4-addition of the diacetylene groups. Several aspects of these compounds generate interest in the monomer and polymer phases. In contrast with other diacetylenes and polydiacetylenes for which structural information is available, the substituent groups on UDD

are chiral. This substituent group chirality means that it is possible to isolate polymerizable crystalline phases consisting of either chiral molecules (R-C≡C-C≡C-R and S-C≡C-C≡C-S) or potentially centrosymmetric molecules (R-C≡C-C≡C-S), where R and S designate opposite handed forms of the substituent



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Table I. Cell Data for Phase I UDD

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
after preliminary examination (~4 h irradiation)	46.251 (7)	10.832 (1)	9.578 (1)	4798
during course of analysis (~19 h irradiation)	46.180 (8)	10.846 (2)	9.588 (2)	4802
at conclusion of analysis (~4.8 days irradiation)	45.982 (7)	10.879 (1)	9.603 (1)	4804

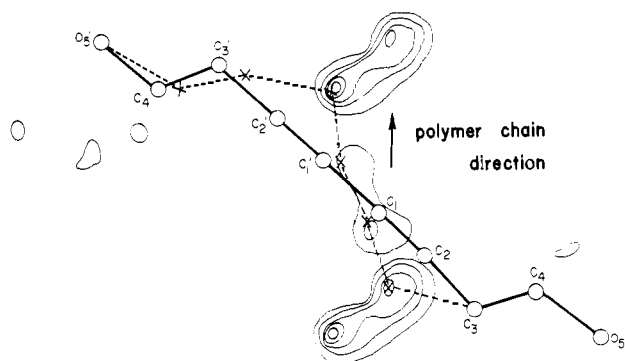


Figure 1. A view of the difference map for the UDD (phase I) crystal in a plane containing the diacetylene rod. The positions of the monomer atoms and bonds are shown by circles and solid lines, respectively. The contours indicate positive electron density in the difference map. The positions of the polymer atoms are indicated by X's (some of the X's lie off the plane of the map shown).

nonhydrogen atoms had been refined by least-squares methods, a difference map yielded the positions for almost all the hydrogen atoms, including those attached to nitrogen. The remaining hydrogen atoms were positioned according to standard geometric criteria. Full-matrix least-squares refinement was continued, varying the positional and anisotropic thermal parameters but keeping the hydrogen atoms fixed with $B_{iso} = 10 \text{ \AA}^2$. The final values of R and R_w were 0.080 and 0.088, respectively, and the "goodness of fit" was 2.15.⁶ The weighting scheme used was $w = 1/[\sigma(F_o)^2 + 0.0004(F_o)^2]$ and the scattering curves were taken from the analytical expressions in the "International Table for X-ray Crystallography".⁷

A difference map showed that the two highest peaks lay in the region between adjacent diacetylene rods; they had heights $\sim 0.5 \text{ e \AA}^{-3}$. These peaks were positioned such that they could represent sites occupied by the atoms C(2) and C(2') in a polymeric structure formed as a solid solution in the monomer. It was also noted that the atoms C(1) and C(1') displayed significant anisotropic motion with the greatest vibrations or apparent vibrations being in the direction toward the satellite peaks. However, it was realized that simply considering these two peaks as minor sites for the atoms C(1) and C(1') in a product molecule would not allow a chemically reasonable polymer structure to be drawn. Nevertheless, these sites were included in a refinement which showed that the sites behaved in a stable fashion and had an occupancy of $\sim 15\%$. Values obtained for R and R_w were 0.073 and 0.081, respectively, and the "goodness-of-fit" was 1.96. A careful examination of the difference map (Figure 1) calculated at the conclusion of the single-site refinement revealed the presence of several additional possible sites for atoms in the central part of the molecule as part of a product polymeric structure. As part of this trial structure for the polymer, we included two sites to explain the elongated thermal ellipsoids for C(1) and C(1'). Least-squares refinement of only the occupancies of the atoms at the major (monomer) and minor (polymer) sites was well behaved and suggested 83:17 as the best overall choice. Refinement was then continued, holding the occupancies fixed, but allowing the positional and anisotropic thermal parameters for the nonhydrogen atoms in the monomer and the positional

(6) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$; "goodness of fit" = $[\sum w|F_o - F_c|^2 / (m - n)]^{1/2}$, where m = number of variables and n = number of adjusted parameters.

(7) "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974, pp 99-102.

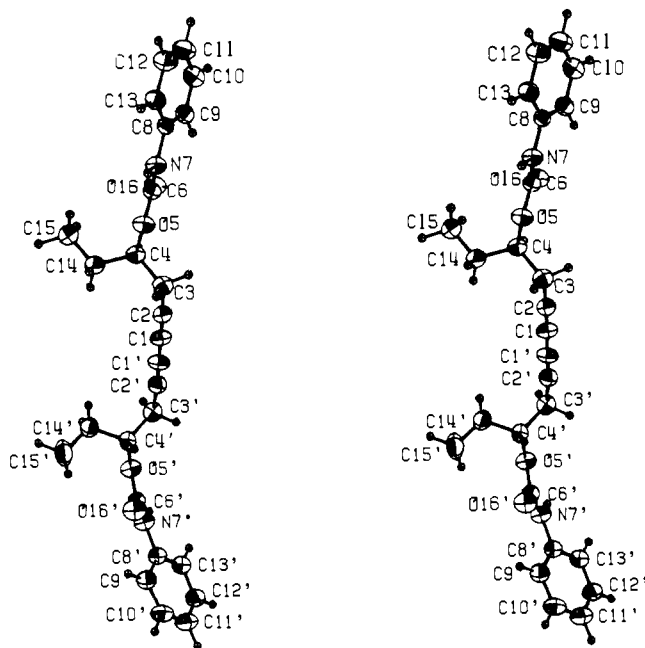


Figure 2. Stereoscopic view of a molecule of UDD monomer at end of "single-site" refinement for phase I. The markedly anisotropic thermal ellipsoids for C(1) and C(1') can be noted.

and isotropic thermal parameters for the atoms in the polymer to vary.⁸ This refinement converged to values of R and R_w of 0.069 and 0.075, respectively, and the "goodness of fit" was 1.84.⁹

The final positional parameters for both major and minor sites are given in Table II. The positional and thermal parameters at the conclusion of the single-site refinement and the thermal parameters of the two-site model and the final values of the observed and calculated structure factors are included as supplementary material.

