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

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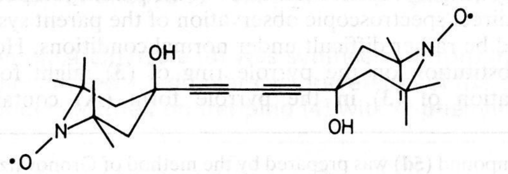
A new polymorph of the title diradical has been characterized by *X*-ray diffraction, vibrational spectroscopy, and magnetic susceptibility; its radiation induced polymerization has not been achieved, but thermal treatment turns the crystals black and explosive decomposition occurs at ~140 °C.

The quest for a molecular based ferromagnet has culminated with the characterization of decamethylferrocenium tetracyanoethenide, $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$, 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 reported[4] 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.



(**1**)

Unlike the 'perfect needle crystal'[4b] habit for the α-phase, we obtain low aspect ratio orange parallelpiped crystals which are also orthorhombic‡ for the β-phase.§ The β-polymorph possesses well separated diagonal chains knitted together by –OH · · · ON hydrogen bonding and forms corrugated sheets in the *ab* plane. The N–O$^{\cdot}$ 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$^{\cdot}$ 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 centre. 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 C(1) · · · C(4) (5.79 Å), C(2) · · · C(4) (6.40 Å), and C(1) · · · 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

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† The diradical (**1**) was synthesized by oxidation of the corresponding bis(piperidine) using H_2O_2 with sodium pertungstate/tetrasodium ethylenediaminetetra-acetate; E. G. Rozantzev, 'Free Nitroxy 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 $\nu_{C\equiv C}$ (Raman) 2236s cm^{-1}. For the bis(piperidine) starting material: i.r. (KBr pellet) $\nu_{OH,NH}$ 3289, 3070s, 3021, $\nu_{C\equiv C}$ (Raman) 2245s cm^{-1}.

‡ *Crystal data:* β-$C_{22}H_{34}N_2O_4$, M = 390.52, orthorhombic space group $Pca2_1$ (No. 29), a = 14.265(1), b = 8.079(3), and c = 18.865(2) Å, U = 2174.1 Å^3, Z = 4, T = −100 °C, D_c = 1.193 g cm^{-3}, μ(Mo-K_α) = 0.76 cm^{-1}, R = 4.8%, R_w = 5.0% for 1322 unique reflections [$(I>3\sigma(I)$] to $\theta_{max.}$ = 54° on a Syntex R3 diffractometer.

§ Since the *Pccn* α-phase and the $Pca2_1$ β-phases are related by $b_\alpha = 2\ b_\beta$ 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 Å^3] are slightly greater than those at −100 °C as expected for thermal contraction; upon collection of a suitable partial data set (0—15°) using b_α (*i.e.*, 2 b_β) 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.

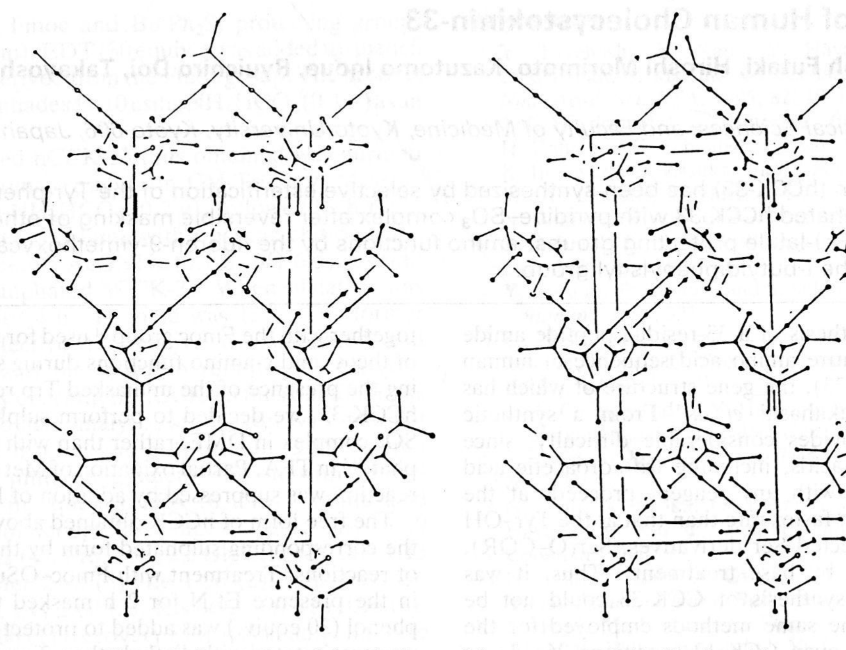

Figure 1. Stereoview of the *ab* plane of the structure of the diradical (**1**).

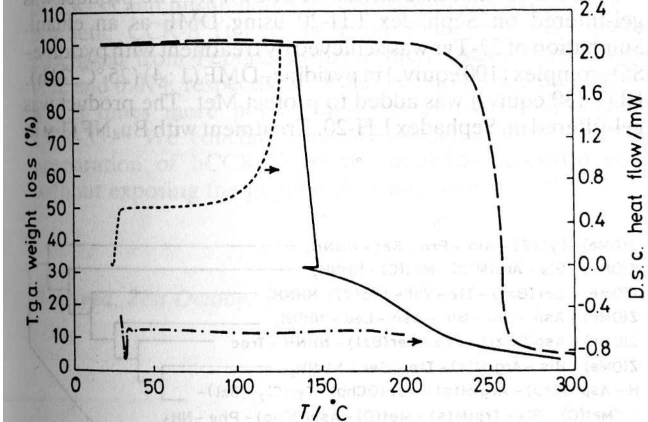

Figure 2. (a) D.s.c. and (b) t.g.a. for the β-phase of the diradical (**1**) under nitrogen (50 cm^3/min) and for the bis(piperidine) starting material: (c) d.s.c. and (d) t.g.a.

Faraday method from 2 to 300 K obeys the Curie–Weiss expression, $\chi_M = C/(T - \theta)$, with $\theta = -2.75$ K. This is comparable to the −2 K value reported for the α-phase. The effective moment, μ_{eff}, is 1.79 μ_B per NO group or 2.47 μ_B per molecule which is lower than that expected for an ideal triplet, *i.e.*, $\mu_{eff.} = 2.83\ \mu_B$, but correlates well for two independent doublets, *i.e.*, $\mu_{eff.} = 2.45\ \mu_B$. 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 μ_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 ~140 °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 ~90 °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 ~90 °C under nitrogen the moment decreases from 2.47 to 1.12 μ_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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