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Structure and Solid-State Polymerization of 1,6-Bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne[1]

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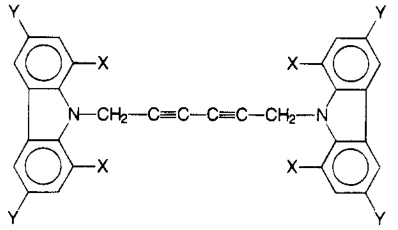
ABSTRACT: Crystals of 1,6-bis(3′,6′-dibromo-*N*-carbazolyl)2,4-hexadiyne (DCHBr$_4$, **1a**) belong to the monoclinic system, space group $P2_1/c$, with $a = 15.408(5)$ Å, $b = 4.120(1)$ Å, $c = 20.032(6)$ Å, $\beta = 95.72(3)°$, $V = 1265.3(11)$ Å^3, and $Z = 2$. Full-matrix least-squares refinement of positional and displacement parameters for all atoms (H atoms fixed at calculated positions), with 1570 reflections ($I > 1.96\sigma(I)$) led to $R = 0.0469$ and $R_w = 0.0448$. The crystal structure of DCHBr$_4$ consists of linear chains of molecules stacked along the crystallographic b axis with an orientation similar to that reported earlier for 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH, **1b**) at $T < 142$ K. Using the accepted structural criteria for solid-state reactivity in diacetylene monomers, DCHBr$_4$ is predicted and found to be markedly less reactive to ^{60}Co γ-rays, UV, and thermal treatment than the room-temperature form of DCH. Prolonged heating of DCHBr$_4$ at $T > 200$ °C leads to solid-state polymerization of this monomer accompanied by thermal decomposition; 3,6-dibromocarbazole was identified as a volatile product of the latter process. The color change accompanying the solid-state polymerization of DCHBr$_4$ suggests applications for this monomer as an irreversible thermochromic sensor. The product of the solid-state reaction is a poly(diacetylene), as determined from resonance Raman spectroscopic measurements.

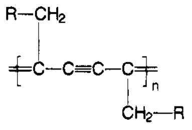
Introduction

The diacetylene monomer 1,6-bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne (DCHBr$_4$, **1a**) was initially synthesized[2] as a model compound for studies of the products of bromination of single crystals of the poly(diacetylene) (PDA, **2**) from 1,6-di-*N*-carbazolyl-2,4-hexadiyne (**1b**)[2–3] by solid-state NMR,[2,3b,4] FTIR,[3c] and Br-EXAFS.[5] The bromination of poly-DCH is an unusual solid-state reaction in which bromine diffuses into the polymer single crystals, resulting in the gain of 3–9 Br atoms per polymer repeat unit.[2,3] The bromination product, which has gained approximately 6 Br atoms per repeat unit, is crystalline,[3] and solid-state NMR studies revealed that the carbazole rings were selectively brominated in the 3 and 6 positions[2,3b,4] and that the poly(diacetylene) backbone was converted to that of a mixed polyacetylene. The mixed polyacetylene structure has been directly observed in Raman spectroscopic studies.[6]

Preliminary experiments suggested that **1a** was insensitive to UV- or γ-irradiation; color changes were observed when solid **1a** was heated at temperatures > 210 °C. This paper presents a complete report of the thermal behavior of **1a** and a comparison to the thermal properties of **1b** and the bis-1,3,6,8-octabromo DCH derivative, DCHBr$_8$, **1c**. Studies of the product of the heating of **1a** allow comparisons to be made to the product of the reaction of poly-DCH with bromine.[2–4] Further, the results of an X-ray structure determination on **1a** provide an opportunity to interpret the structure in terms of the accepted criteria for solid-state reactivity of diacetylene monomers.[7,8]



1a, X = H, Y = Br (DCHBr$_4$)
1b, X = Y = H (DCH)
1c, X = Y = Br (DCHBr$_8$)



