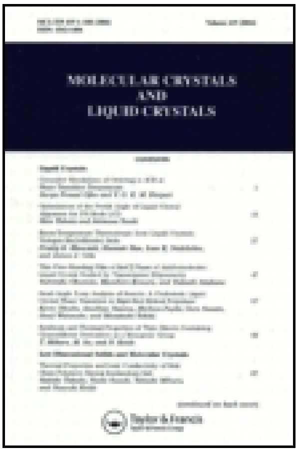

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Crystals of Antiferromagnetic 1,3-Butadiyne and Ferromagnetic 1,3,5-Hexatriyne Both Carrying 4-Chloro-3-(N-tert-butyl-N-oxy-amino)phenyl as Persistent Free Radical Substituent

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Crystals of Antiferromagnetic 1,3-Butadiyne and Ferromagnetic 1,3,5-Hexatriyne Both Carrying 4-Chloro-3-(N-*tert*-butyl-N-oxy-amino)phenyl as Persistent Free Radical Substituent

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Abstract Crystalline samples of 1-[4-choloro-3-(*N*-*tert*-butyl-*N*-oxy-amino)phenyl]-1,3-butadiyne **1** and -1,3,5-hexatriyne **2** have been prepared and were found to exhibit antiferro- and ferromagnetic inter-radical interactions, respectively. In reference to its crystal structure, the former behavior was interpreted in terms of a dimer chain in which $J/k_B = -1.2(3)$ K and $\theta = -0.2$ K. The magnetic susceptibility data of **2** were analyzed in terms of a 1-D Heisenberg model to give $J/k_B = +1.4(8)$ K. Ferromagnetic stacking of the phenyl rings is presumed to to be operative.

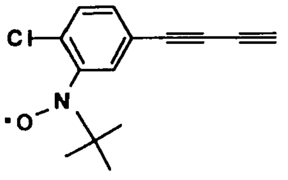
INTRODUCTION

Most organic molecules have closed-shell electronic structures and, therefore, organic compounds are diamagnetic. Even if one or more unpaired electrons are incorporated into an organic molecule to make a persistent free radical, its spin(s) would couple antiferromagnetically with those of neighboring radical molecules in solid states. Such an antiferromagnetic coupling is considered to arise from the Heitler-London exchange between the electron spins with the opposite sign. There are only a few persistent organic radicals known in the literature in which a intermolecular ferromagnetic interaction has been ob-served and well defined in crystalline states.[1,2] We have studied a pair of crystalline 1,3-butadiyne **1** and 1,3,5-hexatriyne **2** carrying a 4-chloro-3-(*N*-*tert*-butyl-*N*-oxyamino)phenyl substituent at position 1 and found that they show quite contrasting magnetic properties, i.e., antiferro- and ferromagnetic intermolecular interaction at cryogenic temperatures, respectively.

RESULTS

Synthesis

1 has been reported previously.[3] The hydroxylamine **5** was obtained by the Cadiot-Chodkiewicz coupling of 1-bromo-3-hydroxy-3-methyl-1-butyne with diacetylene **6**[3] followed by deprotection with sodium hydride. The structure of hydroxylamine **5** was confirmed by IR, ^{1}H-NMR, ^{13}C-NMR spectra. Oxidation of **5** with Fremy's salt gave orange crystals of nitroxide radical **2** (Scheme 1) that were very stable in solution at room temperature but polymerized in a few hours at room temperature in crystalline state.



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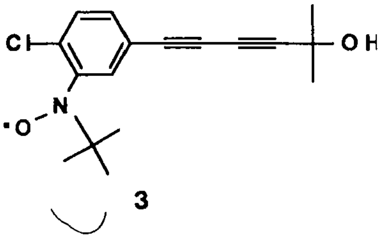

