7.40–7.42 (m, 3 H), 7.60–7.62 (m, 2 H) (The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 10.06 (J = 4.9 Hz))); ^{13}C NMR (270 MHz, $CDCl_3$) δ 124.73, 126.66, 127.57, 128.09, 128.33, 128.45, 128.67, 128.93, 129.05, 129.37, 135.79, 136.05, 138.58, 159.57, 187.77; IR (KBr) 3057, 1658, 1531, 1486, 1476, 1437, 1227, 1042, 935, 760, 744, 696 cm^{-1}; mass spectrum (CI), m/e 445 (M^+ + 1, 56). Anal. Calcd for $C_{21}H_{16}OSe_2$: C, 57.03; H, 3.64. Found: C, 57.19; H, 3.64.

E isomer: Pure *E* isomer could not be isolated because it was formed in low yield.

1,3-Bis(phenylthio)-3-phenyl-2-propen-1-one (Table VI, Entry 9). *Z* isomer: mp 135–139 °C (a yellow solid); ^1H NMR (270 MHz, $CDCl_3$) δ 6.45 (s, 1 H), 7.03–7.13 (m, 10 H), 7.43–7.44 (m, 3 H), 7.52–7.53 (m, 2 H) (The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the two formyl doublets appeared at δ 9.50 (J = 8.1 Hz) and δ 10.47 (J = 6.5 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 121.02, 127.83, 128.01, 128.11, 128.43, 128.66, 128.93, 129.14, 129.32, 132.06, 134.17, 134.67, 137.74, 158.63, 185.19; IR (KBr) 3059, 1661, 1537, 1078, 949, 791, 752, 705, 690, 671, 588 cm^{-1}; mass spectrum (CI), m/e 349 (M^+ + 1, 100). Anal. Calcd for $C_{21}H_{16}OS_2$: C, 72.38; H, 4.62; S, 18.40. Found: C, 72.37; H, 4.61; S, 18.32.

E isomer: Pure *E* isomer could not be isolated because it was formed in low yield.

(*Z*)-1,3-Bis(phenylseleno)-5,5-bis(ethoxycarbonyl)-2,7-octadien-1-one (Table VI, entry 10): mp 66–68 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 1.22 (t, 6 H, J = 7.1 Hz), 2.54 (d, 2 H, J = 8.3 Hz), 2.80 (s, 2 H), 4.15 (q, 4 H, J = 7.1 Hz), 4.88 (d, 1 H, J = 20.5 Hz), 4.93 (d, 1 H, J = 14.0 Hz), 5.35 (octet, 1 H, J = 8.3, 14.0, 20.5 Hz), 6.74 (s, 1 H), 7.34–7.46 (m, 6 H), 7.55–7.60 (m, 4 H) (NOE experiment: Irradiation of the methylene singlet at δ 2.80 resulted in an 11% enhancement of the signal at δ 6.74 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the two formyl doublets appeared at δ 9.74 (J = 7.6 Hz) and δ 9.96 (J = 4.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.07, 38.17, 38.60, 58.02, 61.76, 119.38, 124.52, 126.63, 127.75, 128.92, 129.37, 129.41, 129.50, 131.92, 135.76, 137.22, 155.35, 170.06, 187.45; IR (KBr) 3053, 2982, 1730, 1669, 1543, 1219, 1066, 793, 744, 693 cm^{-1}; mass spectrum (CI), m/e 581 (M^+ + 1, 14). Anal. Calcd for $C_{26}H_{28}O_5Se_2$: C, 53.98; H, 4.87. Found: C, 54.23; H, 4.90.

1,3-Bis(phenylseleno)-6-hydroxy-2-hexen-1-one (Table VI, Entry 11). *Z* isomer: mp 98–100 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 1.55 (quintet, 2 H, J = 6.1, 7.6 Hz), 1.70 (br s, 1 H), 2.26 (t, 2 H, J = 7.6 Hz), 3.29 (t, 2 H, J = 6.1 Hz), 6.71 (s, 1 H, J_{Se-H} = 11.7 Hz), 7.30–7.65 (m, 10 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.26 resulted in a 21% enhancement of the signal at δ 6.71 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.81 (J = 3.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.35, 33.99, 61.06, 122.49, 126.58, 127.08, 128.83, 129.24, 129.29, 129.45, 135.74, 137.23, 161.95, 187.69; IR (KBr) 3326, 3055, 2937, 1664, 1546, 1532, 1085, 809, 742, 693 cm^{-1}; mass spectrum (CI), m/e 427 (M^+ + 1, 8). Anal. Calcd for $C_{18}H_{18}O_2Se_2$: C, 50.96; H, 4.27. Found: C, 51.01; H, 4.34.

E isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 1.87 (quintet, 2 H, J = 5.9, 7.3 Hz), 2.07 (br s, 1 H), 2.88 (t, 2 H, J = 7.3 Hz), 3.62 (t, 2 H, J = 5.9 Hz), 5.94 (s, 1 H), 7.30–7.66 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.69, 32.55, 61.09, 123.48, 126.03, 126.87, 128.88, 129.32, 129.94, 130.07, 135.69 (J_{Se-C} = 8.8 Hz), 136.72, 163.43, 187.74; IR (NaCl) 3368, 3056, 2942, 2874, 1693, 1564, 1557, 1476, 1438, 1338, 1038, 1020, 738, 690 cm^{-1}; mass spectrum (CI), m/e 427 (M^+ + 1, 8).

Acknowledgment. This research was supported in part by a Grant-in-Aid for Developmental Scientific Research (No. 03555183) from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument.

An Approach to Organic Ferromagnets. Synthesis and Characterization of 1-Phenyl-1,3-butadiyne Polymers Having a Persistent Nitroxide Group on the Phenyl Ring

Katsuya Inoue, Noboru Koga, and Hiizu Iwamura*

Contribution from the Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Tokyo 113, Japan. *Received May 3, 1991*

Abstract: 1-[3-(*N-tert*-Butylhydroxyamino)-4-chlorophenyl]-1,3-butadiyne (**3**) was obtained as colorless needles (mp ca. 140 °C from diethyl ether) that polymerized 100% in 24 h at 120 °C to give a black, ethanol-insoluble microcrystalline product. Crystals of **3** are triclinic, space group $P\bar{1}$ (No. 2), with a = 8.496 (3) Å, b = 10.755 (5) Å, c = 8.004 (3) Å, α = 92.77 (4)°, β = 106.51 (3)°, γ = 74.85 (3)°, V = 676.6 (5) Å^3, and d = 1.22 g/cm^3 for Z = 2 ($C_{14}H_{14}ClON$, MW = 247.72). The observed solid-state polymerization is estimated to have taken place along the a/c diagonal. Treatment of **3** with Fremy's salt in THF/H_2O at room temperature gave the corresponding nitroxide radical **4** as red crystals (mp 81.0–82.0 °C, a_N = 13.8 G, g = 2.0066 in hexane). Whereas the planned solid-state polymerization of **4** proceeded neither by heat nor UV and γ irradiation, mixed crystals of **3** and **4** (70:30 to 50:50) did undergo polymerization in 20 h at 140 °C to give a black, ethanol-insoluble solid. A broad X-band ESR signal that showed geometrical anisotropy was observed at ca. 3000 G in addition to resonances at g = 2 due to the isolated (S = $^1/_2$) and exchange-narrowed nitroxide spins. The magnetic susceptibility of the polymer samples measured on a Faraday balance showed that ca. 90% of the nitroxide radical centers were lost during the polymerization. Most of the remaining spins are S = $^1/_2$, and the rest are in a segment where S > $^1/_2$. The latter spins were found to be quenched by an anomalous phase transition at ca. 250 K when the samples were warmed up from cryogenic temperatures.