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Experimental Section

General Procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Raman spectra were recorded using 632.8 nm as the wavelength of excitation using apparatus previously described.[6b] FTIR spectra were measured on a Nicolet 740SX spectrometer. DSC and TGA were obtained using a DuPont 2100 instrument. Samples of DCH, DCHBr$_4$, and DCHBr$_8$ were obtained as previously described.[2]

1,6-Bis(3′,6′-Dibromo-*N*-carbazolyl)-2,4-hexadiyne (DCHBr$_4$, 1a). The FTIR spectrum of this compound dispersed in KBr exhibited the following absorptions (cm^{-1}): 3073, 3055, 2963, 2913, 1594, 1569, 1471, 1437, 1428, 1352, 1332, 1311, 1288, 1258, 1208, 1147, 1097, 1060, 1049, 1022, 931, 887, 867, 832, 802, 785, 737, 649, 558, 492, and 419, in agreement with the previous report.[3c] Diffraction-quality single crystals were grown by slow cooling (82 → 30 °C, 97.5 h) of a saturated solution of **1a** in 3:1 v/v toluene/*N*,*N*-dimethylformamide. Well-formed tan reflective needles were isolated.

Structure Determination of DCHBr$_4$. Oscillation and Weissenberg photographs indicated the crystal selected to be

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

Table 1. Data for the X-ray Diffraction Study of $C_{30}H_{16}N_2Br_4$

(A) Crystal Data at 21(1) °C

crystal system: monoclinic
space group: $P2_1/c$ [C^5_{2h}; No. 14]
$a = 15.408(5)$ Å
$b = 4.120(1)$ Å
$c = 20.032(6)$ Å
$\beta = 95.72(3)°$
$V = 1265.3(11)$ Å^3
$Z = 2$
crystal size: 0.20 × 0.24 × 0.42 mm
formula wt : 724.11
$\rho_{calc} = 1.900$ g-cm^{-3}
$\rho_{obs} = 1.90(1)^a$ g-cm^{-3}
$\mu = 63.24$ cm^{-1} (Mo K$\bar{\alpha}$)

cell constant determination: 12 pairs of $\pm(hkl)$ and refined $2\theta,\omega,\chi$ values in the range $25 \le |2\theta| \le 27°$ (λ(Mo K$\bar{\alpha}$) = 0.71073 Å)

(B) Measurement of Intensity Data

radiation : Mo K$\bar{\alpha}$, graphite monochromator
reflections measured: ±h,+k,+l ($3 \le 2\theta \le 53°$)
scan type, speed: $\theta-2\theta$, vble, 2.93−5.33°/min
scan range: symmetrical, $[1.6 + \Delta(\alpha_2 - \alpha_1)]°$
no. of reflections measured: 3047; 2938 in unique set
standard reflections, period: 70; 020; 24,0,0; 008 reflections; variation $\le \pm 3\sigma(I)$ for each
absorption correction: empirical, normalized transmission factors 0.904−1.000; 114, 406, 0,2,11 reflections
data reduction: as before[b]
statistical information: $R_{av} = 0.013$ ($hk0$ reflections)

(C) Refinement

refinement,[c] with 1570 data for which $I > 1.96\sigma(I)$
weighting of reflections: as before,[c] $p = 0.04$
solution: Patterson, difference-Fourier
refinement:[d] full-matrix least-squares, with
  anisotropic displacement parameters for Br, N, and C atoms
  isotropic displacement parameters for fixed H atoms
  secondary extinction parameter, $5.52(4) \times 10^{-7}$
  $R = 0.0469$; $R_w = 0.0448$; SDU = 1.39
  R (structure factor calcn with all 2938 reflections) = 0.114
final difference map: 6 peaks, 0.38−0.45 e$^-$/Å^3 near Br atoms, random peaks in range −0.25 to +0.37 e$^-$/Å^3

[a] Measured by neutral buoyancy in bromobenzene−chloroform. [b] Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* **1981**, *20*, 4368; all computations in the present work were carried out using the Enraf-Nonius MolEN programs and the Oxford University CRYSTALS package. [c] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. [d] $R_{av} = \sum|I - I_{av}|/\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$; SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (=1570) is the number of observations and n (=164) is the number of parameters.