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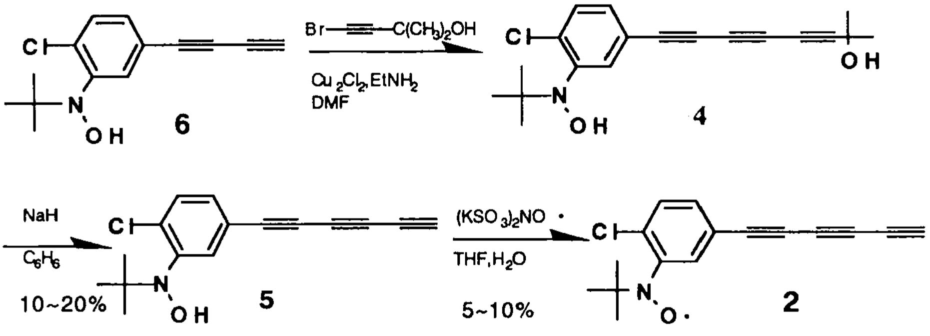
Scheme 1



X-ray Crystal Structure Analyses

Single crystals of **1** are triclinic, space group P1 (#2), with a = 9.113 (1) Å, b = 10.218 (1) Å, c = 7.8759 (6) Å, α = 108.043 (7)°, β = 92.302 (9)°, γ = 102.436(9)°, V = 676.4 (3) Å^3, and d = 1.211 g/cm^3 for Z = 2 ($C_{14}H_{13}ClON$, MW = 246.71). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C-H 0.96 Å, C-C-H 109.5°) and refined isotropically using rigid model. Refinement converged at

R = 0.089 and Rw= 0.128 for 2065 unique reflections, with I > 3σ(I) and 166 variables. The crystal structure is reproduced in Figures 1 and 2.

There are two important arrays of the molecules in the crystal. The first is a column along the b axis in which any adjacent pair of the benzene rings are stacked antiparallel to each other. The distance between the two mean planes is ca. 3.7 Å. The stacked rings are slightly out of phase to form a step-like structure. Secondly, there is a one-dimensional chain across the column along the a/b diagonal (Figure 1). Two molecules stack side-by-side in the chain (Figure 2), where the O/O distance between the adjacent molecules is 3.145(7) Å.

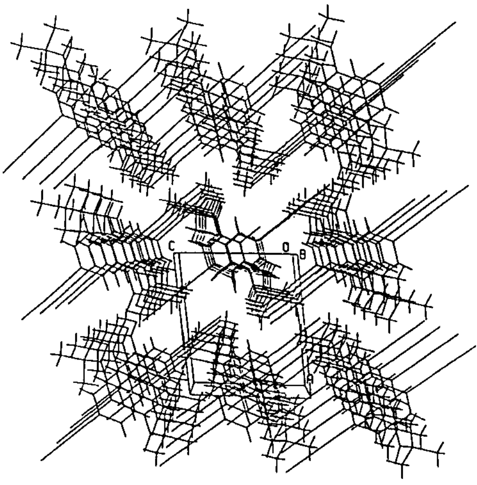


FIGURE 1. Crystal structure of radical 1 viewed along the b axis.

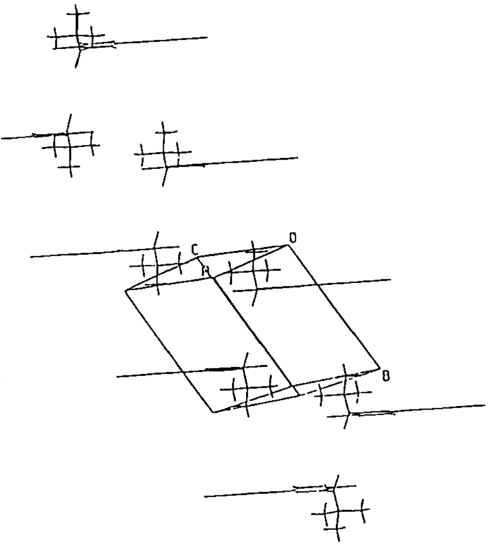


FIGURE 2. Crystal structure of radical 1 viewed along the a/c diagonal.

A single crystal of 2 was subjected to an X-ray crystal structure analysis at 220 K, but polymerization of 2 took place during prolonged exposure to X-rays. Therefore, with a limited set of X-ray data taken over ca. 1 day, only the following crystal lattice parameters were obtained: a single crystal of radical 2 is triclinic, space group P1, with a = 13.77(3) Å, b = 11.75(1) Å, c = 9.65(2) Å, α = 77.1(1)°, β = 105.2(1)°, γ = 81.2(1)°.