Phase II. Pertinent crystal data for the phase II monomer having the same molecular formula and weight as phase I are: monoclinic, $P2_1/c$, $a = 5.181 (2)$, $b = 36.629 (10)$, $c = 6.827 (2) \text{ \AA}$, $\beta = 113.17 (2)^\circ$, $V = 1191 \text{ \AA}^3$, $F(000) = 460.0$, $Z = 2$, $\rho_{calcd} = 1.207 \text{ g cm}^{-3}$, $\rho_{obsd} = 1.203 (5) \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 5.8 \text{ cm}^{-1}$. Cell data were obtained in a fashion similar to that for phase I. Throughout the course of the data collection (39.4 exposure hours) there was slight random fluctuation of the standard reflections, but none of their intensities consistently increased or decreased and the changes were always less than 5% of the original intensity; the cell constants did not change. However, a slight orange tint to the originally colorless crystal was noted at the end of data collection. The $+h, +k, \pm l$ quadrant of reflections up to a maximum of 130° in 2θ (Cu K α) was collected. Of the 2007 unique reflections collected, 1616 had intensities greater than $3\sigma(I)$ and these were used in the subsequent structural analysis. The data were corrected for Lorentz and polarization effects; corrections for absorption and extinction were not warranted.

The structure of phase II was solved by direct phasing methods using the SHELX 76 program.¹⁰ All nonhydrogen atoms were located from an E map and, after refinement of their positions and anisotropic thermal parameters, all hydrogen positions were located from a difference Fourier map. Full matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for H atoms led to final agreement values of $R = 0.038$ and $R_w = 0.052$,⁶ where $w = 1.02/[\sigma(F_o)^2 + 0.0003(F_o)^2]$; the scattering curves were those cited above.⁷ In the final cycle the greatest shift/error was 0.064 and the largest peak in the final difference map was

(8) Minor sites were included for C(1), C(2), C(1'), C(2'), C(3') and C(4'). An attempt was made to include a minor site for C(3), but the parameters did not remain stable upon least-squares refinement and it was removed from the final model. The C(3) (monomer)-C(2) (polymer) distance is quite long (1.84 \AA). It is possible that there is, in fact, more than one site for C(3) polymer and that these sites do not have sufficient occupancy to show up clearly in the difference map or behave in a stable fashion in least-squares refinement.

(9) Several cycles of refinement of the final model with positional and thermal parameters fixed but varying occupancy factors indicated that the occupancies did not change by more than 1%. Thus we present the final model with the occupancies in the 83:17 ratio.

(10) G. M. Sheldrick, SHELX 76, a program for crystal-structure determination, University of Cambridge, England, 1976.

Table II. Final Atomic Parameters for Phase I at the End of the Major and Minor Site Refinement^a

atom	x	y	z
C1	-0.03695 (8)	0.3458 (4)	0.0525 (4)
C2	-0.01884 (8)	0.3430 (4)	-0.0356 (4)
C3	0.00289 (8)	0.3406 (4)	-0.1435 (4)
C4	0.02793 (7)	0.2557 (4)	-0.1057 (4)
O5	0.05002 (4)	0.2794 (2)	-0.2086 (2)
C6	0.07670 (7)	0.3099 (3)	-0.1628 (3)
N7	0.09502 (5)	0.3191 (3)	-0.2726 (3)
C8	0.12473 (7)	0.3528 (3)	-0.2676 (3)
C9	0.13605 (7)	0.4228 (4)	-0.1596 (4)
C10	0.16503 (8)	0.4535 (4)	-0.1631 (4)
C11	0.18234 (8)	0.4174 (4)	-0.2704 (5)
C12	0.17101 (9)	0.3507 (4)	-0.3776 (4)
C13	0.14211 (8)	0.3170 (4)	-0.3780 (4)
C14	0.01992 (8)	0.1202 (4)	-0.1145 (4)
C15	0.04408 (9)	0.0360 (4)	-0.0730 (6)
O16	0.08279 (5)	0.3250 (3)	-0.0412 (2)
C1'	-0.05902 (8)	0.3412 (4)	0.1528 (4)
C2'	-0.07694 (8)	0.3341 (4)	0.2385 (4)
C3'	-0.10062 (8)	0.3201 (4)	0.3417 (4)
C4'	-0.12362 (8)	0.2266 (4)	0.2902 (4)
O5'	-0.14644 (5)	0.2404 (3)	0.3858 (2)
C6'	-0.17296 (7)	0.2574 (4)	0.3305 (3)
N7'	-0.19223 (6)	0.2861 (3)	0.4293 (2)
C8'	-0.22076 (7)	0.3296 (3)	0.4063 (3)
C9'	-0.23794 (8)	0.2863 (4)	0.2993 (4)
C10'	-0.26548 (8)	0.3351 (4)	0.2810 (4)
C11'	-0.27604 (8)	0.4234 (5)	0.3683 (5)
C12'	-0.25896 (8)	0.4649 (4)	0.4765 (4)
C13'	-0.23132 (8)	0.4195 (4)	0.4959 (3)
C14'	-0.11088 (9)	0.0982 (4)	0.2949 (5)
C15'	-0.13148 (11)	0.0054 (4)	0.2331 (6)
O16'	-0.17810 (5)	0.2451 (3)	0.2080 (2)
C1P	-0.0422 (3)	0.298 (2)	0.034 (2)
C2P	-0.0339 (6)	0.285 (3)	-0.100 (3)
C1P'	-0.0530 (4)	0.289 (2)	0.153 (2)
C2P'	-0.0575 (5)	0.273 (2)	0.298 (3)
C3P'	-0.0897 (5)	0.318 (2)	0.322 (2)
C4P'	-0.1151 (3)	0.239 (2)	0.295 (2)
H3A	0.0107 (0)	0.426 (0)	-0.155 (0)
H3B	-0.0059 (0)	0.313 (0)	-0.233 (0)
H4	0.0338 (0)	0.271 (0)	-0.006 (0)
H7	0.0875 (0)	0.288 (0)	-0.357 (0)
H9	0.1231 (0)	0.449 (0)	-0.080 (0)
H10	0.1733 (0)	0.505 (0)	-0.084 (0)
H11	0.2032 (0)	0.440 (0)	-0.271 (0)
H12	0.1836 (0)	0.326 (0)	-0.458 (0)
H13	0.1337 (0)	0.268 (0)	-0.456 (0)
H14A	0.0142 (0)	0.100 (0)	-0.212 (0)
H14B	0.0031 (0)	0.104 (0)	-0.050 (0)
H15A	0.0375 (0)	-0.064 (0)	-0.062 (0)
H15B	0.0520 (0)	0.063 (0)	0.019 (0)
H15C	0.0597 (0)	0.041 (0)	-0.145 (0)
H3'A	-0.1090 (0)	0.402 (0)	0.356 (0)
H3'B	-0.0911 (0)	0.290 (0)	0.430 (0)
H4'	-0.1279 (0)	0.247 (0)	0.192 (0)
H7'	-0.1850 (0)	0.306 (0)	0.515 (0)
H9'	-0.2305 (0)	0.220 (0)	0.236 (0)
H10'	-0.2778 (0)	0.305 (0)	0.203 (0)
H11'	-0.2959 (0)	0.460 (0)	0.353 (0)
H12'	-0.2667 (0)	0.527 (0)	0.543 (0)
H13'	-0.2188 (0)	0.450 (0)	0.573 (0)
H14'A	-0.1073 (0)	0.074 (0)	0.393 (0)
H14'B	-0.0923 (0)	0.094 (0)	0.241 (0)
H15'A	-0.1489 (0)	0.018 (0)	0.302 (0)
H15'B	-0.1229 (0)	-0.081 (0)	0.241 (0)
H15'C	-0.1359 (0)	0.022 (0)	0.135 (0)