Table 2. Atomic Coordinates for $C_{30}H_{16}N_2Br_4$[a,b]

atom	x	y	z	B (Å^2)
Br1	0.29754(5)	0.2184(2)	0.56655(3)	5.25(2)
Br2	−0.04972(4)	0.1978(2)	0.88039(3)	5.22(1)
N	0.3065(2)	0.723(1)	0.8480(2)	2.86(9)
C1	0.4730(3)	0.586(1)	0.9768(2)	3.0(1)
C2	0.4260(3)	0.732(1)	0.9369(2)	3.2(1)
C3	0.3674(3)	0.926(1)	0.8904(2)	3.5(1)
C4	0.3178(3)	0.620(1)	0.7830(2)	2.9(1)
C5	0.3864(3)	0.671(1)	0.7448(3)	3.5(1)
C6	0.3791(3)	0.553(1)	0.6802(3)	3.8(1)
C7	0.3051(4)	0.380(1)	0.6558(2)	3.4(1)
C8	0.2373(3)	0.320(1)	0.6931(2)	3.0(1)
C9	0.2431(3)	0.445(1)	0.7581(2)	2.6(1)
C10	0.1848(3)	0.441(1)	0.8098(2)	2.7(1)
C11	0.1015(3)	0.313(1)	0.8141(3)	3.3(1)
C12	0.0644(3)	0.366(1)	0.8730(2)	3.5(1)
C13	0.1053(4)	0.529(1)	0.9277(2)	3.9(1)
C14	0.1879(3)	0.660(1)	0.9240(2)	3.4(1)
C15	0.2266(3)	0.614(1)	0.8650(2)	2.7(1)

[a] atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$. [b] Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

Table 3. Bond Lengths (Å) and Angles (deg) for $C_{30}H_{16}N_2Br_4$

atom 1	atom 2	distance	atom 1	atom 2	distance
Br1	C7	1.900(5)	C6	C7	1.392(7)
Br2	C12	1.910(5)	C7	C8	1.367(7)
N	C3	1.464(6)	C8	C9	1.396(6)
N	C4	1.396(6)	C9	C10	1.437(7)
N	C15	1.384(6)	C10	C11	1.398(7)
C1	C1	1.381(7)	C10	C15	1.415(6)
C1	C2	1.187(7)	C11	C12	1.379(7)
C2	C3	1.466(7)	C12	C13	1.381(7)
C4	C5	1.382(7)	C13	C14	1.391(8)
C4	C9	1.408(7)	C14	C15	1.388(7)
C5	C6	1.377(7)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C3	N	C4	125.6(4)	C4	C9	C8	119.6(4)
C3	N	C15	125.2(4)	C4	C9	C10	107.3(4)
C4	N	C15	109.2(4)	C8	C9	C10	133.0(4)
C1	C1	C2	179.2(6)	C9	C10	C11	133.7(4)
C1	C2	C3	176.9(5)	C9	C10	C15	106.8(4)
N	C3	C2	112.2(4)	C11	C10	C15	119.5(4)
N	C4	C5	130.1(4)	C10	C11	C12	116.9(4)
N	C4	C9	108.2(4)	Br2	C12	C11	118.1(4)
C5	C4	C9	121.7(4)	Br2	C12	C13	117.8(4)
C4	C5	C6	118.2(5)	C11	C12	C13	124.1(5)
C5	C6	C7	119.9(5)	C12	C13	C14	119.6(5)
Br1	C7	C6	118.8(4)	C13	C14	C15	117.8(4)
Br1	C7	C8	118.2(4)	N	C15	C10	108.5(4)
C6	C7	C8	123.1(4)	N	C15	C14	129.3(4)
C7	C8	C9	117.5(4)	C10	C15	C14	122.2(4)

of excellent quality. It was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2_1 diffractometer. Operations were performed as described previously.[9] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations.[10] Computational work was carried out using either the MolEN[11a] and CRYSTALS-PC[11b] software packages. Details of the structure analysis, in outline form, are presented in Table 1. As noted in Table 1, variation in the intensities of standard reflections was within statistical limits throughout the data collection (21 (1) °C, 86 h). Atomic coordinates for all non-hydrogen atoms appear in Table 2. Selected bond distances and bond angles are given in Table 3.

