Structural and Magnetic Characterization of α- and β-2,4-Hexadiyne-1,6-diyl Bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate) and its Thermal Degradation Product

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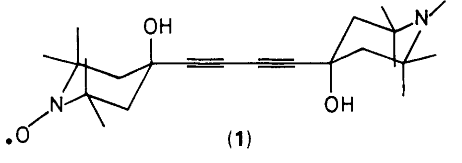
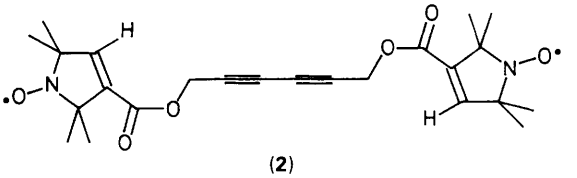
Two polymorphs of the titled diradical have been characterized by *X*-ray diffraction, vibrational spectroscopies, and magnetic susceptibility; its radiation or thermal induced polymerization has not been achieved.

The search for ferromagnetic organic compounds and polymers is the focus of contemporary research.[1—5] Polymerization of di-iminoxyl diacetylene monomers has been suggested as a means to prepare a high spin potentially ferromagnetically coupled polymers[3] and the thermal, photochemical, and glow discharge treatment of 4,4′-(butadiyne-1,4-diyl)-bis-(2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl) (**1**) was reported to form a black polymer of which some samples exhibit field dependent magnetization corresponding to an 'insignificant' amount (0.1%) of a ferromagnet.[3,4] Later, Cao and co-workers reported 0.7% for thermally treated (**1**).[5] 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.[6] Cao and co-workers also reported that 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate) (**2**) exhibits a spontaneous magnetization of 88.5 emuG/mol and a coercive field of 455 G (1 G = 10^{-4} T).[5] The saturation magnetization is characterization of a 1.6% effect; an order of magnitude greater than reported by Ovchinnikov and co-workers.[3]

As part of our continued interest in molecular based ferromagnetic materials,[1a,4] we have prepared (**2**) in an effort to verify and elucidate its ferromagnetic behaviour after polymerization. Compound (**2**) was synthesized by the con-



(**1**)



(**2**)

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† Contribution No. 5117.