The design and synthesis of organic magnets are the subject of increasing current interest.[1] The idea is to establish unprecedented macroscopic spins of long-range order in molecular systems. There appear to be two approaches for the purpose: spin alignment within a molecule and between neighboring molecules. The pros and cons of the two approaches have been discussed.[2] The former approach was highlighted by the synthesis and

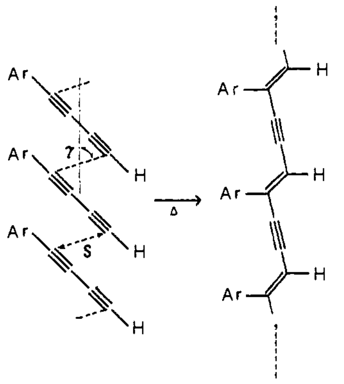
---

(1) (a) Itoh, K. *Bussei* **1971**, *12*, 635. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40. (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114. (d) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (e) Miller, J. S.; Kruisic, P. J.; Epstein, A. J.; Zhang, J. H.; Dixon, D. D.; Calabrese, J. C. *Science* **1988**, *240*, 1185. (f) Iwamura, H. *Oyo Butsuri* **1989**, *58*, 1061–8. (g) Buchachenko, A. L. *Usp. Khim.* **1990**, *59*, 307. (h) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.

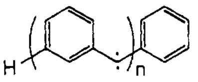
(2) (a) Iwamura, H.; Izuoka, A. *Nippon Kagaku Kaishi* **1987**, 595. (b) Iwamura, H. *J. Phys.* (*Paris*) **1988**, *49*, C8 813. (c) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

0002-7863/91/1513-9803$02.50/0

Scheme I



characterization of tetrakis- and pentakis(m-phenylenecarbene) (**1** and **2**, respectively). These have been demonstrated to be in the ground nonet[3] and undecet[4] states, respectively, the highest spin multiplicities ever reported for purely organic molecules. Whereas the higher analogues had been predicted to be of significance as models for one-dimensional organic ferromagnets[5] and are the targets of our continued synthetic efforts,[6] the synthesis of the precursor diazo compounds becomes more and more difficult and laborious as the chain length increases. Not only are there very few straightforward syntheses for the precursors, but it also becomes difficult to have all of the triplet centers generated without fail and kept intact, a prerequisite for having the expected strong exchange coupling among the carbene centers that are located on the cross-conjugated main chain. Furthermore, it is desirable for the realization of usable macroscopic spins to have stable spins in place of highly reactive triplet carbenes.



1 : n = 4

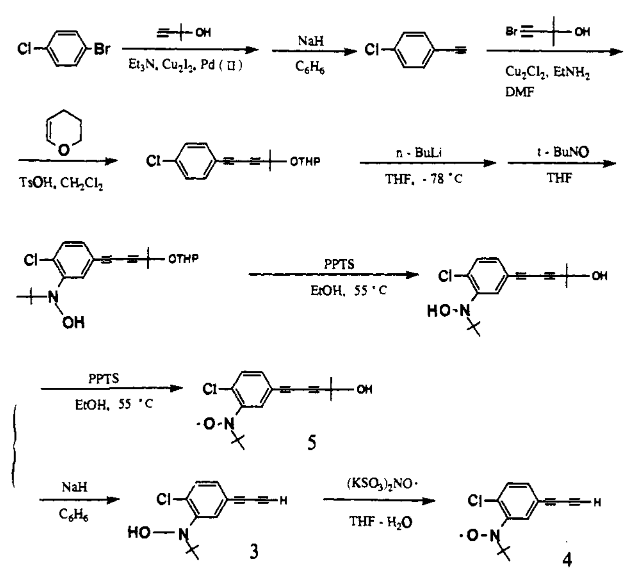
2 : n = 5

In order to overcome these difficulties, we have modified our original strategy and looked for conjugated polymer chains to which persistent radical centers are attached as pendants. In this way, we may be able to construct molecules having hundreds of electron spins and align them by bypassing the site where we are obliged to fail in generating all of the radical centers and keeping them intact.

There are a number of possible conjugated polymer chains:[6] polyacetylenes,[6d] poly(phenylenevinylenes), polyphenylenes, etc., out of which we have chosen poly(phenyldiacetylenes) in this study.

Some 1,3-butadiyne derivatives are known to undergo topochemically controlled solid-state polymerization in crystals.[7] 1-Phenyl-1,3-butadiyne is one of very few examples in which a phenyl ring is conjugated with the diacetylene chromophore and yet often undergoes smooth polymerization (Scheme I).[8] We report here the synthesis of 1-phenyl-1,3-butadiyne derivatives (**3** and **4**), carrying a hydroxyamino and a stable nitroxide group at the meta position on the phenyl ring, respectively, their polymerization in the solid state, and the magnetic properties of the polymer samples.[9]

Scheme II



Results

Synthesis. p-Chlorobromobenzene was coupled with 3-hydroxy-3-methyl-1-butyne in the presence of Cu_2I_2 and $Pd(PPh_3)_2Cl_2$ in triethylamine[10] to give a phenylacetylene (Scheme II). The protecting group was removed by refluxing with sodium hydride in benzene. p-Chloroethynylbenzene was reacted with 1-bromo-3-hydroxy-3-methyl-1-butyne using Cu_2Cl_2 and ethylamine in DMF. The hydroxyl group of the diacetylene was protected with 3,4-dihydro-2H-pyran. When the (p-chlorophenyl)diacetylene ether was treated with n-butyllithium at −78 °C in anhydrous THF and then with 2-methyl-2-nitrosopropane dimer, the resulting product was not due to metal–halogen exchange but ortho-metalation; a [3-(N-*tert*-butylhydroxyamino)-4-chlorophenyl]diacetylene derivative was obtained. Treatment with p-toluenesulfonic acid in ethanol cleaved the ether linkage to give the protected hydroxyamine **5**, which was then reacted with sodium hydride in benzene to give the hydroxyamine **3** as colorless needles. The spectral data were consistent with this structure.

Hydroxyamine **3** was oxidized with Fremy's salt to give the corresponding nitroxide **4** as red crystals. In degassed hexane at 25 °C, the observed ESR spectrum consisting of triplet lines ($g = 2.0066$, $a_N = 13.78$ G) was in good agreement with that of the hindered nitroxide structure.[11] Although the lines had a width of 1.9 G and hyperfine coupling with the ring hydrogens was not explicitly detected, the corresponding coupling was observed for **5** ($g = 2.0066$, $a_N = 13.8$ G, $a_H = 3.1$ (1 H), 2.1 (1 H), and 1.0 (1 H) G).

---

[3] (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. (c) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (d) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147.

[4] Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Izuoka, A.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

[5] Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.

[6] (a) Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 187. (b) Iwamura, H. *Pure Appl. Chem.* **1987**, *59*, 1595. (c) Iwamura, H.; Izuoka, A. *Nippon Kagaku Kaishi* **1987**, 595. (d) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1991**, *24*, 1077.

[7] (a) Wegner, G. *Z. Naturforsch. B* **1969**, *24*, 824. (b) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443. (c) Baughman, R. H. *J. Appl. Phys.* **1972**, *43*, 4362. (d) Sixl, H.; Newman, W.; Huber, R.; Denner, V.; Sigmund, E. *Phys. Rev.* **1985**, *B31*, 142. (e) Eichele, H.; Schworer, M.; Huber, R.; Bloor, D. *Chem. Phys. Lett.* **1976**, *42*, 342. (f) Jones, M. T.; Jansen, S.; Roble, J.; Sandman, D. J.; Velazques, C. S. *Synth. Met.* **1987**, *18*, 427. (g) Chance, R. R.; Baughman, R. H.; Muller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616.

[8] Nakanishi, H.; Matsuda, H.; Okada, S.; Kato, M. In *Frontiers of Macromolecular Science*; Saegusa, T., Higashimura, T., Abe, A., Eds.; Blackwell: Oxford, UK, 1989; p 469.