^a Atoms designated by primes are related to unprimed atoms by the approximate C_2 axis which is nearly along the b axis. Atoms with a P indicate that they represent the polymer. Hydrogen atoms are numbered according to the atom to which they are bonded.

$0.12 \text{ e } \text{Å}^{-3}$. There were few peaks in this map near the diacetylene moiety, the largest representing only $0.07 \text{ e } \text{Å}^{-3}$. The absence of residual electron density near the diacetylene portion of the molecule and the

Table III. Final Positional Parameters for Phase II UDD^a

atom	x	y	z
O5	0.3297 (2)	0.61661 (3)	0.5406 (2)
O16	-0.0812 (2)	0.64176 (3)	0.3199 (2)
N7	0.3294 (3)	0.65290 (4)	0.2814 (2)
C1	0.4048 (4)	0.51300 (4)	0.5031 (3)
C2	0.2392 (4)	0.53531 (4)	0.5068 (3)
C3	0.0405 (4)	0.56309 (4)	0.5140 (3)
C4	0.1799 (3)	0.59628 (4)	0.6471 (3)
C6	0.1701 (3)	0.63758 (4)	0.3750 (2)
C8	0.2326 (3)	0.67611 (4)	0.1008 (2)
C9	-0.0342 (4)	0.67357 (5)	-0.0581 (3)
C10	-0.1126 (4)	0.69659 (5)	-0.2319 (3)
C11	0.0722 (4)	0.72204 (5)	-0.2513 (3)
C12	0.3387 (4)	0.72406 (5)	-0.0948 (3)
C13	0.4204 (3)	0.70151 (4)	0.0807 (3)
C14	0.3913 (4)	0.58807 (6)	0.8676 (3)
C15	0.2638 (6)	0.56741 (9)	1.0007 (4)
H3	-0.075 (4)	0.5717 (5)	0.367 (3)
H3'	-0.085 (4)	0.5506 (5)	0.575 (3)
H4	0.033 (3)	0.6126 (4)	0.652 (2)
H7	0.491 (4)	0.6477 (5)	0.334 (3)
H9	-0.174 (4)	0.6558 (6)	-0.050 (3)
H10	-0.299 (4)	0.6942 (6)	-0.350 (3)
H11	0.021 (4)	0.7389 (5)	-0.373 (3)
H12	0.481 (5)	0.7409 (6)	-0.112 (4)
H13	0.612 (4)	0.7024 (5)	0.192 (3)
H14	0.542 (4)	0.5741 (5)	0.854 (3)
H14'	0.469 (4)	0.6120 (6)	0.936 (3)
H15	0.398 (6)	0.5634 (7)	1.151 (5)
H15'	0.191 (5)	0.5432 (7)	0.938 (4)
H15''	0.089 (6)	0.5803 (8)	0.999 (4)

^a The other half of the molecule is obtained by inversion through the center of symmetry at $1/2, 1/2, 1/2$.

stability of the standard reflections and cell constants upon exposure of the phase II crystal to X-rays were taken as proof that the extent of polymerization in phase II was small and had no significant bearing on the results of the X-ray experiment.¹¹ The final coordinates for UDD phase II are given in Table III. The thermal parameters and structure factors will appear in the microfilm edition.

IV. Results of the Crystal Structure Analysis

(a) **Molecular Structure.** A stereoscopic view of the "molecule" of UDD in phase I at the end of the single-site refinement for all atoms is shown in Figure 2. It can be seen that the thermal ellipsoids for C(1) and C(1') are quite anisotropic because of the omission of the minor sites from the model. Bond lengths and angles at the end of the two-site refinement are given in Table IV. The molecule has no site symmetry, but somewhat approaches C_2 symmetry with the twofold axis running approximately along the b axis. The molecule is in an almost fully extended conformation. The crystal of phase I is a racemate made up of equal numbers of molecules with alternately R,R and S,S configurations at C(4) and C(4'), respectively. The crystal packing is such that along the c axis (the direction of polymerization) nearest-neighbor molecules related by a glide plane are R,R and S,S . The bond lengths in the central part of the diacetylene chain resulting from the two-site refinement are C(3)-C(2) = 1.440 (5), C(2)-C(1) = 1.187 (5), C(1)-C(1') = 1.400 (5), C(1')-C(2') = 1.167 (5),

(11) Since $P2_1/c$ is a uniquely determined space group, there should in principle be no ambiguity in determining crystal symmetry. However, precession photographs of the $h0l$ plane of phase II contain observed reflections which would normally have been assigned as having additional indexes, indicating that no c glide was present. However, subsequent investigation indicated that there were unscreened upper level reflections coming through owing to the long b axis. Refinement of the structure including both observed and unobserved reflections in the space groups $P2_1$ and $P2_1/c$ led to final values of $R = 0.078$, $R_w = 0.109$, and $R = 0.052$, $R_w = 0.054$, for the two models, respectively. Further convincing evidence for the centrosymmetric choice was (1) the refinement in $P2_1$ had not converged after 10 cycles of full-matrix least-squares refinement, (2) the hydrogen atoms moved out of reasonable bonded positions and could not be relocated from a difference map and (3) the esd 's on all the heavy atom bonded distances were a factor of 4 times worse for the $P2_1$ model than the $P2_1/c$ model.

