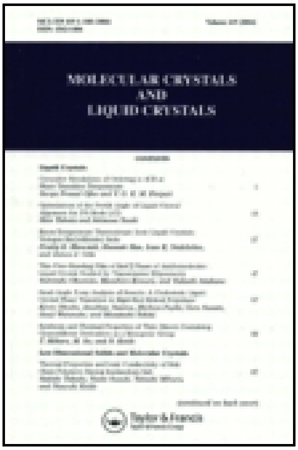

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Magnetic Characterization of 4,4′-(Butadiyne-1,4-Diyl)-Bis-(2,2,6,6-Tetramethyl-4-Hydroxy-Piperidin-1-Oxyl) and its Products on Thermal Treatment

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Version of record first published: 22 Sep 2006.

To cite this article: Jian H. Zhang , Arthur J. Epstein , Joel S. Miller & Charles J. O'connor (1989): Magnetic Characterization of 4,4′-(Butadiyne-1,4-Diyl)-Bis-(2,2,6,6-Tetramethyl-4-Hydroxy-Piperidin-1-Oxyl) and its Products on Thermal Treatment, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 271-276

To link to this article: http://dx.doi.org/10.1080/00268948908037486

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 271–276
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Printed in the United States of America

MAGNETIC CHARACTERIZATION OF 4,4'-(BUTADIYNE-1,4-DIYL)-*BIS*-(2,2,6,6-TETRAMETHYL-4-HYDROXY-PIPERIDIN-1-OXYL) AND ITS PRODUCTS ON THERMAL TREATMENT

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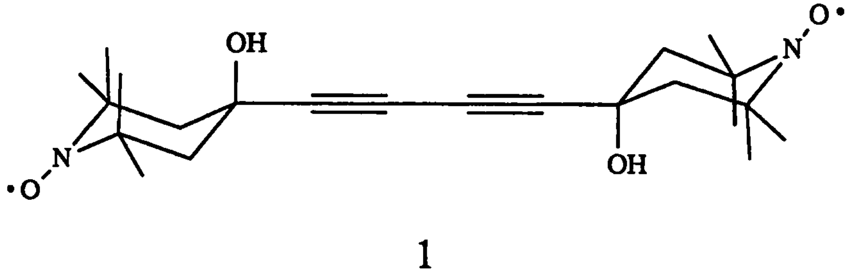
Abstract: The magnetic properties of the title compound have been measured with a superconducting squid susceptometer before and after thermal treatment. The ferromagnetism that has been previously reported by other authors to occur in the title compound following thermal treatment has not been observed. This material (α-phase) and a similar polymorph (β-phase) are shown to exhibit normal (Curie-Weiss) behavior before and after heat treatment and have a maximum ferromagnetic contribution corresponding to 5 ppm iron contamination.

INTRODUCTION

Ferromagnetic and high spin molecular based materials have become the object of increasing interest as several laboratories try to engineer new types of ferromagnetic materials.[1-5] Recently, Ovchinnikov and co-workers[3] have reported the thermal, photochemical, and glow discharge treatment of the titled organic diradical, **1**α, resulting in a black polymeric product. Some samples of this product material were reported to exhibit field dependent magnetization corresponding to a small amount (0.1%) of an organic based ferromagnet. Furthermore, Cao and co-workers[5] report an



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observation of a 0.7% ferromagnetic contribution for thermally treated 1. Later J. Miller and co-workers synthesized and characterized a new but similar polymorph (the β-phase) of the titled compound.[6] The structures for both phases have been determined.[4,6] Both phases crystallize in an orthorhombic lattice and have similar molecular structure.

A series of magnetic measurements on the titled compound and its heat-treated products have been performed in our laboratory to verify the organic ferromagnet properties reported for these materials. Herein we report the experimental details and magnetic data of the α- and β-phases of the titled compound.

EXPERIMENTAL

Magnetic data were recorded with a S.H.E. Corporation VTS superconducting SQUID susceptometer. The sample bucket was fabricated from an Al-Si alloy obtained from S.H.E. Corp. The magnetic susceptibility of the sample bucket was measured independently over the temperature region of 6-300 K at a field of 1 kOe, and the susceptibility data for all samples were then corrected for the bucket contribution. The field dependence of the magnetization of the samples after thermal treatment was measured at the temperature of 6K, 25K and 90 K, and at magnetic fields between 0.1 and 50 kOe. The magnetization data was corrected for the bucket contribution which was obtained at the same temperatures and magnetic fields. Calibration and other measurement procedures for the SQUID susceptometer are reported elsewhere.[7]

Thermal treatment of both α-phase and β-phase was carried out at 95-100 C for 20 hours under an N_2 atmosphere. To minimize exposure to other external sources of ferromagnetic impurities, great care was taken in handling the sample. During all sample manipulations, the sample only came into contact with glass utensils or the Si/Al alloy SQUID sample bucket. The procedure for measuring the magnetic data is as follows: The magnetic susceptibility of the sample was recorded with the sample in the SQUID bucket suspended from a cotton fiber. After the susceptibility was measured as a function of temperature, the holder containing the sample was suspended in a quartz tube which was placed in a heating bath for thermal treatment. After thermal treatment, the holder with sample was immediately placed into the SQUID for susceptibility and magnetization measurements. Only the top of the cotton thread was handled during the sample manipulations following initial measurement of the fresh specimen.