[9] A preliminary report of this work appeared: Koga, N.; Inoue, K.; Sasagawa, N.; Iwamura, H. *Mat. Res. Soc. Symp. Proc.* **1990**, *17*, 39. See also, Iwamura, H.; Sasaki, S.; N. Sasagawa, N.; Inoue, K.; Koga, N. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; p 53.

[10] Sabourin, E. T.; Onopchenko, A. *J. Org. Chem.* **1983**, *48*, 5135.

[11] Calder, A.; Forrester, A. R. *J. Chem. Soc., Chem. Commun.* **1967**, 682.

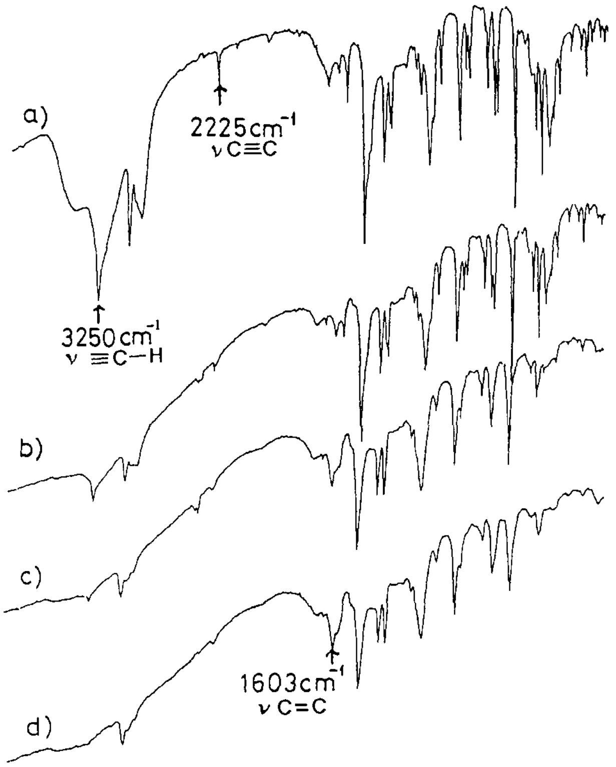


Figure 1. IR absorptions used to monitor the course of the polymerization of diacetylene **3** in a KBr disk at 100 °C: (a) initial, (b) 6 h, (c) 36 h, and (d) 48 h.

Topochemical Polymerization. The solid-state polymerization of crystalline samples of hydroxyamine **3** recrystallized from diethyl ether was monitored by IR absorption on KBr disks (Figure 1). The course of the polymerization was monitored by the decrease of the IR absorptions of the HC≡ and C≡C moieties at 3250 and 2225 cm^{-1}, respectively, and by precipitation in methanol. The polymerization was 50% in 48 h and 76% in 96 h at 96 °C, and 100% in 24 h at 120 °C. When the polymerization was carried out under oxygen, the polymer sample obtained showed a weak triplet ESR pattern characteristic of a nitroxide isolated in solid matrices (vide infra; e.g., Figure 5a), suggesting partial conversion of the hydroxyamino group into the nitroxide. Further chemical oxidation of the totally insoluble black polymers was not successful even under sonication.

Contrary to our expectation, the red triclinic crystals of 1-[3-(*N-tert*-butylnitroxyl)-4-chlorophenyl]-1,3-butadiyne (**4**) did not undergo polymerization on heating or under UV and γ irradiation. Therefore, the last recourse was to prepare mixed crystals consisting of **3** and **4** by cocrystallization from ether and to subject them to heat treatment. The polymerization did take place to give a black-violet powder with metallic luster when **3** was mixed with up to an equal amount of **4**. For example, mixed crystals obtained from **3** and **4** in a ratio of 7:3 satisfactorily polymerized at 120 °C in 20 h.

Thermal Analyses of Solid-State Polymerization. **3** showed an exothermic peak at 140.3 °C when heated at a rate of 4 °C/h on a DSC apparatus. The exothermicity of the solid-state polymerization was 64.0 kcal/mol in fair agreement with the values for other 1-phenyl-1,3-butadiynes.[9] A similar exothermic peak in DSC was observed at 135.7 °C for the 7:3 mixed crystals of **3** and **4**.

Crystal Structure of Hydroxyamine 3. The structure of **3** has been determined by X-ray analysis. Single crystals of **3** are triclinic, space group $P\bar{1}$ (No. 2), with a = 8.496 (3) Å, b = 10.755 (5) Å, c = 8.004 (3) Å, α = 92.77 (4)°, β = 106.51 (3)°, γ = 74.85 (3)°, V = 676.6 (5) Å^3, and d = 1.22 g/cm^3 for Z = 2 ($C_{14}H_{14}ClON$, MW = 247.72). The crystal structure is reproduced in Figures 2 and 3.

One-dimensional stackings of the molecules are found along the c axis (head-to-head) (Figure 3) and the a/c diagonal (head-to-tail) (Figure 3). As far as the 1,3-butadiyne moieties are concerned, there are three nearest-neighbor distances: the C-1/C-1′ distance along the c axis of 8.00 Å, the C-1/C-4′ distance of 4.55 Å, and the C-4/C-4′ distance of 4.72 Å along the a/c diagonal. It is noted that the latter two columnar arrangements along the a/c diagonal are bridged laterally by an intermolecular hydrogen bond between the two hydroxyamino groups (N⋯H⋯O distance of 2.82 Å) as shown in Figure 4.

Polymer samples due to the mixed crystals of **3** and **4** were apparently also crystalline. However, an X-ray powder pattern was considerably broadened, and a broad peak was observed at ca. 2θ = 19° (Cu Kα).

Characterization by ESR Spectroscopy. When studied by ESR, an exchange-narrowed singlet due to neat crystals of **4** was converted into an isolated nitroxide pattern exhibiting hyperfine

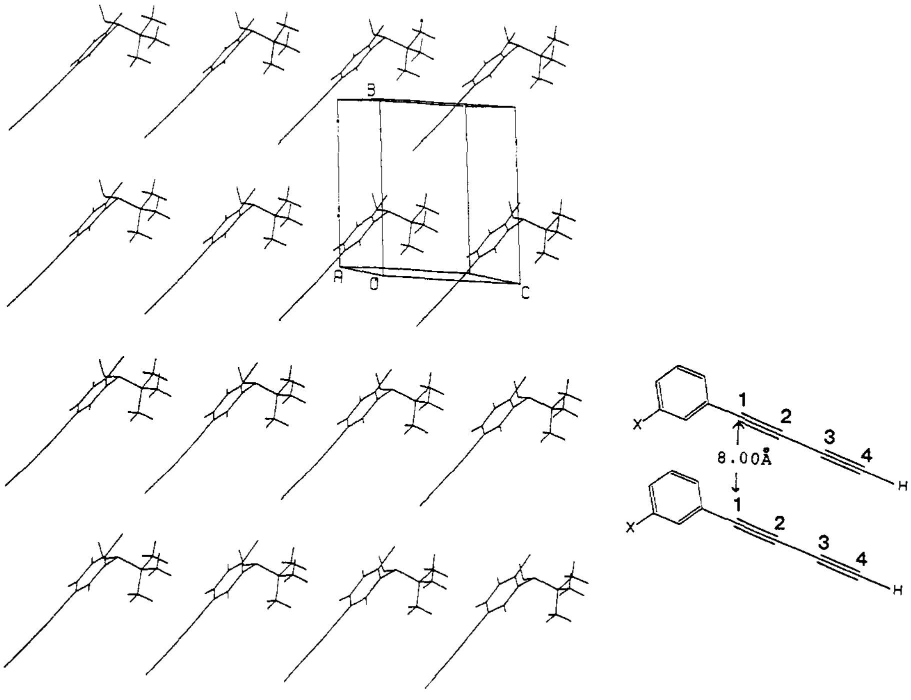


Figure 2. Crystal structure of hydroxyamine **3** viewed along the a axis.