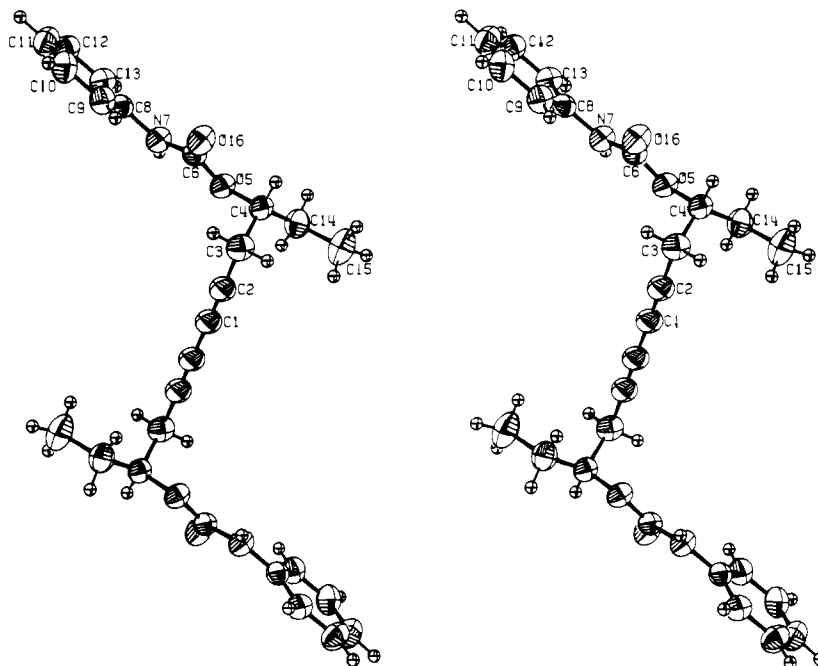


Figure 3. A stereoscopic view of the centrosymmetric UDD phase II molecule. Only half of the atoms are numbered; the remainder would be generated by inversion through the center.

and $C(2')-C(3') = 1.480$ (5) Å. The unequal values for supposedly chemically equivalent bonds may be due to the failure to find separate peaks for $C(3P)$ and $C(4P)$, i.e., the positions of atoms $C(3)$ and $C(4)$ in the polymer.

Figure 3 is a stereoscopic view of the molecule of UDD in phase II with atoms in the asymmetric unit labeled. The symmetry related atoms in the same molecule are henceforth referred to as "prime". Bond lengths and angles are given in Table V. The molecule has $\bar{1}$ site symmetry with the exact center of the $C(1)-C(1')$ bond lying on an inversion center at $1/2, 1/2, 1/2$. The two asymmetric carbon atoms, $C(4)$ and $C(4')$, must show opposite handedness as they are related by an inversion center; therefore, the individual molecule contains both an *R* and an *S* center and is meso. The bond lengths in the diacetylene rod are $C(3)-C(2) = 1.462$ (3), $C(2)-C(1) = 1.192$ (3), and $C(1)-C(1') = 1.383$ (2). While the phase I monomer exhibits an essentially extended conformation, the phase II monomer is significantly bent at $C(4)$ and $C(4')$; the diacetylene plane, containing $C(1)-C(4)$ and $C(1')-C(4')$, and the side chain plane, containing $C(8)$, $N(7)$, $C(6)$, $O(16)$, $O(5)$, $C(4)$, $C(14)$, and $C(15)$, intersect at $C(4)$ and form an angle of 82° ; the torsion angles defined by $C(2)$, $C(3)$, $C(4)$, $C(5)$ and $C(2)$, $C(3)$, $C(4)$, $C(14)$ are 68.6 (2) and -50.9 (2) $^\circ$, respectively.

(b) Crystal Packing A view of the packing of the monomers in phase I looking down the *b* axis is shown in Figure 4a. The molecules form chains along the *c* direction and the chains are stabilized by $N-H \cdots O=C$ hydrogen bonding. The $N(7) \cdots O(16)$ ($x, 1/2 - y, -1/2 + z$) and $N(7') \cdots O(16')$ ($x, 1/2 - y, 1/2 + z$) distances are 3.070 (3) and 2.774 (3) Å, respectively; the $H(7) \cdots O(16)$ and $H(7') \cdots O(16')$ distances are 2.17 and 1.96 Å and the $N(7)-H(7) \cdots O(16)$ and $N(7') \cdots H(7')-O(16')$ angles are 161 and 148° . A representation of the phase I polymer structure is shown in Figure 4b. In this figure, the central portion of the molecule is constructed from the minor sites found in the analysis while the side chains are identical with those for the monomer. In phase II, the monomer molecules pack such that the *a* axis is the direction of polymerization. Reacting nearest-neighbor molecules, each having *R,S* configuration, are related by a unit translation along *a*. A view of the packing looking down the *c* axis is shown in Figure 5. Like the phase I monomer, phase II forms chains of molecules in the direction of polymerization and these are stabilized by $N-H \cdots O=C$ hydrogen bonding. The $H(7) \cdots O(16)$ and $N(7) \cdots O(16)$ distances are 2.26 (2)

and 2.989 (2) Å, respectively, and the $N(7)-H(7) \cdots O(16)$ angle is 152 (2) $^\circ$.

