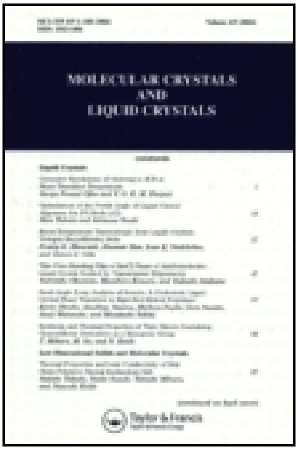

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Synthesis and Characterization of a Diiminoxyl Derivative of 2,4-Hexadiyne-1,6-Diol

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SYNTHESIS AND CHARACTERIZATION OF A DIIMINOXYL DERIVATIVE OF 2,4-HEXADIYNE-1,6-DIOL

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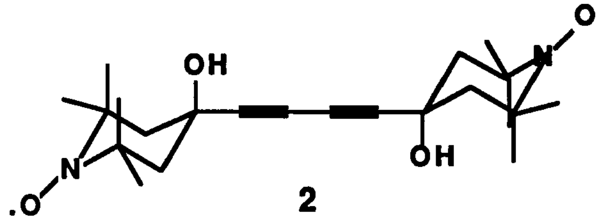
Contribution No. 5187 from the Central Research and Development, E. I. du Pont de Nemours and Co., Inc., Experimental Station 328, Wilmington, DE 19880-0328, U. S. A.

Abstract Two polymorphs of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate) have been prepared and characterized by X-ray diffraction, infrared, Raman, and EPR spectroscopies, and magnetic susceptibility. Based upon accepted structural criteria, both polymorphs should not support single crystal topochemical polymerization; UV, electron beam, and gamma ray induced polymerization has not been achieved for either phase. Thermal treatment, however, turns the crystals black, but magnetic susceptibility studies show no anomalous behavior characteristic of ferromagnetism.

INTRODUCTION

As evidenced by the proceedings of this conference, the search for ferromagnetic organic compounds and polymers is the focus of contemporary research.[1-9] Reports of ferromagnetic polymeric materials have been plagued by ill-defined compositions, low yields, lack of characterization and poor reproducibility.[5-9] This chemistry attempts to take advantage of the fact that some diynes crystallize in such a manner that enables thermal, photochemical, or X-ray induced topochemical polymerization to form a single crystal polymer or polydiynes in a single crystal matrix.[10] Cao and coworkers have recently reported that the the thermal treated product of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-carboxylate), **1**, exhibits a spontaneous magnetization of 88.5 emuG/mol and a coercive field of 455 G.[7] The saturation magnetization is consistent with of a 1.6% bulk effect; an order of magnitude greater than reported by Ovchinnikov and coworkers for thermal treated related 4,4'-(butadiyne-1,4-diyl)-bis-(2,2,6,6-tetramethyl-4-hydroxy-piperidin-1-oxyl), **2**.[6]

1



2

As part of our continued interest in molecular based ferromagnetic materials,[1,2,8] we have prepared **1** in an effort to verify and elucidate its ferromagnetic behavior after polymerization.

PREPARATION AND CHARACTERIZATION

2,4-Hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate) **1**, was synthesized by the condensation of 2,4-hexadiyne-1,6-diol with 2,2,5,5-tetramethyl-1-oxyl-3-pyrrolinecarboxylic acid, Scheme I. After careful purification by multiple flash chromatography, we found that two phases, α and β, could be obtained during recrystallizations. The IR spectra of the two solid phases in KBr pellets or Nujol mulls were quite different, but were identical in CCl_4 solutions. The Raman spectra of both solid phases showed the presence of the acetylenic groups with $\nu_{C\equiv C} = 2263\ cm^{-1}$.

The structures of both phases were determined by X-ray diffraction. The relevant conditions for the X-ray data collection, data reduction and structure refinement are summarized in Table 1, with Tables 2 and 3 listing the bonding and closest non bonding distances, respectively. Figure 1 gives the atom labeling for **1**. The stereoview unit cell projections are shown in Figures 2 and 3. The molecular structure of both phases are essentially equivalent with the average C≡C, CC-CC, and NO distances of 1.186, 1.380, and 1.279 Å, respectively, typical of diiminoxyl diacetylenes.[8,10] The major difference between the pair of phases is their relative conformation around the linear hexadiyne fragment. The α-phase consists of half the molecule

TABLE 1 Summary of X-ray Diffraction Data for the α- and β-phases of 2,4-Hexadiyne-1,6-diyl Bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate),1

