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

Douglas W. Wiley, Joseph C. Calabrese, and Joel S. Miller

Central Research and Development, E.I. du Pont de Nemours and Co. Inc., Experimental Station 328, Wilmington, DE 19880-0328, U.S.A.

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. Polymericization of di-iminoxyl diacetylene monomers has been suggested as a means to prepare a high spin potentially ferromagnetically coupled polymers 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 ferromagnets. Later, Cao and co-workers reported 0.7% for thermally treated (1). 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. 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 = 1/10^4 T). The saturation magnetization is characteristic of a 1.6% effect; an order of magnitude greater than reported by Ovchinnikov and co-workers. As part of our continued interest in molecular based ferromagnetic materials, we have prepared (2) in an effort to verify and elucidate its ferromagnetic behaviour after polymerization. Compound (2) was synthesized by the con-
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 \( \nu_C=O \) peak at 1727 cm⁻¹ and a different 5-peak pattern between 900 and 970 cm⁻¹.

In CCl₄, both phases had identical spectra with \( \nu_C=O \) 1731 s, \( \nu_C=C \) 1629 m, \( \nu_N-O \) 1290 ms, and \( \nu_C-O \) 1185 ms and 1050 s cm⁻¹. The Raman spectra (solid) had a strong \( \nu_C=O \) 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 Δ\( H = 12 \) G, consistent with an unoriented powder pattern for isolated nitroxide spins.

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

| Crystal data: α-C₂₄H₂₆N₂O₆, 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, \( β = 96.18(2)° \), \( U = 1240.2 \) \( \AA^3 \), \( Z = 2 \), \( T = -70°C \), \( D_c = 1.185 \) g cm⁻³, \( μ(\text{Mo-Kα}) = 0.80 \) cm⁻¹, \( R = 6.6% \), \( R_w = 6.6% \) for 873 unique reflections (I > 3σ(I)) to \( θ_{\text{max}} = 52° \) on an 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. |
equivalent bond distances with the average C–C, C=C–C=C, and NO bonds of 1.186, 1.380, and 1.279 Å, respectively. These values are typical of di-iminoxyl diacetylenes. 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 \textit{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 average C=C, C–C=C, and NO bonds of 1.186, 1.380, and 1.279 Å, respectively. These values are typical of di-iminoxyl diacetylenes. 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 \textit{trans} to each other, whereas the β-phase has these groups asymmetrically arranged, Figure 2.

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References