ESR Measurements of Radical 1 and 2

In degassed hexane at 25 °C, the observed ESR spectrum consisted of triplet lines (**1**: g = 2.0066, a_N = 13.8 G, **2**: g = 2.0059, a_N = 13.9 G) in good agreement with the hindered nitroxide structure.[4] Although the lines had a width of 1.9 G and hyperfine coupling with the ring hydrogens was not explicitly detected, the corresponding coupling was observed for **3** (g = 2.0066, a_N = 13.8 G, a_H = 3.1 (1 H), 2.1 (1 H), and 1.0 (1 H) G)(Figure 3).

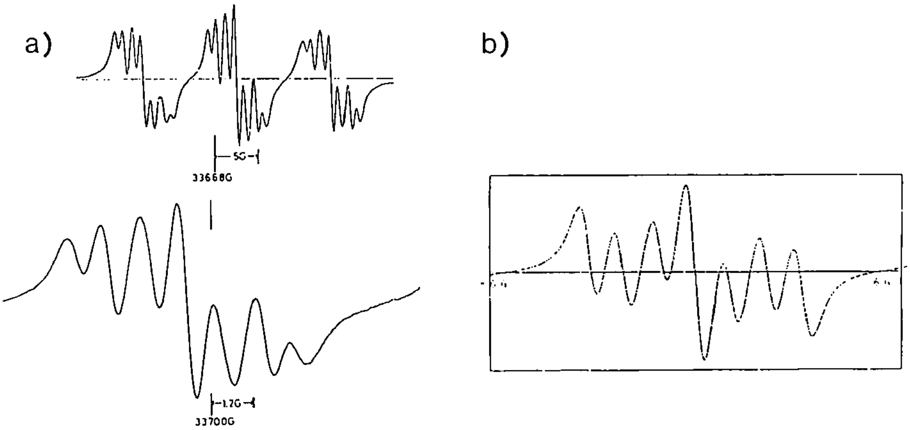


FIGURE 3. The observed (a) and simulated (b) ESR spectra of **3** .

Magnetic Measurements of Crystalline 1 and 2

Temperature dependences of the molar paramagnetic susceptibility χ_M and effective magnetic moment μ_{eff} of **1** and **2** are shown in Figure 4 and Figure 5, respectively.

Figure 6 shows the plot of magnetization vs. external magnetic field over absolute temperature obtained for polycrystalline samples of nitroxide radical **2** by means of a Faraday balance. When simulated with the Brillouin function (Eq. (3)), the average S values were obtained as 0.9 at 2.0 K, 0.7 at 4.2 K, and 0.6 at 10 K (Figure 6).

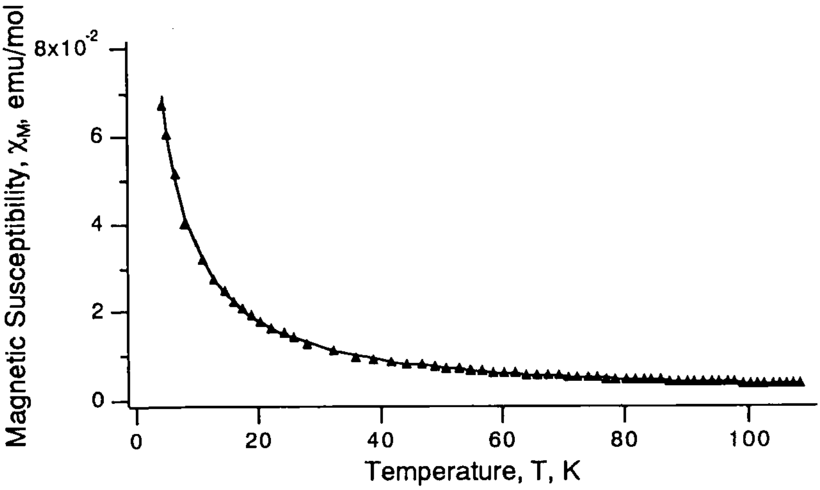


FIGURE 4a. The temperature dependence of molar paramagnetic susceptibility χ_M of **1** at 0.2 T compared with the theoretical one due to eq.1 (solid curve).