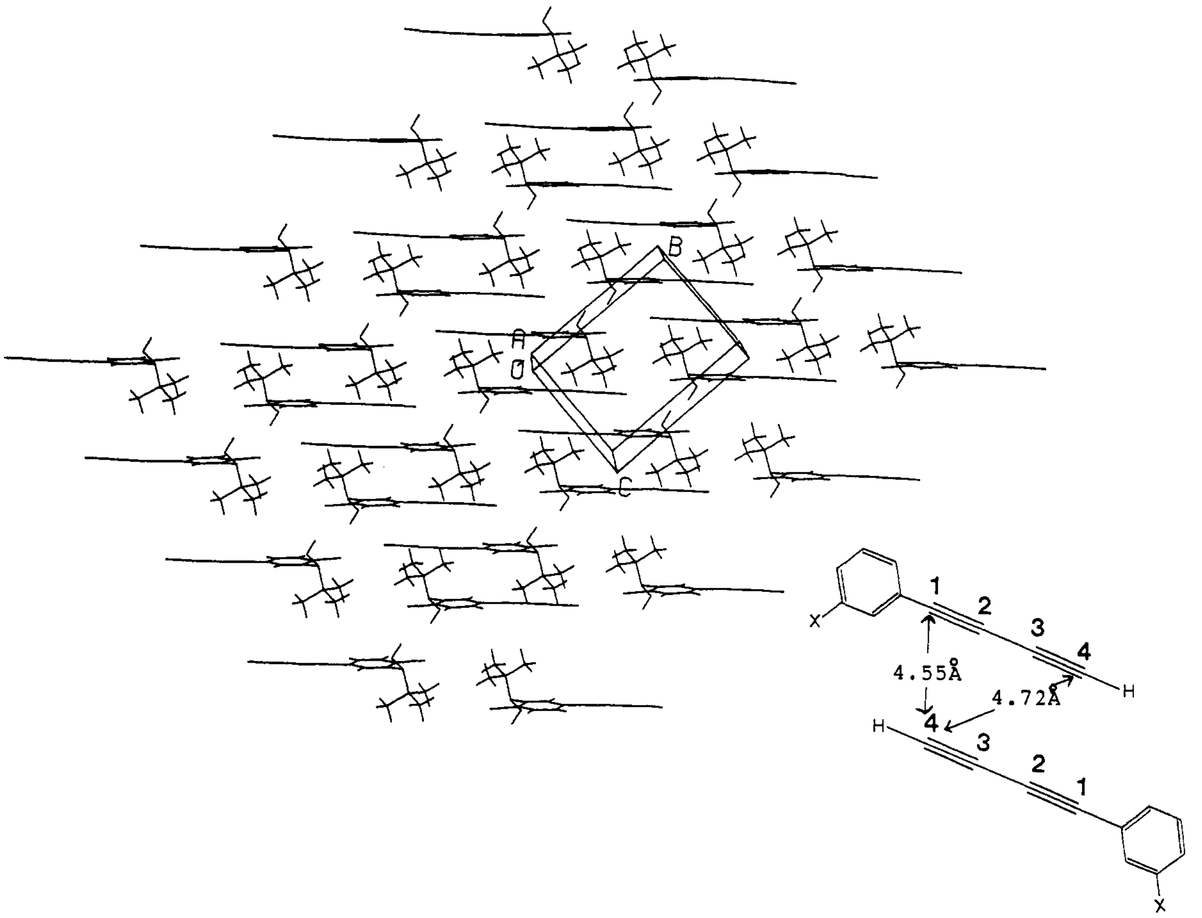


Figure 3. Crystal structure of hydroxyamine 3 projected along the *a*/*c* diagonal.

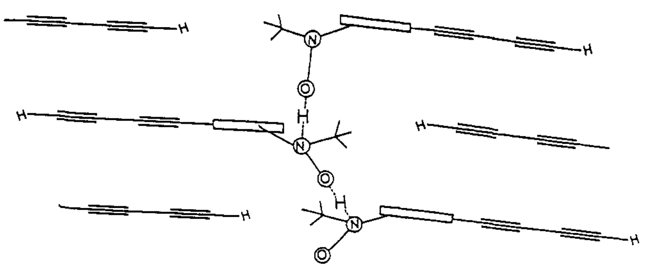


Figure 4. Crystal structure of hydroxyamine 3 showing the hydrogen-bonded network structure of distance N···O = 2.82 Å.

coupling when diluted in the mixed crystals (Figure 5a). This observation strongly suggests that the components 3 and 4 are uniformly mixed to form probably a eutectic mixture rather than forming aggregates of 4 in 3 in the mixed crystals. If the latter were the case, an exchange-narrowed singlet signal should have overlapped with the observed split signals.

After polymerization of the mixed crystals, the ESR pattern of the samples was always an overlap between the exchange-narrowed singlet (at ca. 3360 G) and the isolated triplet (Figure 5b). The pattern was almost independent of the initial composition of 3 and 4. When studied under high modulation, the ESR spectra of powder samples of the mixed polymer of 3 and 4 revealed a broad peak at ca. 3000 G (Figure 5c), which showed geometrical anisotropy when the sample was rotated in an ESR cavity (Figure 5d). This latter peak disappeared when the sample was left at room temperature for a few days.

Magnetic Measurements. Magnetic measurements have been carried out for various samples using a Faraday balance. The reciprocal χ (paramagnetic), χT, and χ vs temperature (T) plots for a sample prepared by polymerization of a 7:3 mixture of 3 and 4 at 140 °C for 20 h are reproduced in Figures 6 and 7. Another portion of the same batch and other samples obtained under similar conditions gave reproducible results.

When the temperature of a freshly prepared sample was decreased in a Faraday balance with the main field of 2 T and field gradient of 5 T/m, the χ values increased in line with a Curie law, plots 1, giving a Curie constant of 7.2×10^{-5} emu K/g. A spin concentration value of 9.6×10^{19} spins/g was obtained by assuming $g = 2.0066$ (by ESR spectrum) and $S = {}^1/_2$. The measurement was started from 4.2 K and was gradually raised to 300 K. The data gave a reasonable Curie relation up until ca. 200 K, plots 2, but deviated upward from the first plots. The values decreased drastically in the 250 K region and leveled off at ca. 300 K. When the temperature was decreased again, the inverse χ values also decreased following another Curie law, plots 3, and deviated from the first and second plots. The occurrence of an irreversible magnetic phase transition at ca. 250 K is suggested.

A freshly prepared sample was subjected to a similar temperature cycle: the temperature was raised from 4.2 to 300 K and lowered back to the cryogenic temperature in the superconducting solenoid without applying the main field ($H = 0$ T). The magnetization curves at 4.2 K before and after the temperature cycle were fitted to Brillouin functions in which $S = 0.65$ with a spin concentration of 1.59×10^{19} and $S = 0.48$ with 1.38×10^{19} spins/g, respectively.

These phenomena were reproduced for the fresh samples but were not observed for the samples kept at room temperature for a few days, a result in good accordance with the appearance of low-field ESR signals.