	α-phase	β-phase
Empirical Formula	$C_{24}H_{30}N_2O_6$	$C_{24}H_{30}N_2O_6$
Formula Weight	442.51	442.51
Crystal Color, Habit	golden yellow, square fiber	yellow, rectangular block
Crystal Dimensions, mm	0.10 x 0.10 x 0.50	0.40 x 0.30 x 0.50
Crystal System	monoclinic	monoclinic
No. Reflections Used for Unit Cell Determination (2θ range)	22	25
Omega Scan Peak Width at Half-height, deg	0.20	0.16
a, Å	5.867 (3)	8.152 (1)
b, Å	21.894 (3)	33.763 (4)
c, Å	9.711 (3)	9.192 (2)
β, deg	96.18 (2)	104.59 (1)
Temperature, °C	-70	-70
V, Å^3	1240.2	2448.4
Space Group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z value	2	4
density$_{calc}$, ρ, g/cm^3	1.185	1.200
μ(Mo), cm^{-1}	0.80	0.81
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	MoK$_a$	MoK$_a$
Scan Type	ω	ω
Scan Rate, deg/min	1.50 - 3.40 (ω)	1.50 - 5.00 (ω)
Scan width, deg w	1.20 - 1.90	1.20 - 1.90
min, max 2q, deg	1.9, 52.0	1.2, 55.0
No. of Reflection Measured	2657	6017
Structure Solution	Direct Methods (MULTAN)	
Hydrogen Atom Treatment	Included in calculated positions (D$_{C\text{-}H}$ = 0.95Å)	
Refinement	Full-matrix least-squares	
Check reflections	2, 29 times	2, 40 times
Variation	4% fluctuation	2 % fluctuation
Psi-scan variation, %	13.4	4.0

Duplicates	140, 1.8 % R-merge	325,1.5%R-merge
Weighting scheme	weights $\propto [\sigma^2(I)+0.0009I^2]^{-1/2}$	
Atoms refined	anisotropic: all nonhydrogen atoms fixed: H	
Parameters varied	145	289
Data/parameter ratio	6.02	11.19
No. Observations (I >3.00σI)	873	3235
No. Variables	261	252
R_u,[a]	0.066	0.047
R_w,[b]	0.066	0.051
Goodness of Fit Indicator	2.01	1.82
Max Shift/Error in Final Cycle	0.00	0.03
Maximum Peak in Final Diff. Map	0.23 e/Å^3	0.25 e/Å^3

[a] $R_u = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ [b] $R_w = (\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o{}^2)^{1/2}$

lying on an inversion center with both pyrroline-carboxylate groups essentially *trans* to each other, whereas the β-phase has these groups asymmetrically arranged, Figure 4. The packing motif of the two phases are similar with the linear hexadiynes aligned in herringbone fashion. The closest interdiyne separations in the α-phase for the 1-carbon of the butadiyne portion of one molecule to the 4- and 3-carbons of the butadiyne portion of the nearest neighboring aligned molecule are 4.14 and 4.42 Å, respectively. In the β-phase, the nearly eclipsed pyrroline carboxylate groups allow a pairing of near neighbors resulting in a somewhat closer approach between the hexadiyne carbons (3.93 and 4.40 Å, respectively). In neither case are the butadiyne portions close enough and positioned correctly to support topochemical polymerization.[10]

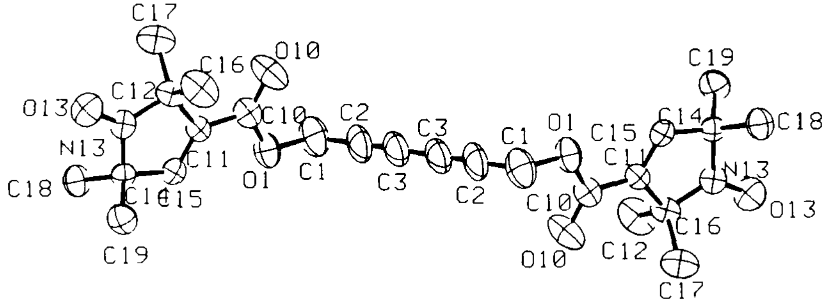


FIGURE 1. Atom labeling for 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), **1**.