Thermal Polymerization of $DCHBr_4$. (a) Heating at 200−210 °C. In a typical experiment, $DCHBr_4$ (110 mg) was placed in a tube and heated in a static argon atmosphere at 200−210 °C for 240 h. After this heating, the material had turned dark violet. X-ray powder diffraction of this material revealed, in addition to all of the monomer reflections, new reflections, not found in the calculated powder pattern of the monomer, at 15.8, 9.9, 8.1, and 5.84 Å. Extraction of this solid with hot toluene gave approximately 5 mg of material, which was not analyzed further.

(b) Heating at 212 ± 6 °C. In a typical experiment, $DCHBr_4$ (100 mg) was heated under a static argon atmosphere in the dark at 212 ± 6 °C for 448 h. In the course of the experiment, a white solid tinged with blue sublimed to the cooler part of the tube; the solid had mp 200−205 °C and was identified as 3,6-dibromocarbazole (lit.[12] mp 212−213 °C) from its mass spectrum and thin-layer chromatogram. The dark violet residue, which largely retained the shape of the original crystals, was twice extracted with 10 mL portions of boiling toluene (2 h reflux for each) to give a residue of 30 mg. X-ray powder diffraction of the residue revealed a largely amorphous material with broad reflections at d = 13.9 and 9.7 Å. The resonance Raman spectrum of this material exhibits shifts at 2128, 1481, and 1464 cm^{-1}. The FTIR spectrum of the material exhibited absorptions quite similar to those of $DCHBr_4$ monomer. The elemental analysis of the dark violet material was as follows: Anal. Found: C, 56.90; H, 2.25; N, 3.50; Br, 35.16. For a composition in which each $DCHBr_4$ unit has lost a 3,6-dibromocarbazole moiety, the calculated analysis is as follows. Calcd for $(C_{18}H_9NBr_2)_x$: C, 54.17; H, 2.27; N, 3.51; Br, 40.05.

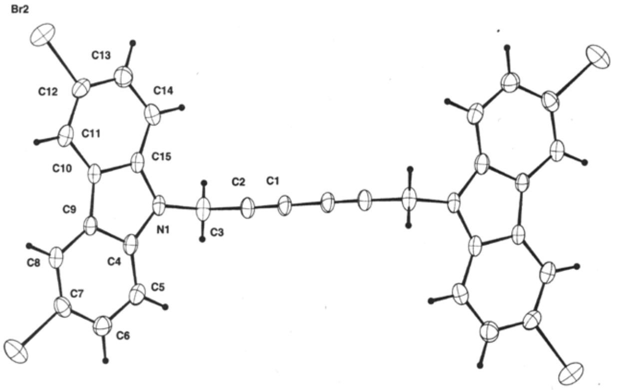


Figure 1. Molecular structure and numbering of DCHBr$_4$; anisotropic displacement parameters are shown as 50% probability ellipsoids.

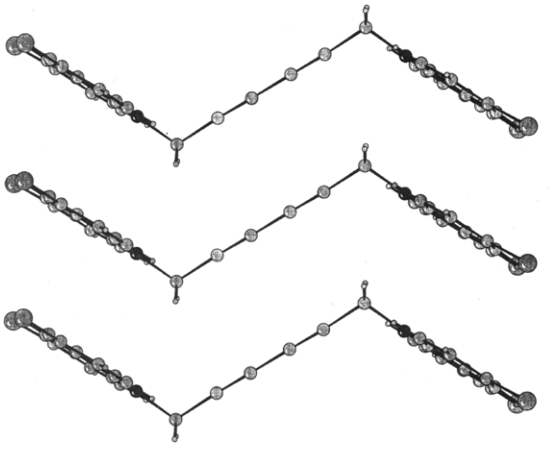


Figure 2. Projection of DCHBr$_4$ showing molecules stacked along the crystallographic b axis.