Discussion

Theoretical Background and Molecular Design. As discussed briefly in the introduction, high-spin oligocarbenes 1 and 2 enjoy their record-holding status as the highest spin organic molecules, but they have some intrinsic disadvantages for realization of macroscopic spins of practical use. First, they are persistent only

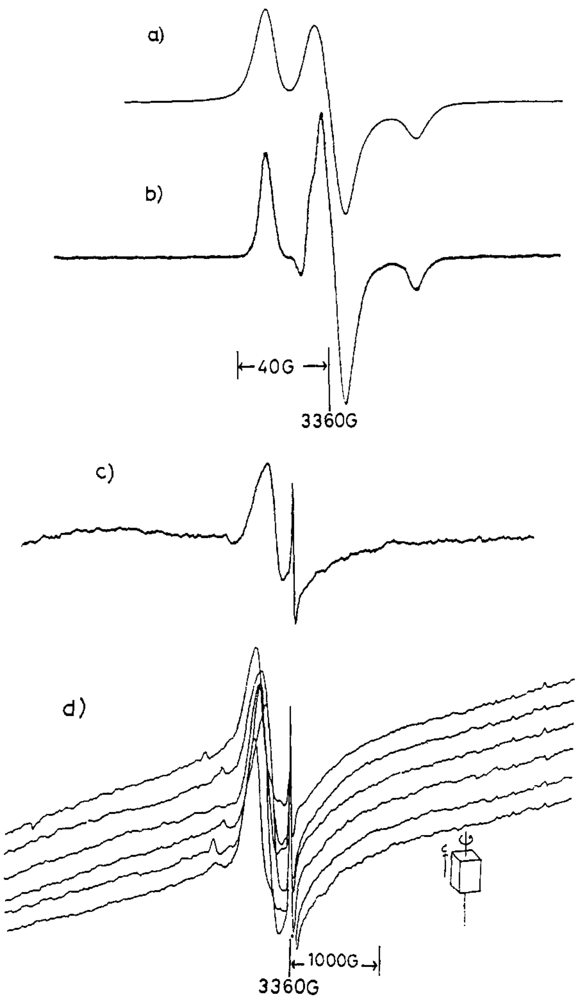


Figure 5. X-Band ESR spectra of mixed crystals of **3** and **4** (7:3): (a) initial, (b) after 12 h at 120 °C, (c) the same sample as b but in high modulation, and (d) demonstration of geometrical anisotropy of a crystalline sample of the polymer thus obtained.

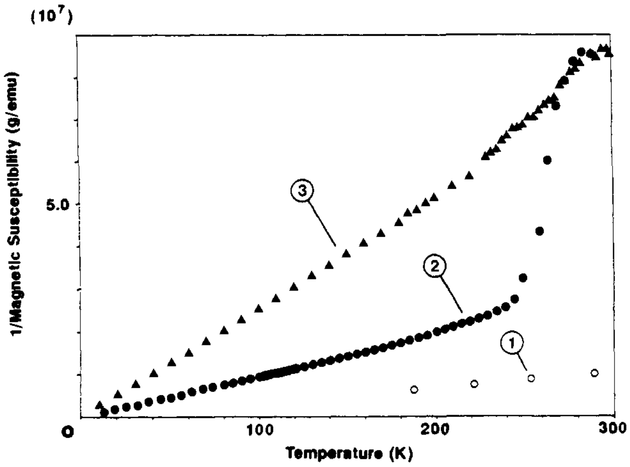


Figure 6. Inverse χ vs temperature plots for the polymer sample obtained from the mixed crystals of **3** and **4** measured under a main field of 2 T. Irreversible temperature dependence is shown.

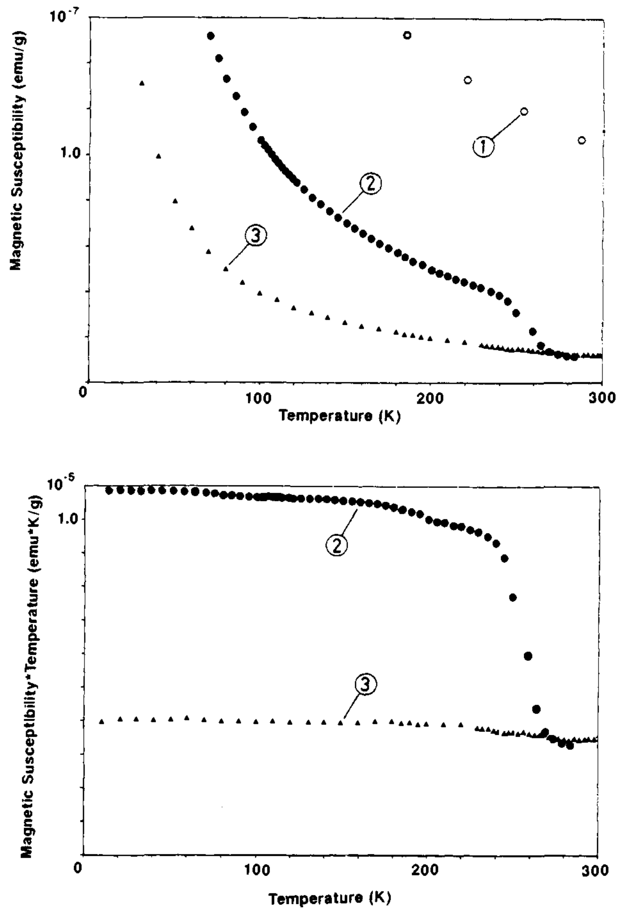


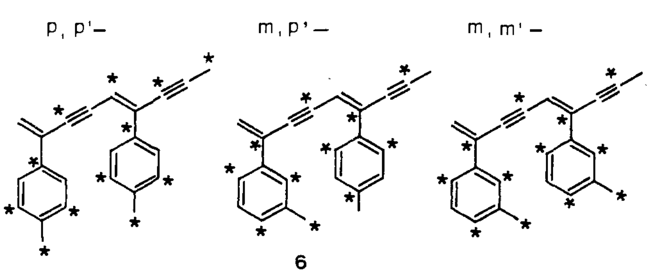
Figure 7. χ vs temperature and χT vs temperature plots for the polymer sample obtained from the mixed crystals of **3** and **4**.

at temperatures lower than ca. 100 K. Second, there are not straightforward polycondensation reactions available for construction of the skeleton. Finally the open-shell centers reside on the cross-conjugated main chain; every carbenic center must be generated and survive without fail for effective exchange coupling among them all. In order to overcome these difficulties, it will be advantageous to introduce other molecular systems. Thus, conjugated polymers having stable radicals as pendants were considered to constitute a new structural basis for designing and constructing high-spin organic molecules that would show interesting magnetic properties.

It is the periodicity of the intervening π-bonds, or in other words, the topology of the π-polyradicals that dictates the alignment of the alpha spins in **1** and **2**.[3,4] The same principle should answer the question of where to place the pendant radical centers on the conjugated polymers. Molecular orbital[12] as well as valence bond[13] theories have been developed for this purpose. According to the latter theory of topological symmetry of alternate π-systems, the spin quantum number S of the ground state is given by eq 1, where n^* and n are the numbers of starred and nonstarred carbon atoms, respectively. Let us take, for example, a dimer unit **6**, in which

$$S = (n^* - n)/2 \qquad (1)$$

radical centers are situated at the *p,p′*-, *m,p′*-, and *m,m′*-positions.



6

Since $n^* = 12$ and $n = 10$ for the *p,p′* and *m,m′* isomers, and n^*

---

(12) (a) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265. (b) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(13) (a) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (b) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101. (c) Klein, D. J. *Pure Appl. Chem.* **1983**, *55*, 299. (d) Alexander, S. A.; Klein, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 3401.

$= n = 11$ for the *m,p′* substitution, the ground states are predicted to be triplet for the former and singlet for the latter. In other words, the exchange interactions between the radical centers attached to the phenyl rings are predicted to be ferromagnetic when they are *p,p′* or *m,m′*, and the coupling is antiferromagnetic for the *m,p′* isomer.