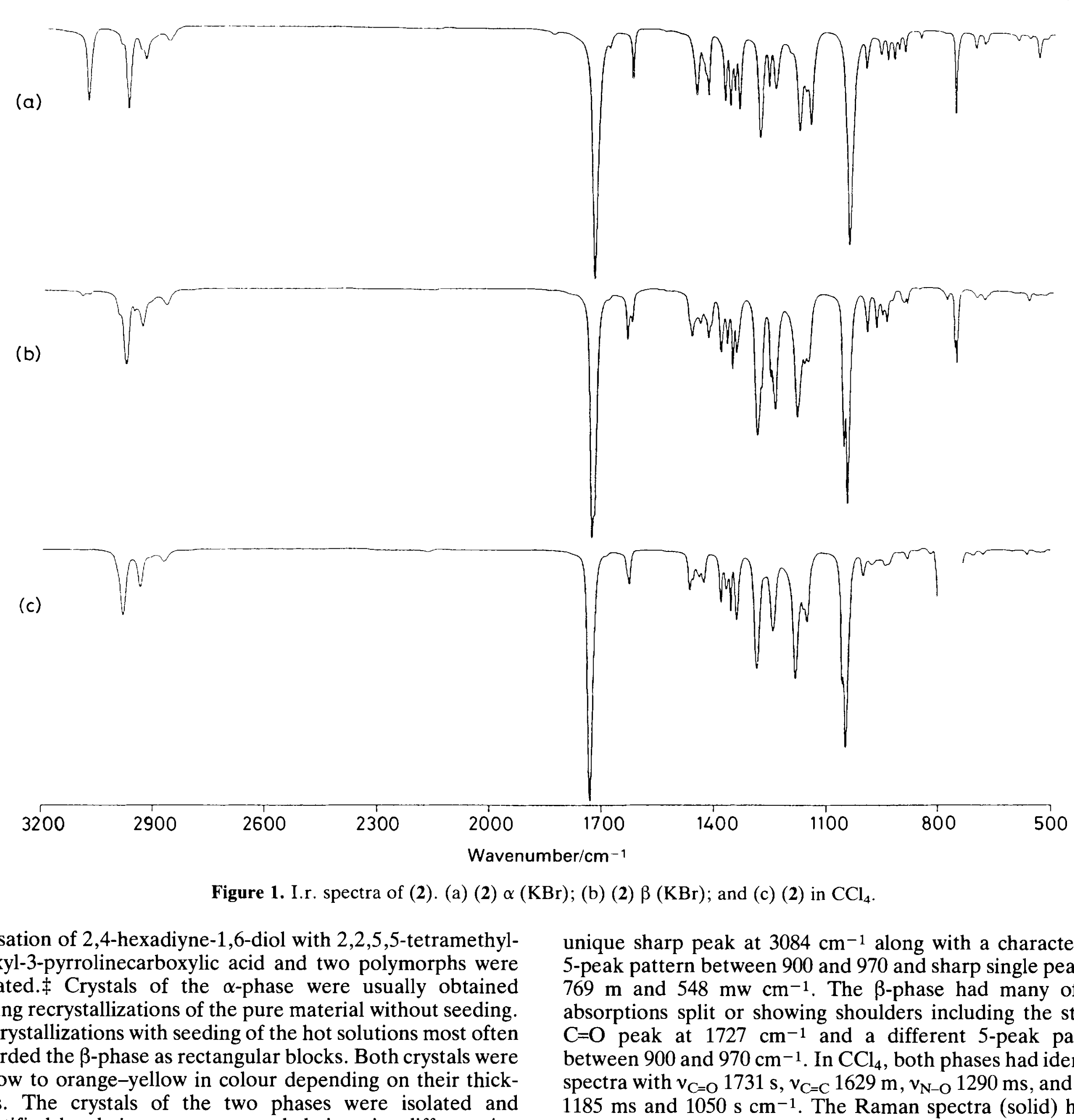

Figure 1. I.r. spectra of (**2**). (a) (**2**) α (KBr); (b) (**2**) β (KBr); and (c) (**2**) in CCl_4.

densation of 2,4-hexadiyne-1,6-diol with 2,2,5,5-tetramethyl-1-oxyl-3-pyrrolinecarboxylic acid and two polymorphs were isolated.‡ Crystals of the α-phase were usually obtained during recrystallizations of the pure material without seeding. Recrystallizations with seeding of the hot solutions most often afforded the β-phase as rectangular blocks. Both crystals were yellow to orange–yellow in colour depending on their thickness. The crystals of the two phases were isolated and identified by their appearance and their quite different i.r. spectra, Figure 1.§ In KBr and Nujol, the α-phase had a unique sharp peak at 3084 cm^{-1} along with a characteristic 5-peak pattern between 900 and 970 and sharp single peaks at 769 m and 548 mw 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 $\nu_{C=O}$ 1731 s, $\nu_{C=C}$ 1629 m, ν_{N-O} 1290 ms, and ν_{C-O} 1185 ms and 1050 s cm^{-1}. The Raman spectra (solid) had a strong C≡C peak at 2263 cm^{-1}. The solid state e.s.r. spectra of both α and β monomers consists of a single line at ~3400 G with ΔH = 12 G, consistent with an unoriented powder pattern for isolated nitroxide spins.

The molecular structures of (**2**) α and (**2**) β‖ have essentially

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‡ A solution of 2,4-hexadiyne-1,6-diol (10 mmole), 2,2,5,5-tetramethyl-1-oxyl-3-pyrrolinecarboxylic acid (21 mmole), dicyclohexyldicarbodianhydride (21 mmole), and 4-dimethylpyridine (1.5 mmol) in 150 ml tetrahydrofuran (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 70 × 45 mm silica column using 3:2 light ether:EtOAc (93% yield). Purification by multiple flash chromatography gave material which showed only one spot by t.l.c. on silica. Development with phosphomolybdic acid gave a much more sensitive analysis than using u.v. on fluorescent plates. *X*-ray quality crystals were obtained from recrystallization from either hexane or i-hexane.

§ Identical elemental analysis and fast atom bombardment (f.a.b.) mass spectra were obtained for both phases. The f.a.b. mass spectra have an anomolous parent peak at 442.10. [The f.a.b. usually is $P + 1$; apparently, the material loses an electron more easily than the conventional addition of H^+]. U.v. spectra (in hexane): λ_{max} (cm^{-1}) (ε) (M^{-1} cm^{-1}) 46 300 (26 060), 40 820sh (3650), 38 460sh (1920), and 25 640 (145).

‖ *Crystal data*: α-$C_{24}H_{30}N_2O_6$, m.p. = 104—105 °C, M = 442.51, monoclinic space group $P2_1/n$ (No. 14), a = 5.867 (3) Å, b = 21.894 (3) Å, c = 9.711 (3) Å, β = 96.18 (2)°, U = 1240.2 Å^3, Z = 2, T = −70 °C, D_c = 1.185 g cm^{-3}, μ(Mo-K_α) = 0.80 cm^{-1}, R = 6.6%, R_w = 6.6% for 873 unique reflections ($I > 3\sigma I$) to θ_{max} = 52° on a Enraf-Nonius CAD4 diffractometer.