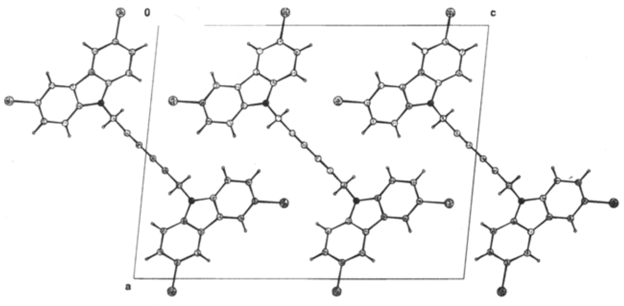


Figure 3. Projection of DCHBr$_4$ down the crystallographic b axis.

Table 4. Lattice Constants for Diacetylene Monomers[a]

monomer	a, Å	b, Å	c, Å	β, deg
DCH(300 K)	13.60(4)	4.55(3)	17.60(4)	94.0(5)
DCH(120 K)	13.38(1)	4.20(4)	18.44(1)	92.0(5)
DCHBr$_4$	15.408(5)	4.120(1)	20.032(6)	95.71(3)
DAH	14.60(5)	4.35(3)	17.92(4)	97.0(5)
ACH	14.33(1)	4.36(1)	18.00(1)	96.1(2)

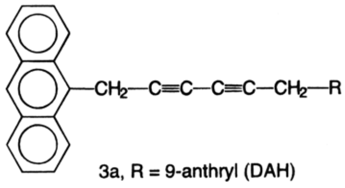
[a] All data in this table are from ref 14 except that of DCHBr$_4$. All crystals are in space group $P2_1/c$.

Results and Discussion

Crystal and Molecular Structure of DCHBr$_4$. Figure 1 shows the molecular structure of DCHBr$_4$. Bond lengths and bond angles lie within the usual ranges for both diyne[13] and carbazole[14,15] groups. Figure 2 shows a projection of DCHBr$_4$ along the b axis, and Figure 3 reveals an ac projection of this monomer. The projection in Figure 2 reveals that the packing of DCHBr$_4$ is not similar to that of DCH at room temperature, but rather to an unreactive low-temperature form of DCH.[14] This is indicated by a comparison of the lattice constants given in Table 4. The b-axis lattice constants of DCHBr$_4$ and the low-temperature DCH phase are similar. The presence of C−Br bonds in DCHBr$_4$ accounts for the expansion of the lattice in DCHBr$_4$ in the a and c directions.

Crystal Structure of DCHBr$_4$ and Solid-State Reactivity. The solid-state reactivity of diacetylene monomers is typically[7,8] discussed in terms of a monomer stacking distance d, an angle ϕ between the diacetylene rod and the stacking axis, and R, the distance between reacting atoms C$_1$ and C$_4'$. For the synthesis of high-quality PDA crystals,[8] optimal values are $d \sim 5$ Å, $\phi \sim 45°$, and $R < 4$ Å. The last criterion appears to be the critical one,[7] and among highly reactive diacetylenes, only DCH, which undergoes a phase transition in the course of polymerization, does not fulfill the $R < 4$ Å criterion.