In poly(1-phenyl-1,3-butadiynes), the radical centers may reside on the same positions of the repeating units to interact ferromagnetically; when the polymer in question consists of m units, $S = (6m - 5m)/2 = m/2$. The prediction is encouraging in that, if we are able to polymerize 1-(substituted phenyl)-1,3-butadiyne regiospecifically in a 1,4-fashion, all of the electron spins could couple ferromagnetically to generate the high-spin polymers. Some prototype dicarbenes and dinitrenes have been prepared to support this discussion.[14]

Polymer Samples. Although sterically protected with the *o*-chlorine atom and *N-tert*-butyl group, the ESR spectrum of monomer **5** showed the presence of hyperfine coupling with the ring hydrogens and that of **4** exhibited a broadened line width of 1.9 G. Some spin densities are expected to be distributed not only over the phenyl ring but, since the hydrogen meta to the nitroxide group has a meaningful hyperfine coupling value, probably also onto the conjugated main chain of the poly(diacetylene), allowing the exchange coupling through bonds between the neighboring nitroxide centers in the ideal poly(diacetylene nitroxide). Further supporting evidence for the nitroxide group in conjugation with the ring is obtained from the dihedral angle O–N–C–C(Cl) of 38.4° in the parent hydroxyamine **3**; the out-of-plane deformation of the nitroxide group should not be much different from this value.

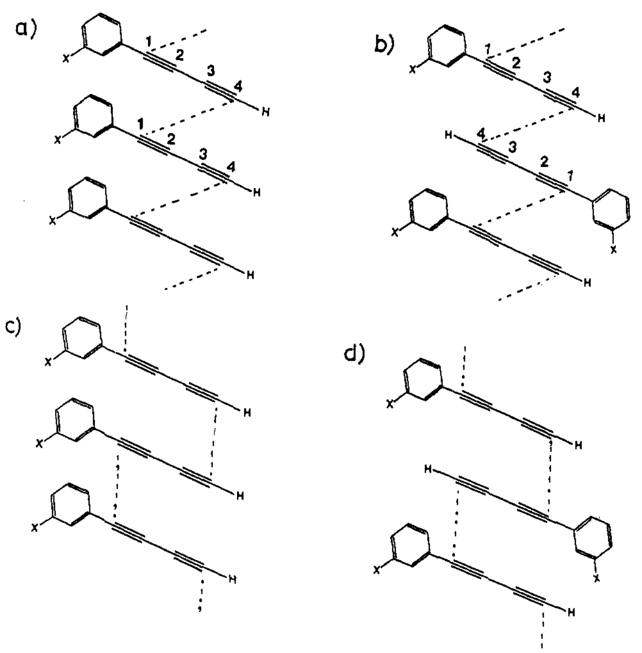
According to Baughman,[7c] the 1,4-addition is possible if 1,3-butadiyne molecules stack in crystals tightly (s = 3.4–4.0 Å) and slanted (γ = 45°), as shown in Scheme I. Whereas the molecules of **3** appear to be stacked head-to-head along the crystal axis c (Figure 2), the nearest distance, C-1 and C-1′, between the neighboring molecules is as large as 8.00 Å. They are too far away to undergo solid-state polymerization. They are stacked rather head-to-tail along the a/c diagonal with the distances between C-1 and C-4′ and C-4 and C-4′ of the neighboring molecules being 4.55 and 4.72 Å, respectively (Figure 3). The crystals did undergo polymerization.

The exothermicity of the solid-state polymerization of 1-phenyl-1,3-butadiynes is usually in the range 35–60 kcal/mol.[9] These values are slightly higher than, but agree in the order of magnitude with, the sum of the bond enthalpies of C–C double (150 kcal/mol) and single bonds (85 kcal/mol) minus that of a triple bond (195 kcal/mol), suggesting that the change of one triple bond into a double bond and an additional single bond in the course of the polymerization process must be mainly responsible for the enthalpy change. The observed exothermic heat flow (64.0 kcal/mol for **3**) corresponds to the upper limit of the typical values and could be interpreted in terms of the strengthening of the hydrogen bond in the polymer or the occurrence of some additional chemical reactions (vide infra).

Operationally there are four modes (Scheme III) of bonding for the polymerization of 1-(substituted phenyl)-1,3-butadiynes, out of which mode b or d would be predicted to be most likely for **3** by application of the principle of least motion. From the topological point of view, modes a and d are mutually equivalent and can serve as ferromagnetic coupling units for the electron spins residing on the all-meta nitroxides. An X-ray powder pattern of the polymer sample of the mixed crystals revealed a broad peak at ca. 2θ = 19° (Cu Kα), suggesting the presence of a periodicity of 4.7 Å corresponding to the polymerization in the a/c diagonal direction.

The observed hydrogen bond interlocking the columnar arrangements of the stacked monomer molecules might be ideal for increasing the dimensionality for the exchange interaction once the high spin alignment is achieved within each column. The dark violet polymer crystals were insoluble in any typical organic solvents. Aeration of the suspension of the polymer sample under supersonic agitation did not induce any meaningful conversion of the hydroxyamine functional group into the corresponding nitroxide as judged by their ESR spectra.

Scheme III



We had expected the chemical inertness of the polymer samples of **3**, since it is well-established that poly(diacetylenes) are not attacked even by bromine. To our dismay, however, the crystals of nitroxide **4** did not polymerize under any typical conditions we tried. We therefore tried to dope the crystals of **3** with **4**. When allowed to polymerize by heating at ca. 140 °C, the mixed crystals underwent polymerization as long as the content of **4** was lower than 50%. The samples obtained from a 30% mixture showed ESR spectra as reproduced in Figure 5 and were found to contain only a few percent of the theoretical spins! Some of these remaining spins in the polymer samples decay further in a few days.

ESR Spectral and Magnetic Properties. Poly(diacetylenes) are known to contain some spins due to the chain terminals and/or defects.[7d–f] The spin concentrations in these samples are ca. 10^{17}, 2 orders of magnitude smaller than those to be discussed in this work.

The low-field broad ESR signal shifted by 100–200 G from the field corresponding to $g = 2$ is explained if we assume the presence of some locally ordered spins exhibiting an ellipsoidal Lorentz field of ca. 50–100 G. Thus, there are three different sites for the spins kept intact after the polymerization: isolated spins ($S = {}^1/_2$), exchange-narrowed spins, and spins in a molecular field of 50–100 G. This last environment of the spins decays with time at room temperature.

Plot 1 in Figure 6 gives a Curie constant of 7.2×10^{-5} emu K/g and a spin concentration of 9.6×10^{19} spins/g. This value corresponds to ca. 4% of the monomer units remaining intact after the polymerization of the mixed crystals. In other words, almost 90% of the nitroxide radicals are lost during the polymerization reactions. There are two possibilities for this apparent loss of unpaired electrons: chemical reactions of the nitroxide during the polymerization reaction or antiferromagnetic coupling in the undesired 1,1′ 4,4′ polymerization products. The observed slightly higher exothermicity of the reaction suggests the former possibility. Other independent observations were all obscured by the presence of a large amount of **3** used in the matrices in the mixed crystal samples.

When a freshly prepared sample was subjected to a temperature cycle, raising the temperature from 4.2 to 300 K and lowering back to the cryogenic temperature in the superconductive solenoid

---

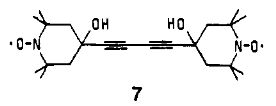
[14] (a) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 1266. (b) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33. (c) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

with the main field of 0 T, some more radical centers were lost. The magnetization curves at 4.2 K before and after the temperature cycle were fitted to Brillouin functions in which $S = 0.65$ with the spin concentration of 1.59×10^{19} and $S = 0.48$ with 1.38×10^{19} spins/g, respectively. The spins in the former sample are considered to consist mainly of the $S = {}^{1}/_{2}$ spins and some $S > {}^{1}/_{2}$. The alignment of the electron spins in such a low concentration is surprising. The spins may not be evenly distributed but instead make an "island" in which they have ferromagnetic exchange interactions; others are just uncorrelated. Comparison with the data after the temperature cycle suggests that the most of the original sites with $S > {}^{1}/_{2}$ were lost during the phase transition at ca. 250 K and that the transition is due to the temperature rather than the magnetic field. Such a loss of the spins during the low-temperature treatment is, to our knowledge, quite novel. We tentatively interpret the result as arising from free radical recombination and/or disproportionation reactions induced by the contraction of the molecular packing in crystals at the cryogenic temperature followed by their annealing at around 250 K. Alternatively, conformational changes in the polymer chains could induce bond shifts with resultant antiferromagnetic coupling among the spin sites through bonds. Actually some poly(diacetylenes) undergo structural phase transitions accompanying thermochromism in these or higher temperature regions.[7g]

Prospect of Strongly Magnetic Poly(diacetylenes). Whereas we had expected to obtain samples that might show at least superparamagnetic properties, the very high spin poly(diacetylenes) have not been obtained in this work. Even though high-spin polymers are obtained, poly(diacetylenes) are basically one-dimensional. Spin alignments in one-dimensional chains are said to be unstable at finite temperatures. Introduction of interchain exchange repulsion (J_2), however weak it may be, is considered to stabilize the spin alignment. According to Tyutyulkov,[15] the Curie temperature can become as high as 1190 K by introduction of $J_2 = 0.001\,85$ eV in one-dimensional polymers, e.g., higher polymers of **1** and **2**.