RESULTS AND DISCUSSION

The molar magnetic susceptibilities corrected for the diamagnetic contribution as a function of temperature for both phases prior to thermal treatment are similar and obey the Curie-Weiss law, $\chi_M = C/(T-\theta)$ with $\theta = -1.88$ K, C = 0.74 emu-K/mole for α-phase and $\theta = -1.71$ K, C = 0.73 emu-K/mole for β-phase. These values of θ are comparable to the -2.0 K and -2.75 K values reported earlier for the α- and β-phase respectively, by the Faraday technique.[3,6] The effective moment, μ_{eff}, is 1.73 μ_b per NO group, or 2.44 μ_b per molecule for the α-phase, and 1.71 μ_b per NO group or 2.41 μ_b per molecule for the β-phase. These values are consistent with two independent S = 1/2 spins. For both phases, the magnetic moments correspond to the spin-only value at room temperature (one electron per NO group) and are nearly temperature independent from room temperature down to 20 K. The magnetic moments for both phases are reduced to 1.50 μ_b per NO group at 6 K. The effective room-temperature moment is markedly larger than the 1.55 per monomer (or 1.10 per NO) reported earlier[3] for the α-phase.

The gram magnetic susceptibility of the heat treated sample of α-phase uncorrected for the diamagnetism of the constituent atoms is plotted as a function of temperature in Figure 1. The large portion of the diamagnetic component in the heated sample results in the negative susceptibility at the high temperatures. This means that the majority of the products that result from heat treatment are diamagnetic. The best fit of the magnetic data to the expression, $\chi = \chi_{para} + \chi_{dia}$, where χ_{para} represents the paramagnetic component that follows the Curie-Weiss behavior and χ_{dia} is the susceptibility of the diamagnetic component, gives the parameters: $\theta = 1.7$ K, C = 2.76×10^{-5} emu·K/g, and $\chi_{dia} = -2.21 \times 10^{-7}$ emu/g. The insets in Figure 1 show the corrected inverse gram magnetic susceptibility of the heat treated α-phase plotted as a function of temperature (**a**) and the inverse molar magnetic susceptibility of the non-heat treated α-phase plotted as a function of temperature (**b**). The β-phase displays similar magnetic behavior before and after heat treatment. The rapid rise in the moments at low temperature that is characteristic of ferromagnetic material has not been observed for the heated samples of either phase.

The field dependences of the magnetization for the α-phase were measured at the temperatures of 6, 25 and 90 K, respectively, and are shown in Figure 2. After