TABLE 2 Distances, Å, for the α- and β-phases of 1

Atoms	α-phase[a]	β-phase[b]
O(13)-N(13)	1.266 (6)	1.272 (2)
O(13')-N(13')		1.272 (2)
O(1)-C(1)	1.423 (8)	1.445 (3)
O(1')-C(1')		1.445 (3)
O(1)-C(10)	1.358 (7)	1.346 (2)
O(1')-C(10')		1.351 (2)
O(10)-C(10)	1.189 (7)	1.193 (2)
O(10')-C(10')		1.200 (3)
N(13)-C(12)	1.464 (7)	1.478 (3)
N(13')-C(12')		1.479 (3)
N(13)-C(14)	1.462 (7)	1.471 (3)
N(13')-C(14')		1.484 (3)
C(1)-C(2)	1.450 (11)	1.458 (3)
C(1')-C(2')	1.460 (3)	
C(2)-C(3)	1.179 (10)	1.189 (3)
C(2')-C(3')		1.192 (3)
C(3)-C(3a,3')	1.378 (17)	1.381 (3)
C(10)-C(11)	1.460 (8)	1.478 (3)
C(10')-C(11')		1.475 (3)
C(11)-C(12)	1.489 (8)	1.510 (3)
C(11')-C(12')		1.519 (3)
C(11)-C(15)	1.311 (8)	1.315 (3)
C(11')-C(15')		1.319 (3)
C(12)-C(16)	1.538 (8)	1.526 (4)
C(12')-C(16')		1.520 (3)
C(12)-C(17)	1.528 (9)	1.514 (4)
C(12')-C(17')		1.526 (3)
C(14)-C(15)	1.489 (8)	1.494 (3)
C(14')-C(15')		1.483 (3)
C(14)-C(18)	1.537 (8)	1.525 (3)
C(14')-C(18')		1.526 (3)
C(14)-C(19)	1.531 (8)	1.521 (3)
C(14')-C(19')		1.520 (3)

[a] symmetric around C(3)-C(3a). [b] asymmetric around C(3)-C(3').

TABLE 3 Nonbonding Distances (<4 Å) for the α- and β-Phases of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), **1**

Atoms	α-phase	β-phase
	Intermolecular Nonbonding Distances	
O(1)...C(16')[a]		3.336 (3)
O(13)...C(1)[b]		3.156 (3)
O(13)...C(15)[c]	3.080 (7)	
O(13')...C(1')[d]		3.117 (3)
O(13')...C(15')[e]		3.259 (3)
O(13')...C(18')[e]		3.375 (3)
	Intramolecular Nonbonding Distances	
O(1')...C(16')		3.153 (3)
O(1')...C(17')		3.143 (3)
O(10)...C(2)	3.056 (10)	3.226 (3)
O(10)...C(3)	3.813 (10)	
O(10)...C(16)	3.304 (8)	3.311 (3)
O(10)...C(17)	3.151 (9)	3.155 (3)
O(10')...C(2')		3.323 (3)

[a] 1-x, 1-y, 2-z. [b] x, y, -1+z. [c] -1/2+x, 1/2-y, 1/2+z

[d] 1+x, y, z. [e] 1/2+x, 3/2-y, 1/2+z

The thermal behaviors of both phases were studied under nitrogen with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Neither phase showed any rapid change below their melting points. Upon melting, an exothermic reaction set in accompanied by darkening with no weight loss until ca. 140-160° C. From these temperatures to a break around 170-180° C, there was an endothermic weight loss of 2.5-4%. Above this the measurements indicated a steady decomposition with 35-40% weight loss by 250-300° C. No additional information was gained by changing the rate of heating (range 2 to 20° C/min).

The magnetic susceptibility of both phases obey the Curie-Weiss expression with $\theta = \sim 0 \pm 2$ K. The effective moment is ~2.45 μ_B per molecule consistent with two independent $S = 1/2$ spins per molecule. Both solid α- and β-phases of the monomer gave nearly identical EPR results. The spectra of 1α and 1β consist of single lines at 2.007 G with ΔH_{pp} = 12 and 20 G, respectively, at 273K.