We hope the interchain interaction with such J_2 values will be obtained when the distance between the moieties of the neighboring chains is 3.0–3.5 Å and the orientation of the overlap between them is appropriately controlled. Actually, a model experiment simulating the stacking overlap between two triplet diphenylcarbene molecules in crystals has been carried out by taking advantage of the [2.2]paracyclophane skeleton.[16b,c] In good agreement with McConnell's Heitler–London spin-exchange model between spin densities of opposite sign on the interacting radicals,[16a] ferromagnetic J_2 values of 0.002–0.003 eV are obtained from the "ortho" and "para" stackings, while $J_2 = -0.006$ eV (antiferromagnetic) for the "meta" overlap. Judging from the X-ray data of the precursor **3** in this work, the hydrogen bond between the polymer chains is expected to contribute to this interchain interaction and stabilization of the spin alignment by added dimensionality.

In 1986 Korshak and Ovchinnikov reported black powdery materials obtained by polymerization of a diacetylene having a symmetrical pair of persistent nitroxide radicals (**7**).[17] A part of this sample was described to show ferromagnetic properties (spontaneous magnetization of ca. 0.022 emu G/g). Even if the expected poly(diacetylene) skeleton is formed in spite of the observed wrong crystal structure of the monomer for topochemical polymerization,[18] the structure of the polymer **4′** (X = Y = TEMPO) is not consistent with our molecular design in two senses. First, radical centers are not conjugated with the main chain; they are too far apart by three saturated carbon atoms to have meaningful exchange coupling. Second, even if there is one, since the structure is symmetric, the interaction is expected to be antiferromagnetic. Actually there are some recent reports contradictory to the Russian claim.[18]



7

In spite of the present negative results and the above controversial data in the literature, we believe that the poly(diacetylene) skeletons have a number of merits worthy of further experimental studies. First, since the polymerization of diacetylenes is effected by heat or irradiation with electrons, γ-ray or UV light in the solid state and topochemically controlled, there is a lower chance of the polymer samples being contaminated with catalysts, often consisting of paramagnetic transition metals. Second, we can expect to obtain crystalline polymers that are more readily characterizable and expected to show firmer spin alignment. Third, since only the exposed part of the sample undergoes polymerization, when the reaction is induced by irradiation, there is a chance of designing an optomagnetic recording device consisting only of organic polymers. Our preliminary results show that 1-[(*p*-diazomethyl)phenyl]-1,3-butadiyne undergoes spontaneous polymerization in neat microcrystals and appears most promising for these purposes.[19]

On the other hand, however, we have to be careful in that the above merits can often become disadvantages as well. Since the polymerization is topochemically controlled, not all diacetylenes are amenable to the reaction. Many diacetylene derivatives have so far eluded our attempts at polymerization. Control of molecular packing in crystals, in other words crystal design, is now needed. Introduction of the technology of liquid crystals or Langmuir–Blodgett membranes may be of help. Second, poly(diacetylenes) are very insoluble in ordinary organic solvents: the radical centers serving as spin carriers have to be introduced in advance. Although the mechanism of the polymerization does not require free radicals and is topochemically controlled, there is a chance of the pendant radicals being intercepted by the polymerization reactions, as observed in this study.

Experimental Section

(A) ESR Spectroscopy and Magnetic Measurements. ESR spectra were recorded by using a Bruker ESP 300 X-band (9.4 GHz) spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter. An Air Products LTD-3-110 liquid helium transfer system was fitted for the low-temperature measurements. The magnetic susceptibility was measured by the Faraday method on an Oxford Instruments magnetic susceptibility system with a 7-T superconducting magnet as described previously.[6d,20]

(B) X-ray Analysis. A large clear platelike single crystal of approximate dimensions $0.48 \times 0.38 \times 0.13$ mm^3 was mounted on a glass fiber support. Diffraction data were obtained on a Rigaku AFC-5R four circle diffractometer with 2θ (max) = 55.2° using graphite monochromated Mo Kα radiation (2.64 cm^{-1}) at 23 °C. The structure was solved in $P\bar{1}$ by direct methods and converged with full-matrix least-squares using the TEXAN Ver. 2.0 program (Molecular Structure Corporation). Crystal data were as follows: $C_{14}H_{14}NOCl$, MW = 247.72, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.496$ (3) Å, $b = 10.755$ (5) Å, $c = 8.004$ (3) Å, $\alpha = 92.77$ (4)°, $\beta = 106.51$ (3)°, $\gamma = 74.85$ (3)°, $V = 676.6$ (5) Å^3, $Z = 2$, $D_X = 1.22$ g cm^{-3}. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C–H 0.96 Å, C–C–H 109.5°, 120° or 180°) and refined isotropically using a rigid model. Refinement converged at $R = 0.081$ and $R_W = 0.102$ for 1973 unique reflections, with $I > 3\sigma(I)$ and 154 variables.

---

(15) (a) Tyutyulkov, N.; Karabunarliev, S. *Int. J. Quantum Chem.* **1986**, *29*, 1325. (b) Tyutyulkov, N.; Polansky, O. E. *Chem. Phys. Lett.* **1987**, *139*, 281.

(16) (a) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. (b) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamrua, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. (c) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(17) (a) Korshak, Yu. V.; Ovchinnikov, A. A.; Shapiro, A. M.; Medvedeva, T. V,; Specktor, V. N. *Pis'ma Zh. Eksp. Teor. Fiz.* **1986**, *43*, 309. (b) Korshak, Yu. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Specktor, V. N. *Nature* **1987**, *326*, 370.

(18) (a) Zhang, J. H.; Epstein, A. J.; Miller, J. S.; O'Connor, C. J. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 271. (b) Sandman, D. J.; Hamill, G. P.; Levinson, M.; Rossoni, P. G.; Yost, E. A.; Papaefthymiou, G. C. *Mat. Res. Soc. Symp. Proc.* **1990**, *173*, 567. (c) Cao, Y.; Wang, P.; Hu, S.; Li, S.; Zhang, J. H.; Zhao, J. *Synth. Met.* **1988**, *27*, B625. (d) Wiley, D. W.; Calabrese, J. C.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 277.

(19) Sasagawa, M.; Koga, N.; Iwamura, H. The 10th IUPAC Conference on Physical Organic Chemistry, August 5–10, 1990, Haifa, Israel.

(20) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238.

(C) Thermal Analysis. Approximately 5-mg samples were sealed in aluminum sample pans and studied at the heating rate of 4 °C/h on a Rigaku TAS 100 thermal analysis system.