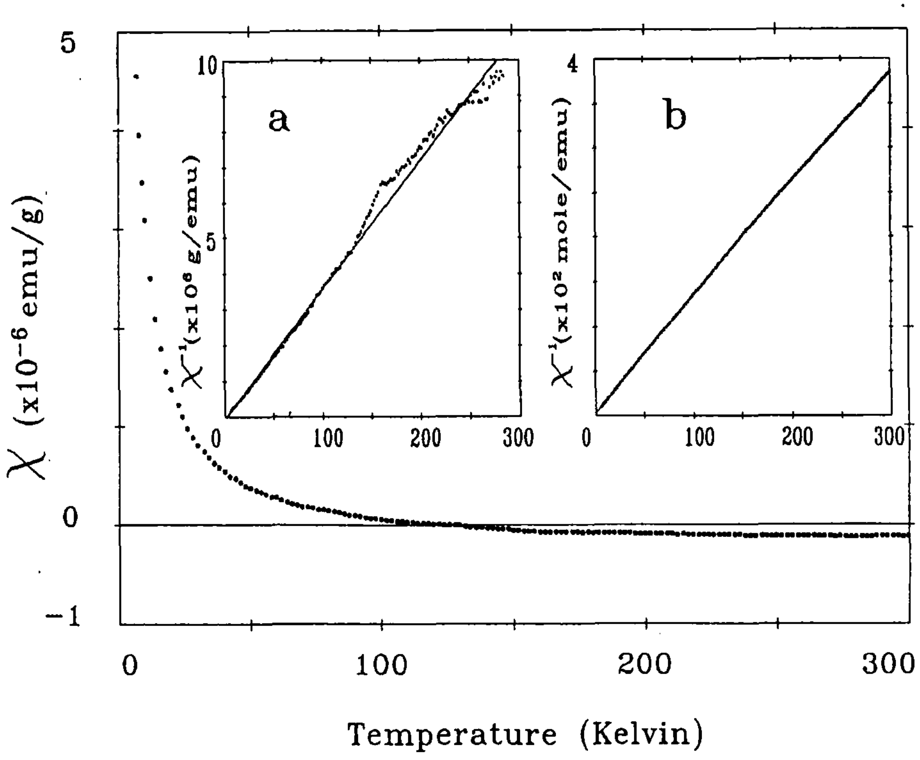

FIGURE 1. The gram magnetic susceptibility plotted as a function of temperature for the α-phase (not corrected for diamagnetism). **a)** Inverse gram susceptibility corrected for diamagnetism. **b)** Inverse molar susceptibility of the non-heat treated α-phase.

careful bucket correction is made, the field dependences of the magnetization are linear at each temperature and do not show any evidence of the existence of ferromagnetic behavior. If sufficient care is not exercised when converting the raw magnetic data to M(H), spurious results that imply ferromagnetic behavior may be obtained. The magnetic signals from the heat-treated materials that are being measured are very small when compared to the large magnetic contributions from the bucket and support fibers. The precision required by these experiments calls for a correction for each individual data point. We accomplish this by measuring the empty sample bucket under identical conditions. After these extremely careful corrections are made, the spurious ferromagnetic signals disappear and normal

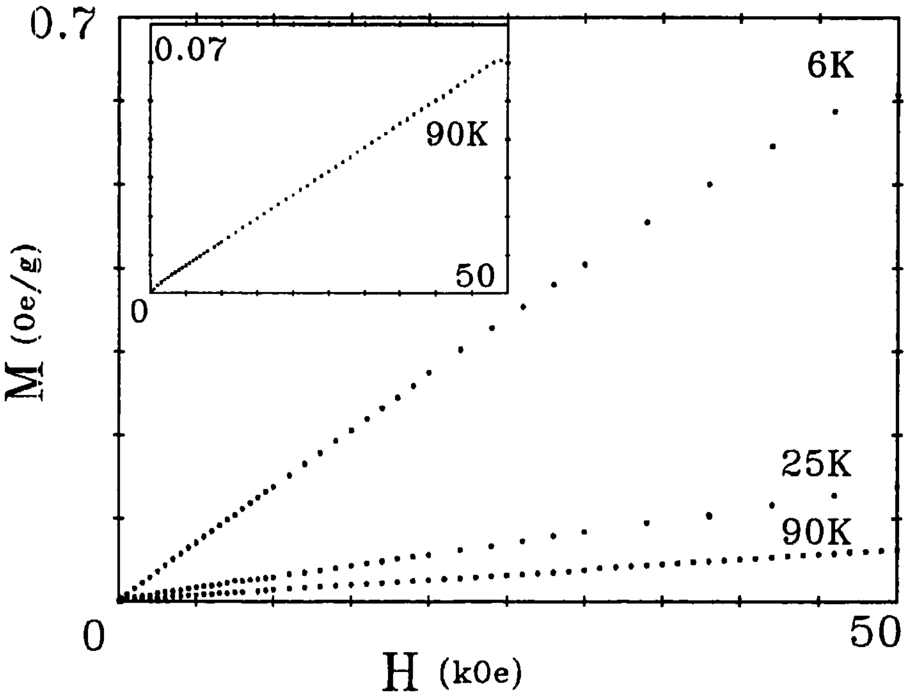

FIGURE 2. Field dependent magnetization plotted at three different temperatures for the heat treated α-phase. The inset shows an expanded scale for the M vs. H recorded at 90 K.

paramagnetic behavior is observed. The value of the upper limit of ferromagnetic saturation magnetization may be estimated from the extrapolation of the magnetization curve recorded at 90 K to zero applied field. The zero field magnetization at 90 K is extrapolated to 0.002 emu/gram. This value would correspond to about 5 ppm by weight of iron contamination which is consistent with x-ray fluorescence analysis on samples prior to thermal treatment.

It is concluded that the magnetic data of both phases of the titled organic diradical compound and their thermal treated products do not provide evidence that any polymeric or organic material present possesses ferromagnetic behavior. The large portion of diamagnetic components from decomposition and the paramagnetic monomers remaining on thermal treatment account for the magnetic behavior observed for the heated samples.

ACKNOWLEDGMENTS: CJO wishes to acknowledge support from a grant from the Louisiana Education Quality Support Fund administered by the Board of Regents of the state of Louisiana and the donors of the Petroleum Research Fund administered by the American Chemical Society.

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