V. Discussion

The X-ray structural study on phase I crystals of UDD indicates that polymerization occurs by reaction of $R-C \equiv C-C \equiv C-R$ and $S-C \equiv C-C \equiv C-S$ molecules related by a *c*-glide plane. Consequently, the polymer structure is $[=(R)C-C \equiv C-C-(R)=(S)C-C \equiv C-C(S)=]_n$, rather than the alternative halved or doubled repeat structures. This unusual synthesis of a polymer with regularly alternating substituents of different chirality evidences the power of solid-state reactions as a synthetic method.

The structure of UDD phase II reveals that the polymerization reaction must take place between translationally related (along the *a* axis) $R-C \equiv C-C \equiv C-S$ molecules. Thus, the polymer formed is $[=(R)C-C \equiv C-C(S)=]$.

The structural work provides information relevant to a better understanding of the solid-state synthesis of polydiacetylenes. The continuous change in cell parameters during X-ray irradiation (Table I), which is often observed for diacetylene reactions,¹²⁻¹⁴ and the appearance of product molecules in the electron density maps provide clear indication that phase I UDD polymerizes as a single-phase reaction. Product polymers in polymerizing monomer phases have previously been observed in electron density maps for only two materials, S_2N_2 ^{15,16} and a cyclic diacetylene.¹⁷

The phase I polymer appears to be isomorphous with the starting monomer phase, while the phase II polymer has only a liquid crystal-like degree of order. This difference in perfection does not imply a difference in reaction uniqueness for the two phases, since in both cases the monomer lattice symmetry elements are possible symmetry elements for the polymer chain. The X-ray

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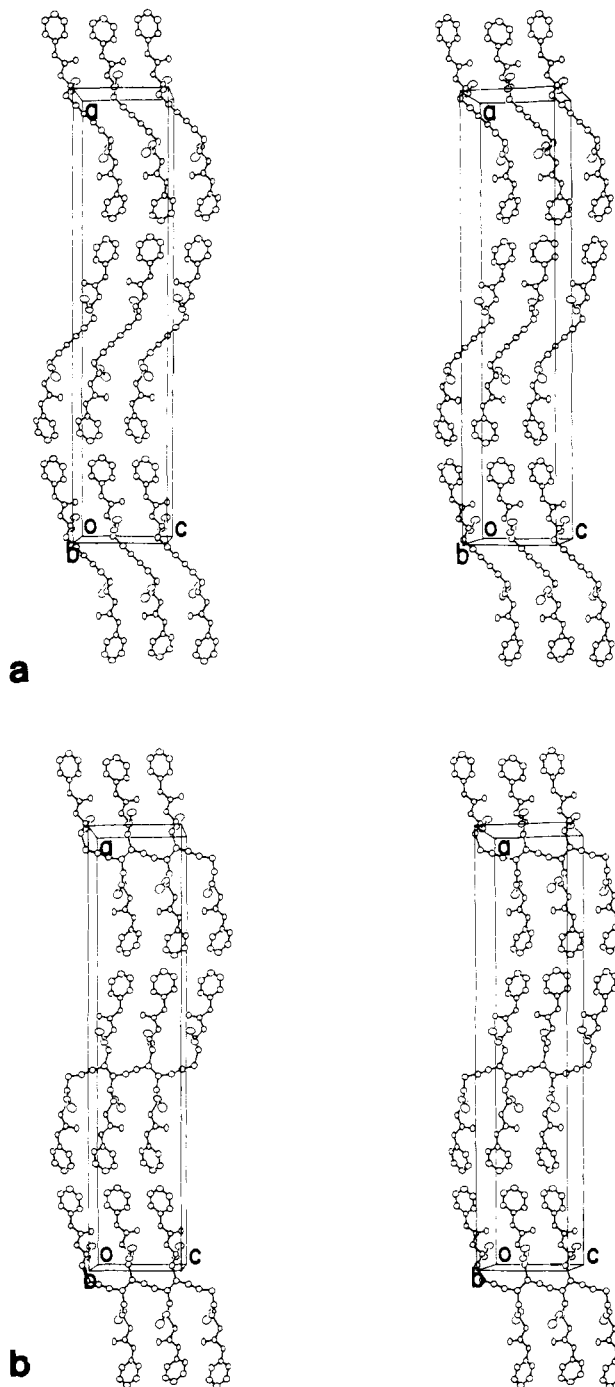


Figure 4. (a) Stereoscopic view of the packing of monomer UDD molecules in the phase I unit cell. The a axis is vertical and the c axis is horizontal. (b) Stereoscopic view of the packing of polymer UDD molecules in the phase I unit cell. This structure for the polymer is obtained by combining the position of the side-chain atoms from the monomer with the polymer positions for the central portion obtained from the two-site refinement.

study shows no evidence for solid-solution formation in the case of phase II. However, formation of a small amount of disordered polymer would not have been detected.

The monomer site symmetry for both phase I (unity) and phase II ($\bar{1}$) is a possible symmetry for the monomer unit in the polymer chain and the symmetry relationship between mutually reacting monomer units (c glide and a translation, respectively) is a possible symmetry relationship between neighboring monomer units in trans polydiacetylene. Consequently, the introduction of disorder is not required by symmetry elements in the parent phase which cannot be accommodated in an ordered product structure.^{1,12}

A number of ideas have been advanced to predict reactivity

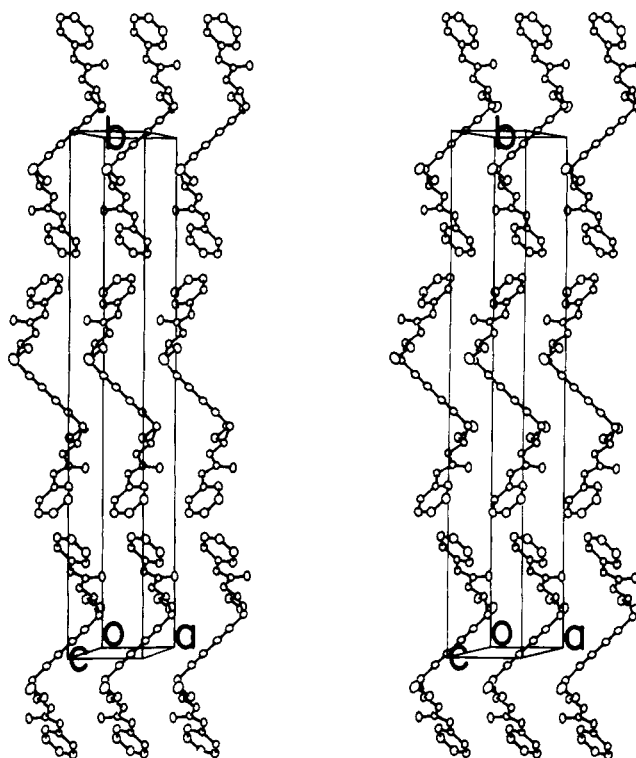


Figure 5. Packing diagram for UDD phase II monomer. The reference molecule is in the center of the cell sitting on the inversion center at $1/2, 1/2$. The direction of polymerization is a .

in diacetylene crystals. In the case of UDD, neither phase is extremely reactive, but phase I is significantly more reactive than phase II and forms a much more ordered crystalline product.