(D) Materials. (*p*-Chlorophenyl)acetylene. A mixture of 25 g (0.13 mol) of 4-bromochlorobenzene and 25 g (0.30 mol) of 3-methyl-1-butyn-3-ol in 200 mL of triethylamine was heated under reflux in the presence of 0.05 g of $Pd(Ph_3P)_2Cl_2$, 0.05 g of Cu_2I_2, and 0.1 g of Ph_3P for 8 h until the displacement reaction was complete. The reaction mixture was cooled and filtered, and the solvent was removed by distillation. The residue was transferred to a flask containing 200 mL of benzene and 1.0 g of sodium hydride. The mixture was heated under reflux for 3 h, cooled, filtered, and concentrated by evaporation of the solvent. The residue was steam-distilled, and the distillate was recrystallized from methylene chloride to yield 15 g (84% overall yield) of the (chlorophenyl)acetylene as colorless crystals: mp 44.5–45.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.11 (1 H, s), 7.31 (2 H, dt, J = 8.7, 2.1 Hz), 7.43 (2 H, dt, J = 8.7 and 2.1 Hz).

1-(*p*-Chlorophenyl)-5-methyl-1,3-hexadiyn-5-ol. A solution of 26 g (0.16 mol) of 1-bromo-3-methyl-1-butyn-3-ol in 160 mL of DMF was added to a mixture of 15 g (0.11 mol) of the (chlorophenyl)acetylene, 260 mg (2.6 mmol) of Cu_2Cl_2, 12.4 g (0.19 mol) of 70% aqueous ethylamine, and 0.1 g of hydroxyamine hydrochloride in 300 mL of DMF over a 24-h period at room temperature. Twenty milliliters of 10% aqueous potassium cyanide was added to the reaction mixture. The mixture was extracted with benzene, and the organic layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent in vacuo gave an oil. The crude product was chromatographed upon silica gel with hexane/ether (1:1) as an eluent to give 15 g (64.2%) of the diacetylene as white crystals: mp 102.0–103.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.58 (6 H, s), 2.06 (1 H, br s), 7.29 (2 H, dt, J = 9.0, 2.1 Hz), 7.40 (2 H, dt, J = 9.0, 2.1 Hz).

Tetrahydropyranyl Ether. A solution of 2.0 g (9.2 mmol) of the diacetylene, 2.0 g (23.8 mmol) of 3,4-dihydro-2*H*-pyran, and 0.05 g of *p*-toluenesulfonic acid monohydrate in 20 mL of methylene chloride was stirred at room temperature for 4 h. The reaction mixture was washed with 20 mL of saturated aqueous sodium bicarbonate solution, dried over $MgSO_4$, and concentrated by evaporation of the solvent under reduced pressure to yield 2.7 g (99%) of white crystals: mp 70.5–71.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.5–1.9 (6 H, m), 1.55 (3 H, s), 1.59 (3 H, s), 3.4–4.0 (2 H, m), 5.0–5.1 (1 H, m), 7.30 (2 H, d, J = 8.7 Hz), 7.42 (2 H, d, J = 8.7 Hz).

Protected Hydroxyamine 5. To a solution of 100 mg (0.331 mmol) of the protected diacetylene in 50 mL of THF cooled at −78 °C was added dropwise 0.25 mL (1.2 equiv) of 1.6 M *n*-butyllithium in hexane. The mixture was stirred at −78 °C for 3.5 h, and to this solution was added dropwise a solution of 300 mg of 2-methyl-2-nitrosopropane in 3 mL of THF. The mixture was stirred at −78 °C for 4 h and at room temperature for 1 h. The reaction was quenched by the addition of 10 mL of water and treated with ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to yield a pale yellow solid. Recrystallization from ether hexane (1:1) gave 103 mg (80%) of colorless crystals: mp 127.0–128.0 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (9 H, s), 1.55 (3 H, s), 1.59 (3 H, s), 1.5–1.9 (6 H, m), 3.5–4.0 (2 H, m), 5.05–5.07 (1 H, m), 6.10 (1 H, br s), 7.20 (1 H, dd, J = 8.3, 1.9 Hz), 7.26 (1 H, d, J = 8.3 Hz), 7.77 (1 H, d, J = 1.9 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.3, 25.2, 25.3, 29.6, 30.3, 31.9, 62.4, 63.3, 68.4, 71.5, 74.0, 85.6, 96.3, 120.2, 130.0, 130.5, 132.0, 132.5, 147.1.

1-[3-(*N-tert*-Butylhydroxyamino)-4-chlorophenyl]-1,3-butadiyne (3). A mixture of 100 mg (0.26 mmol) of the protected hydroxyamine and 10 mg of pyridinium *p*-toluenesulfonate in 50 mL of ethanol was heated at 55 °C for 3 h. The reaction mixture was cooled, poured into 200 mL of water, and extracted with ether. The organic layer was dried over magnesium sulfate and concentrated in vacuo. To the benzene solution (50 mL) of the residue was added 10 mg of sodium hydride. The mixture was heated under reflux for 1 h, cooled, and filtered, and the filtrate ws evaporated at room temperature to yield pale yellow solids. Recrystallization from ether hexane (1:1) gave 55 mg (86%) of colorless triclinic crystals: mp ca. 140 °C (polymerization); ^1H NMR (270 MHz, $CDCl_3$) δ 1.20 (9 H, s), 2.50 (1 H, s), 5.36 (1 H, br s), 7.23 (2 H, dd, J = 8.2, 1.9 Hz), 7.29 (2 H, d, J. − 8.2 Hz), 7.76 (1 H, d, J = 1.9 Hz). Anal. Found: C, 67.66; H, 5.86; N, 5.65; Cl, 14.18. Calcd for $C_{14}H_{14}NOCl$: C, 67.88; H, 5.70; N, 5.65; Cl, 14.31.

1-[3-(*N-tert*-Butylnitroxyl)-4-chlorophenyl]-1,3-butadiyne (4). A 5-mL aqueous solution of 500 mg of Fremy's salt was added dropwise to a mixture of 2 g of K_3PO_4 and 100 mg (0.40 mmol) of **3** in water/THF (3:1). The reaction mixture was stirred at room temperature for 3 h and then extracted with ether. The organic layer was washed with cold water, dried over magnesium sulfate, and concentrated under reduced pressure at room temperature to yield a red oil. The crude product was crystallized from *n*-pentane/ether (10:1) to give 75 mg (76%) of red crystals: mp 81–82 °C; ESR (X-band, hexane) $g = 2.0066$, $a_N = 13.8$ G. Anal. Found: C, 68.31; H, 5.48; N, 5.71; Cl, 14.36. Calcd for $C_{14}H_{13}NOCl$: C, 68.16; H, 5.31; N, 5.68; Cl, 14.37.

Acknowledgment. This work was supported by the Ministry of Education, Science, and Culture (Grant Nos. 63430006 and 01648002) and the Mitsubishi Science Foundation. We thank Drs. Hikaru Ichida and Akiko Kobayashi for their assistance in the X-ray crystal and structure analysis.

Registry No. 3, 129541-86-2; **3** (homopolymer), 129541-87-3; **3**/**4** (copolymer), 129541-89-5; **4**, 129541-88-4; **5**, 136881-86-2; **5** hydroxyamine derivative, 136881-85-1; ClC_6H_4-*p*-Br, 106-39-8; $HC\equiv CC(Me)_2OH$, 115-19-5; ClC_6H_4-*p*-$C\equiv CH$, 873-73-4; $BrC\equiv CC(Me)_2OH$, 2063-19-6; *t*-BuNO, 917-95-3; ClC_6H_4-*p*-$C\equiv CC\equiv CC(Me)_2OH$, 136881-87-3; 3,4-dihydro-2*H*-pyran, 110-87-2; 1-(*p*-chlorophenyl)-5-methyl-1,3-hexadiyn-5-ol tetrahydropyranyl ether, 136881-88-4; 1-[3-(*N-tert*-butylhydroxyamino)-4-chlorophenyl]-5-methyl-1,3-hexadiyn-5-ol tetrahydropyranyl ether, 136881-89-5.

Supplementary Material Available: Listing of crystallographic data and processing descriptions, final atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and an ORTEP drawing for compound **3** (9 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.