Crystal data: β-$C_{24}H_{30}N_2O_6$, m.p. = 108—109 °C, M = 442.51, monoclinic space group $P2_1/n$ (No. 14), a = 8.152 (2) Å, b = 33.763 (4) Å, c = 9.192 (2) Å, β = 104.59 (1)°, U = 2448.4 Å^3, Z = 4, T = −70 °C, D_c = 1.200 g cm^{-3}, μ(Mo-K_α) = 0.81 cm^{-1}, R = 4.7%, R_w = 5.1% for 3235 unique reflections ($I > 3\sigma I$) to θ_{max} = 55° on a Enraf-Nonius CAD4 diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

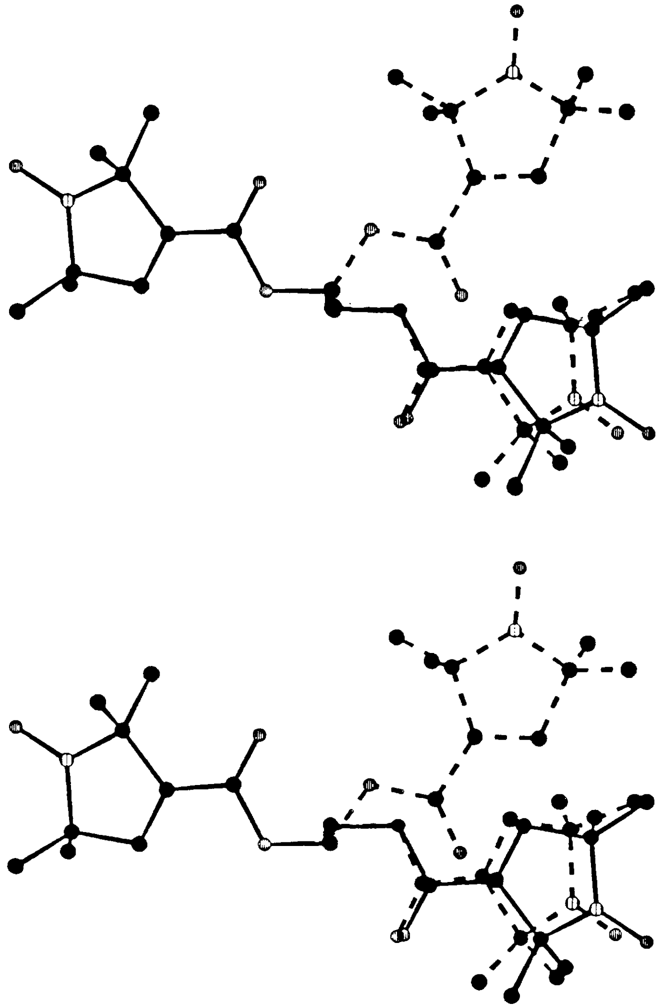

Figure 2. Stereoview of the molecular conformation for the α-and β-phases of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate), (**2**) α (solid bonds) and (**2**) β (dashed bonds).

equivalent bond distances with the average C≡C, CC–CC, and NO bonds of 1.186, 1.380, and 1.279 Å, respectively. These values are typical of di-iminoxyl diacetylenes.[4,6] 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 lying on an inversion centre with both pyrroline carboxylate groups essentially *trans* to each other, whereas the β-phase has these groups asymmetrically arranged, Figure 2.

The packing motif of the two phases are similar with the linear hexadiynes aligned in a 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 neighbouring 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 neighbours resulting in a somewhat closer approach between the hexadiyne carbons (3.93 and 4.40 Å, respectively). In neither case are the butadiyne atoms close enough to support topchemical polymerization.[6]

The molar magnetic susceptibility corrected for the diamagnetic core correction, χ_M, between 2—320 K was fit by the Curie–Weiss expression, $\chi_M = C/(T - \theta)$, where the parameters are: $\theta = 2.54$ K, $C = 0.75$ emuK/mol and $\theta = -2.87$ K, $C = 0.74$ emuK/mol for α- and β-phases, respectively. The effective moment, μ_{eff}, is 1.73 ± 0.01 μ_B per NO group, or 2.44 ± 0.01 μ_B per molecule for both phases. These values are consistent with two independent $S = 1/2$ spins. For both phases, the magnetic moment is essentially temperature independent down to 2 K. Similar data are not reported by Cao and co-workers.[5] 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 p.p.m. by weight of equivalent iron.

The thermal behaviours of both phases were studied with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Neither phase under nitrogen 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).

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 u.v. irradiations.¶ No change was noted for either γ-ray or electron beam irradiations. Some darkening was observed after 72 h exposure to u.v. radiation. The magnetic susceptibility measurements showed a reduced moment of 2.16 μ_B per original monomer unit. Longer exposure (162 h) caused additional darkening and the moment reducing to 2.09 μ_B.

Thermal treatment of (**2**) 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 μ_B 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. Experiments carried out in Pyrex tubes were 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 °C overnight, an amorphous dark melt resulted which still had $\mu_{eff} = 1.69$ μ_B. In both the radiated and heated samples, no anomalous behaviour as reported by Cao[5] was observed in the temperature dependence of the magnetic moment over the range of 1.5—300 K.

In conclusion, the α- and β-2,4-hexadiyne-1,6-diyl bis-(2,2,5,5-tetramethyl-1-oxyl-3-carboxylate) (**2**) 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 couple only extremely weakly, 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 behaviour. 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 (**2**) as well as their thermal degradation products do not provide evidence that any polymeric or organic material present possesses ferromagnetic coupling or ferromagnetic behaviour.

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

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