The quest for a polymeric ferromagnet: A new polymorph of 1,4-bis(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)butadiyne (invited)

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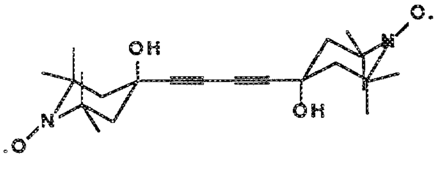
A new polymorph of 1,4-bis(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)butadiyne has been prepared and characterized by x-ray diffraction, infrared and Raman spectroscopies, and magnetic susceptibility. Unlike the *Pccn-α* phase, the β phase belongs to the $Pca2_1$ space group [$a = 14.265(1)$ Å, $b = 8.079$ (3) Å, and $c = 18.865(2)$ Å, $V = 2174.1$ Å^3, $Z = 4$, $T = -100$ °C, $R_u = 4.8\%$, $R_w = 5.0\%$). The C≡C, CC–CC, and NO distances are 1.201, 1.391, and 1.293 Å, respectively. The only intermolecular interactions are 1.844-Å–OH · · · ON hydrogen bonding interactions. The vibrations $\nu_{\mathrm{OH,NH}} = 3289, 3070, 3021$, ν_{NO} (IR) $= 1341$, and $\nu_{\mathrm{C\equiv C}}$ (Raman) $= 2236\ \mathrm{cm}^{-1}$ are present. The solid-state motif is that of pleated sheets. UV, electron beam, and γ-ray induced polymerization has not been achieved; however, thermal treatment turns the crystals black. Thermogravimetric analysis under nitrogen reveals an explosive decomposition at ~ 140 °C. Between 2 and 300 K the susceptibility obeys the Curie–Weiss expression with $\Theta = -2.75$ K. The effective moment is $2.47\mu_B$ per molecule which is consistent with two independent $S = \frac{1}{2}$ spins per molecule. Upon thermal treatment (17 h at 90 °C) the resultant black material exhibits a reduced Curie–Weiss susceptibility of $1.12\mu_B$ and $\Theta = -2.87$ K. Unlike the α phase evidence for ferromagnetic behavior has not been observed.

Highly magnetic materials, i.e., ferro- or ferrimagnetic, have close approach of the spin containing moieties (i.e., covalent or metallic bonded 1D, 2D, or 3D network structures) where the magnetic sites are *d* or *f* orbital transition, lanthanide, or actinide metal based. Examples of highly magnetic molecular based compounds with *p* or even *d* orbitals contributing to the cooperative magnetic properties were until recently unknown. A molecular solid is comprised of low molecular weight molecules or ions (organic, organometallic, main group, polymer, and/or inorganic coordination complex) that do not possess extended covalent bonding in the solid state and dissolution into conventional aqueous or organic solvents leads to solvation of the individual ions or molecules that were used to prepare the molecular solid. These chemical features make this class of materials distinct from classically studied *d* and *f* shell metal or metal oxide ferro- and ferrimagnetic materials. This broad range of phenomena combined with the anticipated modulation of the physical properties via conventional synthetic organic chemistry as well as the ease of fabrication enjoyed by organic materials may lead to their use in future generations of electronic and/or photonic applications.

In accompanying papers the magnetic[1] and ^{57}Fe Mössbauer[2] properties of the bulk ferromagnet $\mathrm{Fe^{III}(C_5(CH_3)_5)_2]^{\cdot +}\ [TCNE]^{\cdot -}$ are discussed.[3-5] In this paper we focus on recent results in our laboratory aimed at the preparation of the polymeric ferromagnetic materials based dinitroxide diacetylenes first reported by Ovchinnikov and co-workers,[6] while Torrance presents the status of his endeavors to prepare an polymeric organic ferromagnet based upon the iodine oxidation of 1,3,5-triaminobenzene.[7]

Specific 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.[8] Ovchinnikov and co-workers have recently reported[7] the thermal, photochemical, and glow-discharge treatment of 1,4-bis(2,2,8,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)butadiyne [see diagram below (**1**)] to form a black polymer of which some samples exhibit field dependent magnetization corresponding to an "insignificant" amount (0.1%) of a ferromagnet. The orthorhombic *Pccn* structure (i.e., α phase) of the monomer diyne, although not reported in detail, is stated to be unfavorable for single-crystal topochemical polymerization. Due to our ongoing interest in molecular based ferromagnetic materials,[3] we have prepared a diacetylene **1**[9] in an effort to verify and elucidate its ferromagnetic behavior after thermal, electron beam, or γ-ray treatment and have characterized the new but similar β polymorph:



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Unlike the "perfect needle crystal"[6(b)] habit for the α

phase, we obtain low aspect ratio orange parallelpiped crystals which are also orthorhombic [$a = 14.265(1)$ Å, $b = 8.079(3)$ Å, and $c = 18.865(2)$ Å, $V = 2174.1$ Å^3, $Z = 4$, $T = -100$ °C, $Pca2_1$ (No.29), $R = 4.8\%$, $R_w = 5.0\%$, and residual background electron density of $0.19e^-/\text{Å}^3$] for the β phase.[10] The β polymorph possesses well separated diagonal chains knit together by –OH · · · ON hydrogen bonding and forms corrugated sheets in the ab plane. The N–O· and –OH · · · ON distances average 1.293 and 1.844 Å, respectively. The α phase possesses a hydrogen bonded helical chain structure and average N–O· and –OH · · · ON distances of 1.282 and 1.71 Å, respectively. Thus, they are 0.01 and 0.13 Å shorter than in the β phase. The C_4 diyne moiety is linear and the molecule as a whole possesses a nearly perfect noncrystallographic inversion center. Typical of diynes the average C≡C is 1.201 Å whereas the central C–C bond is 1.391 Å. The closest C_4 diyne separations are C1 · · · C4 (5.79 Å), C2 · · · C4 (6.40 Å), and C1 · · · C3 (6.31 Å) and based on accepted structural criteria should not support single-crystal topochemical polymerization.[8] The chair conformation of the monomer as well as the hydrogen bonded knit structure is shown in Fig. 1.

The molar magnetic susceptibility χ_M measured by the Faraday method from 2 to 300 K obeys the Curie–Weiss expression, $\chi_M = C/(T - \Theta)$, with $\Theta = -2.75$ K (Fig. 2). This is comparable to the -2 K value reported for the α phase. The effective moment, μ_{eff}, is $1.79\mu_B$ per NO group or $2.47\mu_B$ per molecule which is lower than that expected for an ideal triplet, i.e., $\mu_{\text{eff}} = 2.83\mu_B$, but correlates well for two independent $S = \frac{1}{2}$ spins, i.e., $\mu_{\text{eff}} = 2.45\mu_B$. Contribution to the susceptibility from a singlet state is not observed in this temperature range. The effective moment is markedly larger than the $1.55\mu_B$ per monomer observed for the α polymorph.[6(b)] Differential scanning calorimetry (DSC) under nitrogen shows the onset of a reaction between 60 and 80 °C with catastrophic decomposition as evidenced by thermogravimetric analysis (TGA) at 140 °C. This is in contrast to the bis(piperidine) starting material which is stable up to 200 °C and does not decompose explosively (Fig. 3).

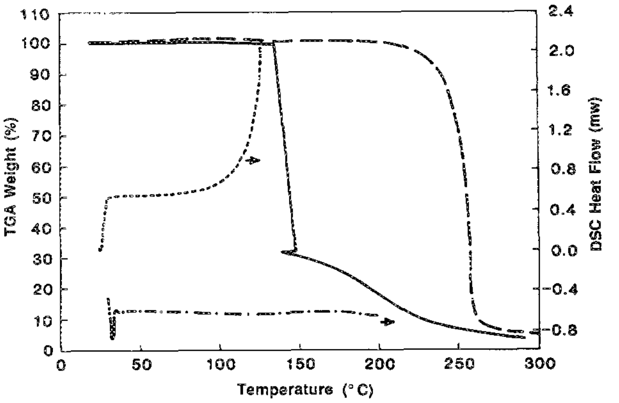

FIG. 2. Reciprocal molar magnetic susceptibility, $\chi_{M^{-1}}$, as a function of temperature for for the β phase of 1,4-bis(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)butadyne, **1**, (a) and **1** heated for 17 h at 90 °C in under nitrogen (b).