The nearest neighbor $C(sp)---C(sp)$ intermolecular distances do not explain the order of reactivity. In phase I, the shortest distance between reacting $C(2)$ and $C(2')$ atoms is 3.944 (5) Å, while the corresponding distance in II is 3.559 (2) Å.

In previous studies^{1,12} the reactivity of diacetylene phases has been correlated with the root-mean-square atom displacements (R_D) for the atoms in the diacetylene rod during formation of an unstrained polymer chain segment by reaction of two diacetylene molecules. The idea behind the correlation of reactivity with R_D is that the structural component of the activation free energy for polymerization is generally expected to increase in proportion to R_D . While the atom displacements for substituent atoms will not be negligible, previous work dealing with the reaction of parallel, coplanar diacetylene rods has shown that R_D adequately represents relative atom displacements for reaction in different phases. Application of the R_D criterion requires that the structure of the polymer be known, especially in cases for which nonplanar backbones are likely possibilities. In the case of UDD phase I, the neighboring diacetylene rods in the reaction direction are not translationally equivalent but are related by a glide plane. The projection of the two neighboring diacetylene rods onto the best plane containing the reference rod and some neighboring groups is shown in Figure 6. From this figure it can be seen that the reference rod is translated by 2.0 Å from the plane containing the two neighboring rods and is crossed with respect to these neighboring rods by an angle of 6° . However, reasonably well-determined positions for the polymer atoms $C(1P)$, $C(2P)$, $C(1P')$, and $C(2P')$ are known from the analysis. Using these polymer positions, R_D for phase I is 0.95 Å, a value which is consistent with moderate reactivity.^{1,12} Also, the center to center distance between mutually reacting monomer rods is 5.164 Å.

Although the structure of phase II polymer is not known, it is reasonable to assume that the coplanar arrangement of mutually reacting diacetylene rods in the monomer phase will be replaced by a coplanar polymer backbone involving these atoms. Such is the case for all known polydiacetylene structures which result from

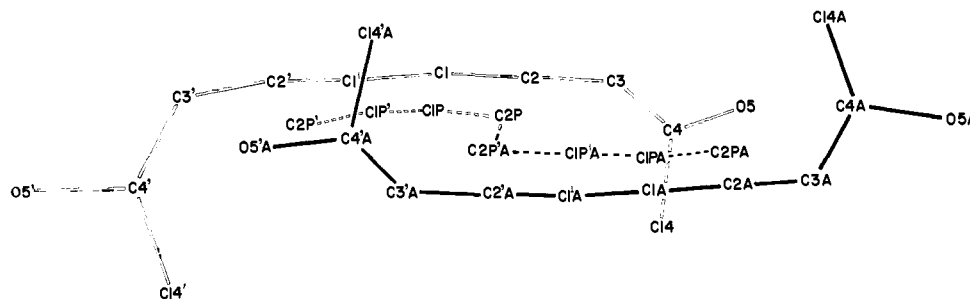


Figure 6. A view of the projection of the central portion of the UDD phase I molecule at $x, 1/2 - y, -1/2 + z$ (dark lines) onto the best plane defined by the atoms C(1), C(2), C(3), C(1'), C(2'), C(3'), C(14), and C(14') of the reference molecule. The position of the polymer that would be produced by reaction between these two diacetylenes is shown by discontinuous lines. It can be seen that the polymeric structure is more planar than the starting monomer array.

Table IV. Bond Lengths (Å) and Angles (Deg) for Phase I UDD after the Major and Minor Site Refinement

Bond, Å			
C(1)-C(2)	1.187 (5)	C(4')-C(14')	1.515 (6)
C(1)-C(1')	1.400 (5)	O(5')-C(6')	1.343 (4)
C(2)-C(3)	1.440 (5)	C(6')-N(7')	1.336 (4)
C(3)-C(4)	1.520 (5)	C(6')-O(16')	1.208 (4)
C(4)-O(5)	1.440 (4)	N(7')-C(8')	1.412 (4)
C(4)-C(14)	1.522 (6)	C(8')-C(9')	1.379 (5)
O(5)-C(6)	1.345 (4)	C(8')-C(13')	1.390 (5)
C(6)-N(7)	1.354 (4)	C(9')-C(10')	1.384 (5)
C(6)-O(16)	1.211 (4)	C(10')-C(11')	1.365 (6)
N(7)-C(8)	1.415 (5)	C(11')-C(12')	1.378 (6)
C(8)-C(9)	1.388 (4)	C(12')-C(13')	1.376 (5)
C(8)-C(13)	1.384 (5)	C(14')-C(15')	1.506 (6)
C(9)-C(10)	1.374 (5)	C(1P)-C(1P')	1.25 (2)
C(10)-C(11)	1.360 (6)	C(1P)-C(2P)	1.35 (3)
C(11)-C(12)	1.362 (6)	C(2P)-C(3)	1.84 (3)
C(12)-C(13)	1.378 (5)	C(1P')-C(2P')	1.42 (3)
C(14)-C(15)	1.494 (6)	C(2P')-C(3P')	1.58 (3)
C(1')-C(2')	1.167 (5)	C(3P')-C(4P')	1.47 (3)
C(2')-C(3')	1.480 (5)	C(4P')-O(5')	1.69 (2)
C(3')-C(4')	1.548 (6)	C(4P')-C(14')	1.55 (2)
C(4')-O(5')	1.402 (4)	C(2P)-C(2P')*	1.59 (4)