From the crystal structure of DCHBr$_4$, $d = 4.12$ Å, $\phi = 59.3°$, and $R = 3.912$ Å. On the basis of the observed values of d and ϕ,[7,8] DCHBr$_4$ is expected and found to be significantly less reactive than DCH. While DCH is completely polymerized by 30−50 Mrad of ^{60}Co γ-radiation,[7] DCHBr$_4$ is recovered unchanged after such exposure. Further, while DCH is extensively polymerized by exposure to 370 nm light[13] at 20 °C for 48 h under an argon atmosphere, DCHBr$_4$ shows no evidence of reaction after similar treatment. DCH undergoes a single-crystal-monomer to polycrystalline-polymer transformation on heating at 100−120 °C.[16] As will be described in detail below, DCHBr$_4$ must be heated for extended periods above 200 °C to initiate significant thermal reaction. In this respect, the reactivity behavior of DCHBr$_4$ is reminiscent of that of two other monomers which are structurally related to DCH, namely 1,6-di-(9′-anthryl)-2,4-hexadiyne (DAH, **3a**) and 1-(9′-anthryl)-6-(9′-carbazolyl)-2,4-hexadiyne (ACH, **3b**). The lattice constants[14] of DAH and ACH are listed in Table 4. DAH and ACH are not reactive to high-energy radiation and can be polymerized with decomposition near their melting points.[14] For example, heating of DAH leads to a dark brown undefined product, while heating of ACH at 250 °C for 2 h results in anisotropic blue-brown coloration.[17] Further heating of ACH leads to a black undefined substance.[17] Our compositional and structural characterization of the products of the thermal reaction of DCHBr$_4$ is given below.



3a, R = 9-anthryl (DAH)

3b, R = 9-carbazoyl (ACH)

Differential Scanning Calorimetry and Thermogravimetric Analysis of DCH, DCHBr$_4$, and DCHBr$_8$. As noted above, DCHBr$_4$ is thermally less reactive than DCH. Hence, we deemed a comparative DSC−TGA study of these monomers and DCHBr$_8$ of interest. In DSC experiments carried out under an argon atmosphere at a heating rate of 10 °C/min, DCH, DCHBr$_4$, and DCHBr$_8$ undergo exothermic processes at 228.5, 320.3, and 333.7 °C, respectively. For DCH and DCHBr$_4$, the temperatures of the DSC exotherms correlate

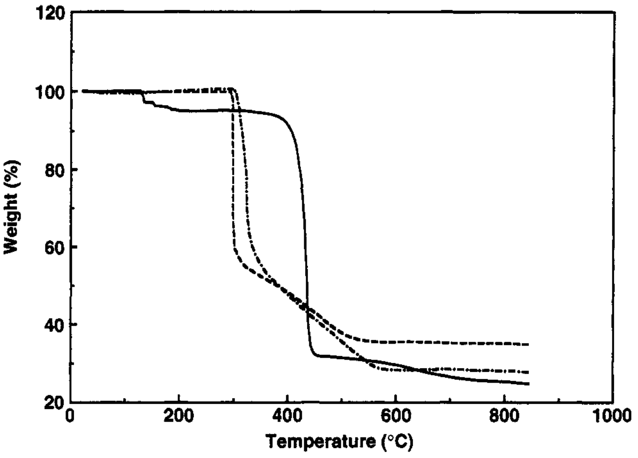


Figure 4. Thermogravimetric analysis of DCH (—), DCHBr$_4$ (- - -), and DCHBr$_8$ (-··-).

with the relative reactivity anticipated on the basis of structural considerations. The TGA experiments were carried out under argon at a heating rate of 10 °C/min. DCH loses approximately two-thirds of its weight between 360 and 440 °C. In contrast to the behavior of DCH, DCHBr$_4$ and DCHBr$_8$ seem to lose weight in at least two stages. For example, DCHBr$_4$ loses about 41% of its weight in the narrow temperature range 297–302.5 °C. We note that 3,6-dibromocarbazole has been isolated as a product of the thermal reaction of DCHBr$_4$ above 200 °C and that the loss of a dibromocarbazolyl moiety from DCHBr$_4$ involves a weight loss of 44.5%. In the temperature range 310–340 °C, DCHBr$_8$ loses about 40% of its weight. The percentage weight loss of a tetrabromocarbazolyl group from the DCHBr$_8$ monomer would be 46%. The TGA behavior of DCH, DCHBr$_4$, and DCHBr$_8$ is shown in Figure 4.