Ultraviolet irradiation of several samples below 60 °C within a spiral mercury arc lamp (2 h) or a Rayonet Photochemical reactor (~300-nm peak output, 4 h) as well as 2-Mrad radiation from a ^{60}Co γ-ray source and 5-Mrad electron beam radiation under ambient conditions failed to alter the appearance of the crystals. Thermal treatment at ~90 °C leads to transformation from the orange color to black. The black product is amorphous and exhibits a substantially reduced moment, e.g., after thermal treatment for 17 h at ~90 °C under nitrogen the moment decreases from 2.47 to $1.12\mu_B$ (Fig. 2). The reasons for the loss of susceptibility

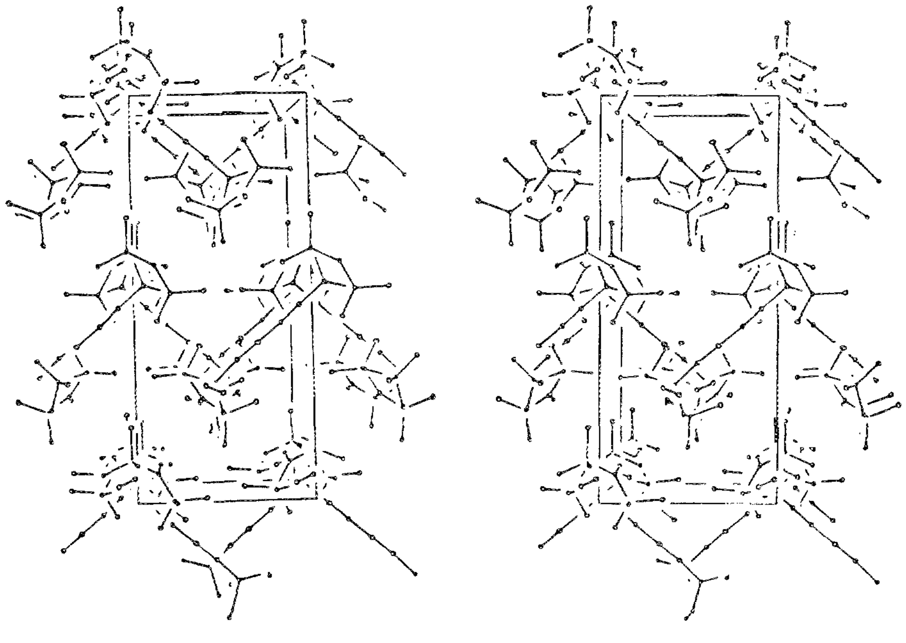

FIG. 1. Stereoview of the *ab* plane of 1,4-bis(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)butadyne (see diagram **1**).

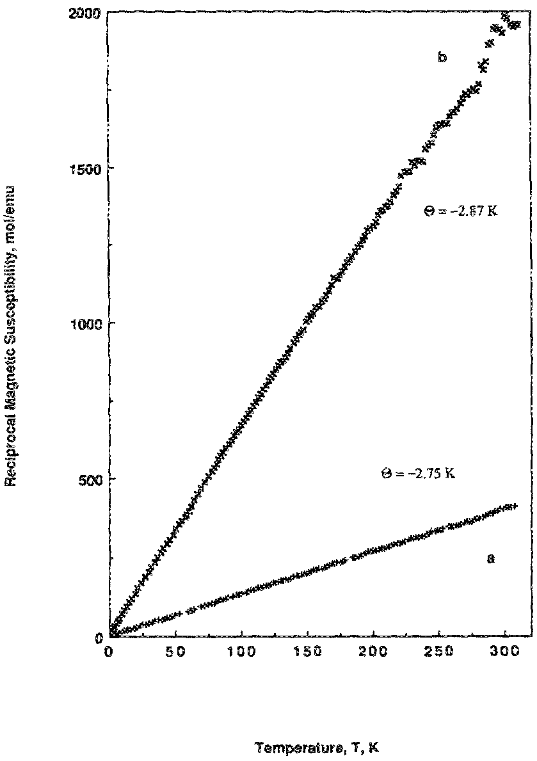

FIG. 3. DSC (- - -) and TGA (——) for the β phase of 1,4-bis(2,2,6,6-tetramethyl-4oxy-4-piperidyl-1-oxy)butadyne, **1**, under nitrogen (50 cm^3/min) and the bis(piperidine) starting material (- - -: DSC and -·-·-·: TGA).

with thermal treatment as well as preparation of the α phase are under active investigation.

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[10] Since the *Fccn*-α and the $Pca2_1$-β phases differ by $b_\alpha = 2\, b_\beta$ we verified that the room-temperature unit cell parameters [$a = 14.390(2)$ Å, $b = 8.168(1)$ Å, and $c = 18.720(1)$ Å, $V = 2200.3$ Å^3] are slightly greater than those at −100 °C as expected for thermal contraction and upon collection of a suitable partial data set (0–15°) using b_α (i.e., $2\, b_\beta$) we do not observe any reflections with odd values for k. Additionally, an exhaustive review of the film data does not reveal evidence that b should be doubled to that noted for the α phase.