

A New Polymorph of 4,4'-(Butadiyne-1,4-diyl)-bis-(2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl)

Joel S. Miller,^{a*} Daniel T. Glatzhofer,^{a,b} Joseph C. Calabrese,^a and Arthur J. Epstein^b

^a Contribution No. 4429, Central Research and Development, E. I. du Pont de Nemours and Co., Inc., Experimental Station E328, Wilmington, DE 19898, U.S.A.

^b Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH 43210-1106, U.S.A.

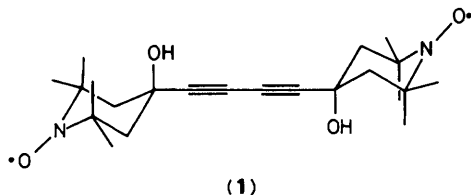
A new polymorph of the title diradical has been characterized by X-ray diffraction, vibrational spectroscopy, and magnetic susceptibility; its radiation induced polymerization has not been achieved, but thermal treatment turns the crystals black and explosive decomposition occurs at $\sim 140^\circ\text{C}$.

The quest for a molecular based ferromagnet has culminated with the characterization of decamethylferrocenium tetracyanoethenide, $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$, which has bulk ferromagnetic behaviour.¹ The search for ferromagnetic organic compounds and polymers, however, maintains academic interest.²⁻⁴ 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.⁵ Ovchinnikov and co-workers have recently reported⁴ the thermal, photochemical, and glow discharge treatment of the diradical (**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 unfavourable for single crystal topochemical polymerization. Because of our continuing interest in molecular based ferromagnetic materials,⁶ we have prepared (**1**)[†] in an effort to verify and elucidate its

ferromagnetic behaviour after thermal or γ -ray treatment and have characterized a similar but new polymorph, *i.e.*, the β -phase, of the monomer.

Unlike the 'perfect needle crystal'^{4b} habit for the α -phase, we obtain low aspect ratio orange parallelepiped crystals which are also orthorhombic[‡] for the β -phase. § The β -polymorph possesses well separated diagonal chains knitted together by $-\text{OH} \cdots \text{ON}$ hydrogen bonding and forms corrugated sheets in the *ab* plane. The N-O \cdot and $-\text{OH} \cdots \text{ON}$ distances average 1.293 and 1.844 Å, respectively. The α -phase possesses a hydrogen bonded helical chain structure and average N-O \cdot and $-\text{OH} \cdots \text{ON}$ 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 centre. Typical of diynes the average $\text{C}\equiv\text{C}$ is 1.201 Å whereas the central C-C bond is 1.391 Å. The closest C_4 diyne separations are C(1) \cdots C(4) (5.79 Å), C(2) \cdots C(4) (6.40 Å), and C(1) \cdots C(3) (6.31 Å) and based on accepted structural criteria should not support single crystal topochemical polymerization.⁵ The chair conformation of the monomer as well as the hydrogen bonded structure is shown in Figure 1.

The molar magnetic susceptibility, χ_M , measured by the



(1)

[†] The diradical (**1**) was synthesized by oxidation of the corresponding bis(piperidine) using H_2O_2 with sodium pertungstate/tetrasodium ethylenediaminetetra-acetate; E. G. Rozantsev, 'Free Nitroxyl Radicals,' Plenum, New York, 1970, pp. 227-228. It was purified by precipitation from methanol with water followed by recrystallization from methanol/water or ethyl acetate and gave satisfactory elemental analyses; *i.r.* (KBr pellet) ν_{OH} 3360s, ν_{NO} 1341s $\nu_{\text{C}\equiv\text{C}}$ (Raman) 2236s cm^{-1} . For the bis(piperidine) starting material: *i.r.* (KBr pellet) $\nu_{\text{OH,NH}}$ 3289, 3070s, 3021, $\nu_{\text{C}\equiv\text{C}}$ (Raman) 2245s cm^{-1} .

[‡] Crystal data: β - $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_4$, $M = 390.52$, orthorhombic space group *Pca*2₁ (No. 29), $a = 14.265(1)$, $b = 8.079(3)$, and $c = 18.865(2)$ Å, $U = 2174.1$ Å³, $Z = 4$, $T = -100^\circ\text{C}$, $D_c = 1.193$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 0.76$ cm^{-1} , $R = 4.8\%$, $R_w = 5.0\%$ for 1322 unique reflections [$I > 3\sigma(I)$] to $\theta_{\text{max.}} = 54^\circ$ on a Syntex R3 diffractometer.