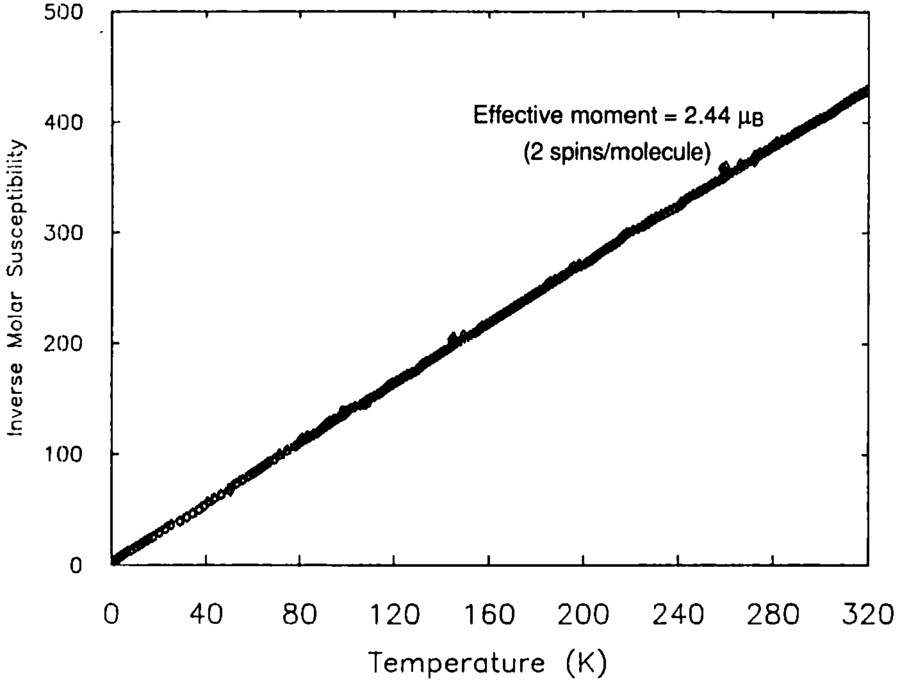


FIGURE 5. Reciprocal molar magnetic susceptibility, χ_M^{-1}, as a function of temperature for either polymorph of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), 1.

ATTEMPTED POLYMERIZATION

In order to induce topochemical polymerization, we have studied the effects of both radiation and heat. The α and β monomers were subjected to γ-ray, electron beam, and UV irradiations. No change was noted for either γ-ray or electron beam irradiations. Some darkening was observed after 72 h exposure to UV. The magnetic susceptibility measurements showed a reduced moment of 2.16 μB per original monomer unit. Longer exposure (162 h) caused additional darkening with the moment reduced to 2.09 μB.

Thermal treatment of 1 caused was carried out either under TGA conditions in N_2 or in Pyrex tubes under vacuum. Isothermal calorimetry on both phases at 90° C for 10 h under N_2 showed essentially no weight loss, slight darkening, and a decrease in μ_{eff} to 2.35 μB per original monomer unit.

At 95° C for 55 h, there was more darkening, 2.2% weight loss and a further decrease in the moment to 1.69 μ_B. The experiments were carried out in Pyrex tubes placed in a temperature controlled small tube heater. At 90° C for 12 days, the quite dark solids showed a decrease in moment to 0.89 μ_B. When samples were heated at 99° overnight, an amorphous dark melt resulted in a dark solid which still had μ_{eff} = 1.69 μ_B. In both the radiated and heated samples, no anomalous behavior as reported by Cao and co-workers[5] was observed in the temperature dependence of the magnetic moment over the range of 1.5 - 300 K. Careful analyses of the field dependent magnetization for magnetic field up to 19.5 kG for several samples showed that any ferromagnetic impurities are present in less than 2 ppm by weight of equivalent iron.

CONCLUSION

In conclusion, the α- and β-2,4-hexadiyne-1,6-diyl bis-(2,2,5,5-tetramethyl-1-oxyl-3-carboxylate), **1**, diacetylene monomer is a well behaved magnetic system comprised of a pair of independent doublets without evidence for a significant triplet. Since the spins on this diacetylene monomer essentially do not couple, it seems unlikely that should the desired single crystal polymer form that it would possess spin coupling that could lead to high spin or ferromagnetic behavior. A preferred model diacetylene monomer should have a spin coupled triplet ground state as well as the ideal solid state structure enabling topochemical polymerization.

The magnetic data of both phases of **1** as well as their thermal degradation products do not provide evidence that any polymeric or organic material present possesses ferromagnetic coupling or ferromagnetic behavior.

EXPERIMENTAL SECTION

Magnetic susceptibility were determined by the Faraday method. IR and Raman spectra were recorded on a Perkin Elmer 283B spectrometer.[11] C, H and N analyses were performed by Micro-Analysis, Inc., Wilmington, Delaware. Temperature dependent EPR spectra were recorded on an updated Bruker ER 200 D-SRC with an ESP 1600 data system using an ER

4111 VT temperature controller. The γ-ray irradiation (2.5 Mrad) from a ^{60}Co source was carried out by Neutron Products Inc., Dickerson, MD and and electron beam irradiation (5 Mrad) was performed by Electron Technologies Corp., South Windsor, CT. The UV source was a 450 watt medium pressure mercury arc lamp. In all cases sample temperatures did not exceed 60-65 C.