A-B-C, deg			
C(1')-C(1)-C(2)	176.0 (4)	N(7')-C(6')-O(5')	110.7 (3)
C(1)-C(2)-C(3)	179.3 (4)	O(16')-C(6')-O(5')	123.2 (3)
C(2)-C(3)-C(4)	111.4 (3)	C(8')-N(7')-C(6')	125.7 (3)
O(5)-C(4)-C(14)	107.8 (3)	C(9')-C(8')-C(13')	120.1 (3)
O(5)-C(4)-C(3)	105.2 (3)	C(9')-C(8')-N(7')	122.3 (3)
C(14)-C(4)-C(3)	113.1 (3)	C(13')-C(8')-N(7')	117.6 (3)
C(6)-O(5)-C(4)	117.5 (3)	C(10')-C(9')-C(8')	119.2 (4)
N(7)-C(6)-O(16)	126.6 (3)	C(11')-C(10')-C(9')	121.2 (4)
N(7)-C(6)-O(5)	109.3 (3)	C(12')-C(11')-C(10')	119.4 (4)
O(16)-C(6)-O(5)	124.1 (3)	C(13')-C(12')-C(11')	120.7 (4)
C(8)-N(7)-C(6)	126.4 (3)	C(8')-C(13')-C(12')	119.4 (3)
C(9)-C(8)-C(13)	120.7 (3)	C(15')-C(14')-C(4')	111.3 (4)
C(9)-C(8)-N(7)	122.0 (3)	C(2P)-C(1P)-C(1P')	168.0 (20)
C(13)-C(8)-N(7)	117.3 (3)	C(3)-C(2P)-C(1P)	116.0 (20)
C(10)-C(9)-C(8)	118.6 (3)	C(4)-C(3)-C(2P)	116.3 (9)
C(11)-C(10)-C(9)	121.0 (4)	C(1P)-C(1P')-C(2P')	165.0 (20)
C(12)-C(11)-C(10)	120.1 (4)	C(3P')-C(2P')-C(1P')	104.0 (20)
C(13)-C(12)-C(11)	120.8 (4)	C(4P')-C(3P')-C(2P')	122.0 (20)
C(8)-C(13)-C(12)	118.7 (3)	O(5')-C(4P')-C(3P')	125.4 (13)
C(15)-C(14)-C(4)	113.5 (4)	C(14')-C(4P')-C(3P')	118.6 (14)
C(1)-C(1')-C(2')	177.7 (4)	O(5')-C(4P')-C(14')	96.4 (9)
C(3')-C(2')-C(1')	176.6 (4)	C(6')-O(5')-C(4P')	124.9 (6)
C(4')-C(3')-C(2')	110.9 (3)	C(15')-C(14')-C(4P')	125.8 (7)
O(5')-C(4')-C(14')	111.6 (3)	C(2P')*-C(2P)-C(1P)	115.8 (23)
O(5')-C(4')-C(3')	103.4 (3)	C(2P')*-C(2P)-C(3P)	128.0 (20)
C(14')-C(4')-C(3')	109.3 (3)	C(2P')*-C(2P')-C(3P')	132.3 (21)
C(6')-O(5')-C(4')	115.8 (3)	C(2P')*-C(2P')-C(1P')	123.6 (21)
N(7')-C(6')-O(16')	126.0 (3)		

* An asterisk indicates atom related by the glide plane to those given in Table II.

the reaction of translationally equivalent monomer molecules. This result is consistent with the polymer chain repeat (4.8 (1) Å) observed from the rotation photographs on phase II polymer. If this assumption is made, R_D for reaction is 0.77 Å.¹⁸ The mo-

Table V. Bond Lengths (Å) and Angles (Deg) for UDD Phase II^a

C(1)-C(1')	1.383 (2)	N(7)-C(8)	1.417 (2)
C(1)-C(2)	1.192 (3)	C(8)-C(9)	1.384 (2)
C(2)-C(3)	1.462 (3)	C(8)-C(13)	1.392 (2)
C(3)-C(4)	1.519 (2)	C(9)-C(10)	1.380 (2)
C(4)-C(14)	1.503 (2)	C(11)-C(12)	1.376 (3)
C(4)-O(5)	1.460 (2)	C(10)-C(11)	1.380 (3)
O(5)-C(6)	1.348 (2)	C(12)-C(13)	1.378 (3)
C(6)-N(7)	1.349 (2)	C(14)-C(15)	1.519 (4)
C(6)-O(16)	1.214 (2)	N(7)-H(7)	0.79 (2)
C(1')-C(1)-C(2)	179.5 (2)	N(7)-C(8)-C(9)	122.9 (1)
C(1)-C(2)-C(3)	178.9 (2)	N(7)-C(8)-C(13)	117.7 (1)
C(2)-C(3)-C(4)	113.7 (1)	C(9)-C(8)-C(13)	119.3 (2)
C(3)-C(4)-O(5)	109.3 (1)	C(8)-C(9)-C(10)	119.9 (2)
C(3)-C(4)-C(14)	115.2 (1)	C(9)-C(10)-C(11)	121.0 (2)
O(5)-C(4)-C(14)	106.3 (1)	C(10)-C(11)-C(12)	118.9 (2)
C(4)-O(5)-C(6)	116.0 (1)	C(11)-C(12)-C(13)	121.0 (2)
O(5)-C(6)-N(7)	110.3 (1)	C(12)-C(13)-C(8)	119.9 (2)
O(5)-C(6)-O(16)	124.1 (1)	C(4)-C(14)-C(15)	112.4 (2)
N(7)-C(6)-O(16)	125.6 (2)	C(6)-N(7)-H(7)	115 (1)
C(6)-N(7)-C(8)	126.1 (1)	C(8)-N(7)-H(7)	119 (1)

^a The C-H bonds range from 0.97 to 1.02 Å, the aromatic C-C-H angles from 110 to 122°, and the aliphatic C-C-H and H-C-H angles from 100 to 113°.

nomer center-to-monomer center vector (reaction direction) is 5.181 Å and the angle between this vector and the diacetylene rods is 46.1°. Although the observed reaction modes for phase I and for phase II UDD are those which result in the lowest possible R_D , in accordance with the prediction of the least motion principle, the order of reactivity for phase I and phase II is not correctly predicted by the simplified least motion theory. Perhaps this discrepancy arises because the calculated atomic displacements refer to the mutual reaction of neighboring molecules in a monomer phase (chain initiation) rather than to the average atomic displacements for formation of a long chain in a structure of specified monomer-to-polymer conversion. The rate of chain initiation might well be highest for the phase II polymer, consistent with the least motion calculations, but a shorter chain propagation distance in phase II could result in the lower overall reactivity compared with phase I. A shorter chain propagation distance in phase II is not unreasonable in light of the larger reaction direction strains (molecular displacements) required for polymerization, as compared with the case for phase I.