Thermal Solid-State Polymerization of DCHBr$_4$. In our initial characterization of DCHBr$_4$ crystals, we found that heating them at 200–210 °C in a capillary tube in a melting point apparatus resulted in a pink coloration after about an hour. On continued heating, the crystals turned violet and opaque while retaining the shape of the original crystal. Additionally, thin films of DCHBr$_4$ and DCHBr$_8$ slowly turn red on heating at approximately 200 °C, and these materials may have application as thermochromic sensors in this temperature range. As these color changes are reminiscent of those typically found for a diacetylene polymerization, we set out to perform the thermal polymerization on a macroscopic scale and to characterize the products of the process with respect to the degree of conversion of monomer to polymer, evidence for the backbone structure of polymer formed, and the crystallinity of the polymeric product.

To obtain detectable conversion of monomer to polymer, it was necessary to heat the monomer at 210 ± 10 °C for at least 2 weeks. For example, heating at 200–210 °C for about 10 days gave significantly less than 5% polymer, as determined after monomer extraction with hot toluene. Nevertheless, as noted above in the Experimental Section, the X-ray powder pattern of this material before extraction revealed several reflections not found in either the observed or calculated powder pattern of DCHBr$_4$ and hence might be associated with a polymer chain in the monomer crystal or a modified monomer structure. In experiments carried out at 210 °C and higher temperatures, a white solid with a bluish tinge sublimes to the space above the material undergoing polymerization. As noted in the Experimental Section, this white solid was identified as 3,6-dibromocarbazole. Hence, in addition to polymerization, the thermal process leads to a decomposition. We are unable to specify whether this is a decomposition of DCHBr$_4$ monomer or of the resultant polymer. We note that PDA–DCH undergoes thermal decomposition at temperatures above 360 °C,[3c,18] and carbazole and *N*-methylcarbazole were reported[18] to be volatile products of the decomposition.

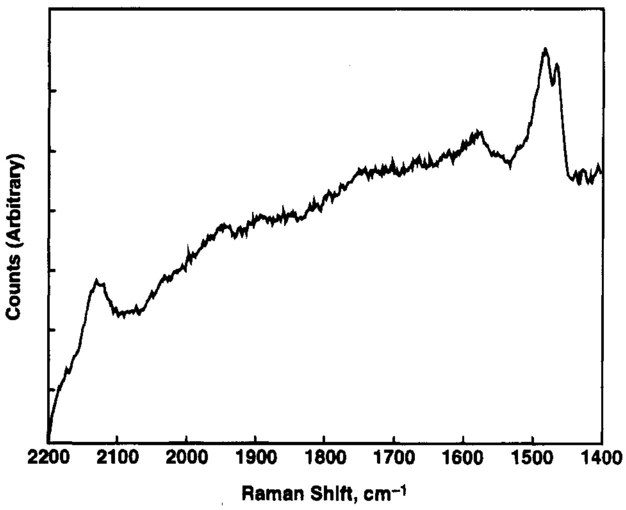


Figure 5. Raman spectrum (632.8 nm excitation) of polymerized DCHBr$_4$.

The polymer obtained on heating above 210 °C has a low crystallinity. If not carefully extracted with boiling toluene, as described in the Experimental Section, the X-ray powder diffraction shows only the major reflections of DCHBr$_4$ monomer.

Raman spectroscopy, especially resonance Raman spectroscopy, is a sensitive probe of PDA structure and properties, especially in samples less well-defined than completely polymerized single crystals.[19] Accordingly, using conditions previously reported,[6b] the spectrum of the polymer product was recorded on "needle" pieces of the dark violet polymer product. A Raman spectrum, observed on a weak luminescent background, was recorded and is displayed in Figure 5. As shown in Figure 5, relatively broad Raman-shifted lines are observed at 2128 cm^{-1} (assigned to the normal mode associated with triple-bond stretching) and 1481 and 1464 cm^{-1} (in the region associated with the normal mode involving double-bond stretching). We note that the spectrum in Figure 5 in the region of double-bond stretching is clearly different from that observed[6] for poly-DCH, which has gained 5–6 Br atoms per repeat unit. The broad feature in Figure 5 found at a shift of 1550–1600 cm^{-1} varies in intensity from sample to sample. In a sample which was heated to 230 °C, it was the only observable feature in the spectrum. The presence of these Raman-shifted lines associated with triple- and double-bond stretching is sufficient to assign a PDA backbone as the structure of the polymeric product of DCHBr$_4$ thermal reaction. It is not clear at present whether the two shifted lines at 1481 and 1464 cm^{-1} should be associated with a Fermi resonance, as in the case of poly-DCH,[19] or whether they might be due to PDA chains in different environments. The latter situation might involve, for example, a PDA backbone with two dibromocarbazole side groups and a PDA backbone with only one such side group as a result of the thermal decomposition process described above.