2,4-Hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-carboxylate) ,1. A solution of 5.53 g (30 mmol) 2,4-hexadiyne-1,6-diol, 1.57 g (14.3 mmol) 2,2,5,5-tetramethyl-1-oxyl-3-pyrrolinecarboxylic acid, 6.19 g (30 mmol) dicyclohexyldicarbo-dianhydride, and 0.24 g (2 mmol) 4-dimethylpyridine in 200 mL THF was stirred overnight. Filtration of the insoluble dicyclohexylurea and removal of the solvent gave crude product which was roughly purified by passing through a 200 x 45 mm silica column using 3:2 pet ether:EtOAc to give 11.78 g (93%)of 1 as a yellow oil which slowly solidified. Purification by multiple flash chromatography gave material which showed only only one spot by TLC on silica. [Development with phosphomolybdic acid gave a much more sensitive analysis than using UV on fluorescent plates.] Analytical and X-ray quality crystals were obtained by recrystallizations of the pure material from hexane or *i*-hexane. The α-phase was obtained randomly by recrystallization without seeding as flat rectangular plates or square fibers, mp 104-105° C. Recrystallization with seeding of the hot solutions most often afforded the β-phase as rectangular blocks, mp 108-109° C. Both crystals were yellow to orange-yellow in color depending on their thickness. Although we were not able to get a-phase in a reproducible manner, we were able to get it often enough for these studies. The crystals of the two phases were identified by their appearance and their characteristic IR spectra. In KBr and Nujol, the α-phase had an unusual sharp peak at 3084 cm^{-1} along with a characteristic 5-peak pattern between 900 and 970 and sharp single peaks at 769m and 548mw cm^{-1}. The β-phase had many of the absorptions split or showing shoulders including the strong C=O peak at 1727 cm^{-1} and a different 5-peak pattern between 900 and 970 cm^{-1}. In CCl_4, both phases had identical spectra with $\upsilon_{C=O}$ = 1731s, $\upsilon_{C=C}$ = 1629m, $\upsilon_{N-O\cdot}$ = 1290ms, and υ_{C-O} = 1185ms and 1050s cm^{-1}. The analytical samples were dried under vacuum at 65° C for 2 hrs. Anal. Calc'd for $C_{24}H_{30}N_2O_6$: C = 65.1, H = 6.8, N = 6.3, and MW = 442.51. Found for the α-phase: C = 65.2, H = 7.1, and N = 6.3. Found for the β-phase: C = 65.3, H = 7.1, and N = 6.3. Both phases gave identical FAB mass spectra with an anomalous parent peak at 442.10. [The

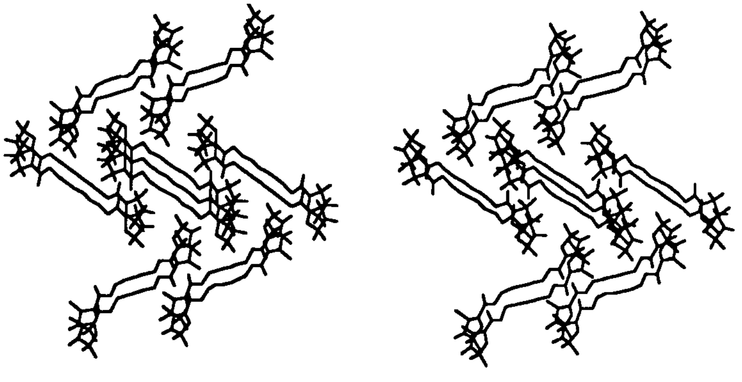


FIGURE 2. Stereoview of the unit cell of the α-phase of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), **1α**.

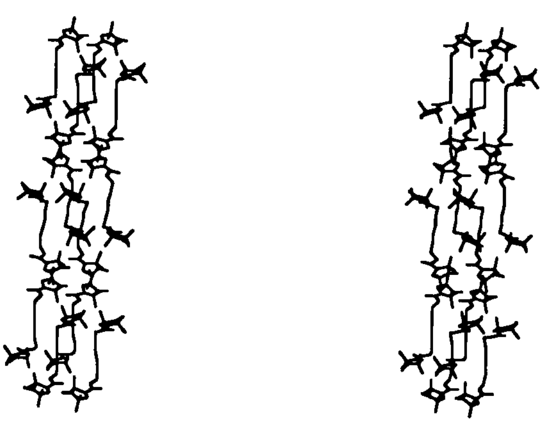


FIGURE 3. Stereoview of the unit cell of the β-phase of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), **1β**.