A possible explanation for the lower structural order in the phase II polymer relates to the larger displacements of molecular centers required for the phase II polymerization. More specifically, the normal length of a $=C-C\equiv C-C=$ backbone segment in a polydiacetylene is about 4.9 Å.¹² Assuming this approximate chain dimension, polymerization of the phase I crystals requires about a 2.0% increase in length in the reaction direction, while the

(18) This value is obtained by considering the motion along the straight line between monomer and presumed polymer position. If one considers the motion to be simultaneous and proportional rigid body rotation and center of mass translation of the diacetylene rod, a quite similar value (0.82 Å) is obtained.

corresponding required change for phase II crystals is about a 5.7% decrease. It is interesting to note for phase I that a 0.025 Å increase (0.25%) in *c*-axis length was observed at a monomer to polymer conversion of 17%.

Diacetylenes are known which polymerize to high perfection crystals despite similarly large dimensional changes to those required for phase II,^{13,14} but these monomers do not have the additional structural constraints imposed by hydrogen bonding. The lower percent conversion for the γ -ray irradiated phase II crystals (17% vs. 70% for phase I after 50 Mrads of ⁶⁰Co γ -ray irradiation), again a possible consequence of the larger dimensional changes required for polymerization than for phase I, likely contributes to the low degree of order in the monomer-extracted polymer.

Another possible explanation for the difference in reactivity involves a significant difference in the arrangement of side chains. When polymerization occurs, there must be movement of the side chains toward the center of the molecule along the main axis of the side chains. In phase I, the side chain is virtually fully extended (Figure 4a). There would appear to be little hindrance for a cooperative movement of the side chains toward the center with preservation of the hydrogen bonding. The contraction of the molecule in this direction is reflected in the decrease (0.27 Å) in the *a*-axis length during X-ray irradiation (Table I). In phase II, the molecule adopts a much more "zig-zag" shape with the substituent ethyl groups protruding into a crevice in the adjacent molecules (this direction is normal to the view in Figure 5). Thus there could be more resistance to a cooperative contraction in the direction normal to the polymer direction.

The strong fluorescence observed for the phase I UDD polymer is consistent with the blue-shifted absorption spectra, relative to other polydiacetylenes which do not significantly fluoresce. Eximer emission from phenyl rings is excluded as an origin of this fluorescence, since the monomer and polymer have similar structures (evidenced by the quite similar powder diffraction spectra) and the structure of the phase I monomer indicates little overlap between phenyls. The UDD polymer fluorescence is clearly due to the polymer backbone. Chance¹⁹ and Bhattacharjee et al.²⁰ have observed strong fluorescence from solutions of soluble

(19) R. R. Chance, unpublished results.

polydiacetylenes having blue-shifted absorption spectra, for which a nonplanar backbone is suggested.

The blue-shifted polymer absorption spectra do not reflect a low molecular weight for the phase I polymer, since the mechanical properties in the chain direction indicate a reasonably high molecular weight. Consequently, polymer backbone strain provides the most reasonable explanation for the blue shift. Tensile stress in the polymer chain direction is known to cause large blue shifts in the absorption spectra of other polydiacetylenes.²¹ However, the effective stress on the polymer backbone in UDD, provided by minimization of side-group energy, can be much more complicated. Since the mutually reacting diacetylene rods in phase I crystals are nonplanar, retention of this structural feature in the polymer would decrease the effective conjugation, providing a blue-shifted spectra. Patel et al.²² have suggested that low monomer-to-polymer conversion and blue-shifted absorption spectra result from backbone strain in another polymerizable diacetylene, 2,4-hexadiyne-1,6-bis(*m*-tolylurethane). In this case, diacetylene rods for mutually reacting molecules (which are related by a glide plane, as for phase I UDD) form an angle of 72°. Additional structural and spectroscopy studies on the polymerized diacetylene crystals are required to further clarify the relationship between polymer electronic structure and backbone configuration.

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Registry No. UDD, 79664-55-4.

Supplementary Material Available: Thermal and positional parameters for phase I after two-site refinement, atomic coordinates and thermal parameters after single-site refinement, bond lengths and angles from single-site refinement, and thermal parameters and structure factors for phase II UDD (62 pp). Ordering information is given on any current masthead page.

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Mechanisms for the Photooxidation of Protoporphyrin IX in Solution^{1,2}

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Abstract: Protoporphyrin IX dimethyl ester (**1a**) is photooxidized upon irradiation in aprotic organic solvents in the presence of oxygen to yield a mixture of hydroxyaldehydes (**2** and **3**) (photoporphyrins), monoformylmonovinyldeuteroporphyrins (**4** and **5**), and diformyldeuteroporphyrin (**6**). Studies of the reaction under a variety of conditions show that the major portion of all of these products arises via a singlet oxygen path. The formyl products **4-6** can also arise via reaction of the protoporphyrin π cations with superoxide, but this path can be shown to be of only minor importance when only the porphyrin and oxygen are involved in direct irradiation of the porphyrin. Quenching of singlet oxygen by ground-state **1a** occurs with a rate constant $k_p = 8.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; this value is comparable to that measured for other free-base porphyrins but considerably lower than that observed for open-shell metalloporphyrins and for free-base chlorins. The relatively low limiting quantum yield obtained for reaction of **1a** indicates that net physical quenching is the result of most porphyrin-singlet oxygen interactions.

Porphyrins and their metal complexes are among the most widely used sensitizers in photooxidation processes;^{3,4} in addition

several naturally occurring porphyrins have been implicated as the light absorbing agents in photodynamic action.⁵⁻⁹ Conse-