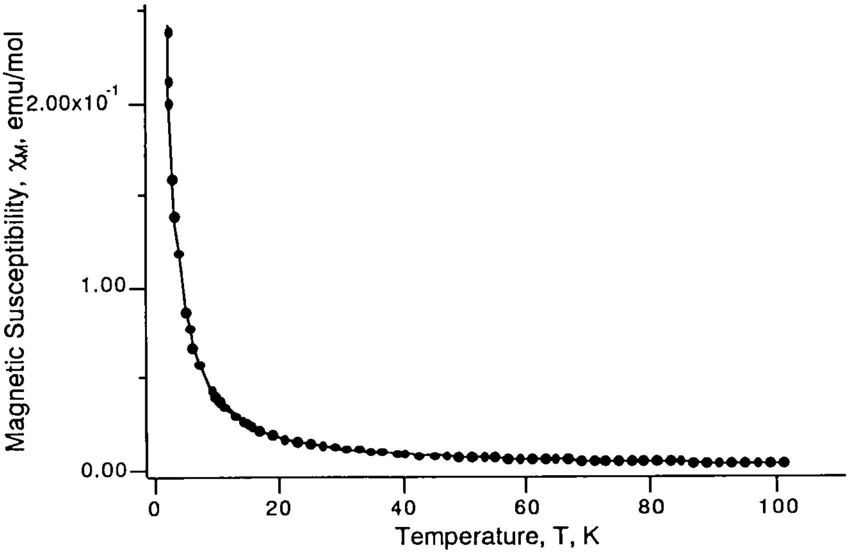


FIGURE 4b. The temperature dependence of molar paramagnetic susceptibility χ_M of **2** at 0.1 T compared with the theoretical one due to eq.2 (solid curve).

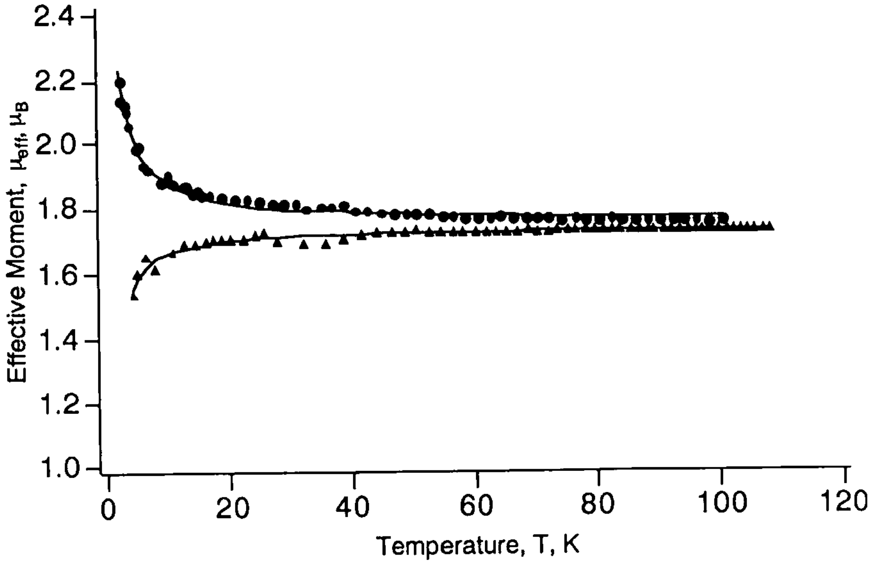


Figure 5. The temperature dependences of effective magnetic moment μ_{eff} of polycrystalline nitroxide radicals **1** (▲) and **2** (●) observed at 0.2 and 0.1 T, respectively, fitted to a theoretical curve based on Eq. (1) and Eq. (2), respectively.

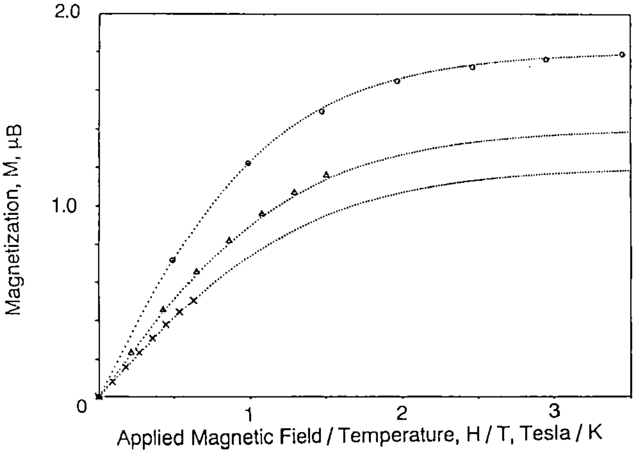


FIGURE 6. The field dependence of magnetization of the polycrystals of nitroxide radical **2** at 2.0 (○), 4.2 (△), 10 (×) K. The dotted curves are theoretical ones for S = 0.9, 0.7, and 0.6, respectively.