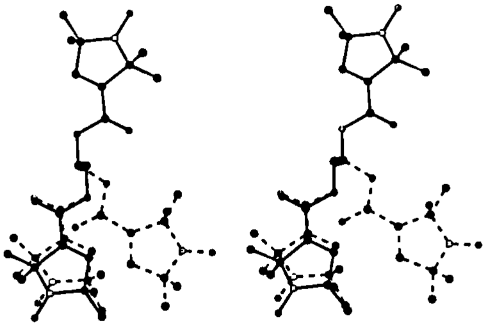


FIGURE 4. Stereoview of the molecular conformation for the α- and β-phases of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), **1α** and **1β**.

FAB should have been P+1; apparently, the material loses 1 electron more easily than the conventional addition of H^+.] Raman (solid) $\upsilon_{C\equiv C}$ =2263 cm^{-1}. UV spectrum (in hexane): λ_{max}, cm^{-1} (ε, $M^{-1}cm^{-1}$) 216 (26,060), 245sh (3650), 260sh (1920), and 390 (145) nm. The magnetic susceptibility of both phases were essentially identical, Figure 5.

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REFERENCES

1. J. S. Miller, J. C. Calabrese, R. W. Bigelow, A. J. Epstein, J. H. Zhang, and W. M. Reiff, *J. Chem. Soc., Chem. Commun.* 1026 (1986). J. S. Miller, J. C. Calabrese, H. Rommelmann, S. Chittapeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.109*, 769 (1987). S. Chittapeddi, K. Cromack, J. S. Miller, and A. J. Epstein, *Phys. Rev. Lett. 58*, 2695 (1987).
2. J. S. Miller and A. J. Epstein, *J. Am. Chem. Soc. 109*, 3850 (1987). J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev. 88*, 201(1988). J. S. Miller and A. J. Epstein *NATO ASI, 168B*, 159 (1987). J. S. Miller, A. J. Epstein and W. M. Reiff *Acc. Chem. Res. 23*, 114 (1988).
3. K. Itoh, and K. Takai, *Mol. Cryst. Liq. Cryst. 125*, 251(1985). H. Iwamura, *Pure & Appl. Chem. 58*, 187 (1986).
4. R. Breslow, *Mol. Cryst. Liq. Cryst. 125*, 261 (1985).
5. J. B. Torrance, S. Oostra, and A. Nazzal, *Syn. Met. 19*, 708 (1987). J. B. Torrance, P. S. Bagus, I. Johannsen, A. Nazzal, S. S. P. Parkin, and P. Batail, *J. Appl. Phys. 63*, 2962 (1988).
6. (a) Yu. V. Korshak, A. A. Ovchinnikov, A. M. Shapiro, T. V. Medvedeva, and V. N. Specktor, *Pisma Zh. Eksp. Teor. Fiz. 43*, 309 (1986). (b) Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, and V. N. Specktor, *Nature 326*, 370 (1987). (c) A. L. Buchachenko, R. P. Shibaeva, L. P. Rozenberg, and A. A. Ovchinnikov, *Khim. Phys. 6*, 773 (1987).
7. Y. Cao, P. Wang, Z. Hu, S. Ki, L. Zhang, and J. Zhao, *Solid State Commun. 68*, 817 (1988) and*Syn. Met. 27*, B625 (1988).
8. J. S. Miller, D. T. Glatzhofer, R. Laversanne, S. Chittipeddi, P. Vaca, T. B. Brill, M. D. Timken, C. J. O'Connor, J. H. Zhang, J. C. Calabrese, and A. J. Epstein, submitted.
9. A. A. Ovchinnikov and V. N. Specktor, *Syn. Met. 27*, B615 (1988).
10. H. Bassler, *Adv. Poly. Sci. 63*, 1 (1984). R. H. Baughman and R. R. Chance, *Ann. N. Y. Acad. Sci. 313*, 705 (1978). D. Bloor and R. R. Chance, "Polydiacetlyenes," NATO ASI, Series E, *#102*, (1985).
11. B. Chase, *Microchimica Acta, 3*, 81 (1987).