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Supporting Information Available: Tables of anisotropic displacement parameters, calculated H-atom positions, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A preliminary account of portions of this work was presented in the Symposium on X-ray and Electron Diffraction from Polymers, 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 5–10, 1992, Abstracts of Papers, Part III, POLY 171; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 284.

(2) Eckert, H.; Yesinowski, J. P.; Sandman, D. J.; Velazquez, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 761.

(3) (a) Sandman, D. J.; Elman, B. S.; Hamill, G. P.; Velazquez, C. S.; Samuelson, L. A. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 89. (b) Sandman, D. J.; Elman, B. S.; Hamill, G. P.; Velazquez, C. S.; Yesinowski, J. P.; Eckert, H. *Mol. Cryst. Liq. Cryst. Lett.* **1987**, *4*, 77. (c) Sandman, D. J.; Elman, B. S.; Hamill, G. P.; Hefter, J.; Velazquez, C. S. In *Crystallographically Ordered Polymers*; Sandman, D. J., Ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; pp 118–127.

(4) Yesinowski, J. P.; Eckert, H.; Sandman, D. J.; Velazquez, C. S. In *Crystallographically Ordered Polymers*; Sandman, D. J., Ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; pp 230–252.

(5) Lester, J. E., unpublished experiments performed at the National Synchrotron Light Source, Brookhaven National Laboratory.

(6) (a) Sandman, D. J.; Chen, Y. J.; Elman, B. S.; Velazquez, C. S. *Macromolecules* **1988**, *21*, 3112; (b) Hankin, S.; Sandman, D. J. *Polym. Commun.* **1990**, *31*, 22. (c) Hankin, S.; Sandman, D. J. *Mol. Cryst. Liq. Cryst.* **1990**, *186*, 197.

(7) Enkelmann, V. *Adv. Polymer Sci.* **1984**, *63*, 91.

(8) Baughman, R. H.; Chance, R. R. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 705.

(9) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932. Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113.

(10) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101. Cromer, D. T.; Ibers, J. A. *Ibid.*, pp 148–150.

(11) (a) *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands, 1990. (b) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS-PC User Guide*, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985, 1993.

(12) Pielichowski, J.; Kyziol, J. *Monatsh. Chem.* **1974**, *105*, 1306.

(13) Sandman, D. J.; Haaksma, R. A.; Foxman, B. M. *Chem. Mater.* **1991**, *3*, 471.

(14) Enkelmann, V.; Schleier, G.; Eichele, H. *J. Mater. Sci.* **1982**, *17*, 533.

(15) Kimura, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2268.

(16) Enkelmann, V.; Leyrer, R. J.; Schleier, G.; Wegner, G. *J. Mater. Sci.* **1980**, *15*, 168.

(17) Schleier, G., Ph.D. Thesis, Universität Freiburg, 1980.

(18) (a) Bradner, F. P.; Shapiro, J. S. *Makromol. Chem.* **1992**, *193*, 389. (b) Bradner, F. P.; Shapiro, J. S. *Polymer* **1992**, *33*, 4366. (c) Bradner, F. P.; Shapiro, J. S.; Hunter, D.; Pomery, P. *Polymer* **1993**, *34*, 1811.

(19) (a) Batchelder, D. N.; Bloor, D. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley-Heyden: New York, 1984; Vol. 11, pp 133–209. (b) Hankin, S.; Sandman, D. J., In *Structure–Property Relations in Polymers*; Urban, M. W.; Craver, C. D., Eds.; ACS Advances in Chemistry 236; American Chemical Society: Washington, DC, 1993; pp 243–262.

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