§ Since the *Pccn* α -phase and the *Pca*2₁ β -phases are related by $b_\alpha = 2b_\beta$ we verified that the room temperature unit cell parameters [$a = 14.390(2)$, $b = 8.168(1)$, $c = 18.720(1)$ Å, $U 2200.3$ Å³] are slightly greater than those at -100°C as expected for thermal contraction; upon collection of a suitable partial data set ($0-15^\circ$) using b_α (*i.e.*, $2b_\beta$) 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.

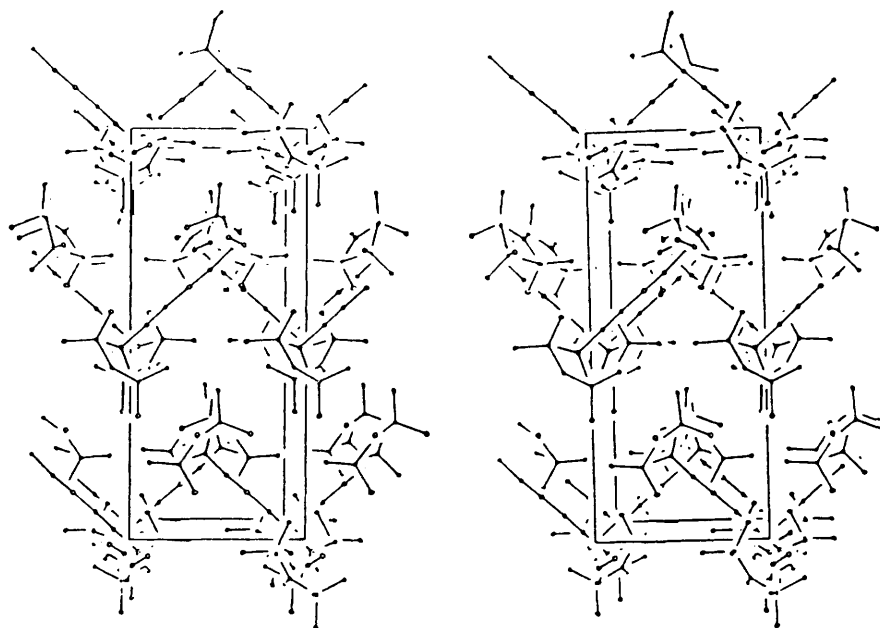


Figure 1. Stereoview of the *ab* plane of the structure of the diradical (1).

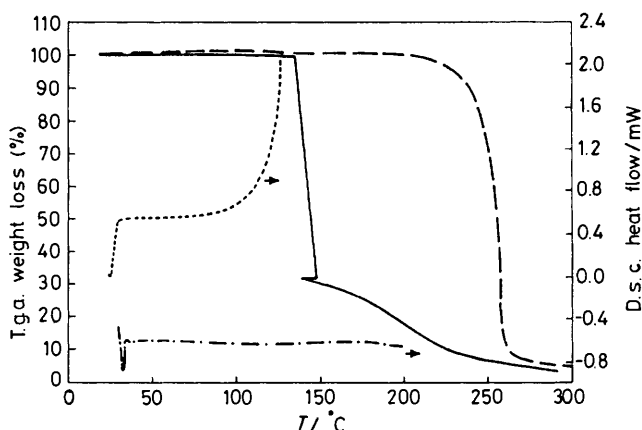


Figure 2. (a) D.s.c. and (b) t.g.a. for the β -phase of the diradical (1) under nitrogen ($50 \text{ cm}^3/\text{min}$) and for the bis(piperidine) starting material: (c) d.s.c. and (d) t.g.a.

Faraday method from 2 to 300 K obeys the Curie–Weiss expression, $\chi_M = C/(T - \theta)$, with $\theta = -2.75 \text{ K}$. 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 doublets, *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 reported for the α -polymorph.^{4b} Differential scanning calorimetry (d.s.c.) under nitrogen shows the onset of a reaction between 60 and 80 °C with catastrophic decomposition as shown by thermogravimetric analysis (t.g.a.) at $\sim 140^\circ\text{C}$. This contrasts with the bis(piperidine) starting material which is stable up to 200 °C and does not decompose explosively (Figure 2).

U.v. irradiation of several samples below 60 °C within a spiral mercury arc lamp (2 h) or a Rayonet photochemical

reactor (*ca.* 300 nm peak output, 4 h) as well as 2 Mrad radiation from a ^{60}Co γ -ray source and 5 Mrad radiation from an electron beam failed to alter the appearance of the crystals. Heating at $\sim 90^\circ\text{C}$ leads to a colour change from orange to black. The black product is amorphous and exhibits a substantially reduced moment, *e.g.*, after 17 h at $\sim 90^\circ\text{C}$ under nitrogen the moment decreases from 2.47 to $1.12 \mu_B$. The reason for the loss of susceptibility on heating as well as preparation of the α -phase is under active investigation.

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