DISCUSSION

Magnetic susceptibility of 1

Dimer-like structures are found in one-dimensional chain of radical **1** in the crystals (Figure 1 or 2). We therefore applied exchange-coupled linear chain models for the magnetic susceptibility of **1** and used a modified Bleaney-Bowers equation:

$$\chi_M = \frac{2Ng^2\mu_B^2}{k_B(T-\theta)\{3+\exp(-2J/k_BT)\}} \qquad (1)$$

where N is the number of spin pairs, and J is the exchange integral between adjacent molecules in the dimer. Eq. (1) was well fitted to the susceptibility data in the whole temperature range studied to give the optimized exchange coupling parameter: J/k_B = -1.2(3) K, using a fixed value of θ = -0.2 K and g = 2.006 (Figure 4a and 5).

Magnetic susceptibility of 2

The χ_M values in the higher temperature range 10 - 100 K were fitted to a Curie-Weiss law with θ = +2.5 K. A 1-D Heisenberg model (Eq. (2))^5 was applied with success to the observed susceptibility data in the whole temperature range studied. The exchange coupling parameter was optimized by a least-squares-method to give: J/k_B = +1.4(8) K, using a fix-ed value of g = 2.0059 (Figure 4b and 5).

$$\chi_M = \frac{Ng^2\mu_B^2}{4k_BT}\left(\frac{1+5.798X+16.903X^2+29.377X^3+29.833X^4+14.037X^5}{1+2.798X+7.0087X^2+8.654X^3+4.574X^4}\right)^{\frac{2}{3}} \qquad (2)$$

where

$X = J/2k_BT$

Magnetization of 2

The magnetization curves for paramagnetic samples are dictated by the spin quantum number S at the constant external magnetic field over absolute temperature and simulated by the Brillouin function (Eq. (3)). The apparent S values of **2** increased from the theoretical 0.5 to 0.9 at 2.0 K as the temperature was decreased through 10.0 K (Figure 6), supporting the operation of a ferromagnetic intermolecular interaction.

$$M = NgS\mu_B\left\{\frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}a\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}a\right)\right\} \qquad (3)$$

where

$$a = \frac{gSH\mu_B}{k_BT}$$

CONCLUSION

The crystals of nitroxide radicals **1** and **2** contain stoichiometric amounts of spins. Crystals of **1** were found to have several directions in which the molecules are expected to have special intermolecular interactions. A chain along the a/b diagonal contains a side-by-side dimer-like structure with the O/O distance between the adjacent molecules of 3.145(7) Å. The J/k_B value for the coupling between the nearest radical molecules was found to be -1.2(3) K from the modified dimer model. According to a theory based on Heitler-London spin exchange between positive spin density on one molecules and negative spin density on another,[7] the antiparallel dimer-stackings of radical-substituted benzene rings are predicted to have ferro- and antiferromagnetic exchange couplings for full and partial overlaps, respectively.[8] The crystal structure of **1** has the columnar structure of the latter type as well (Figure 7a). The resulting antiferromagnetic interaction is considered to add to that of direct interaction between the oxygen atoms of the neighboring nitroxide radical centers.

While the crystal structure of **2** was not fully solved, it is highly likely that the molecules would form one-dimensional arrays of the phenyltriacetylene units as in **1** and many other diacetylene derivatives.[9] The crystals of **2** proved to be Heisenberg ferromagnetic solids from the magnetic measurements; the J/k_B value was found to be +1.5 K from a 1-D Heisenberg model. Such a ferromagnetic interaction may be interpreted to arise from a subtle change in the relative orientation of the adjacent molecules in the one-dimensional stacking in the crystals.[7,8] For example, the antiferromagnetic

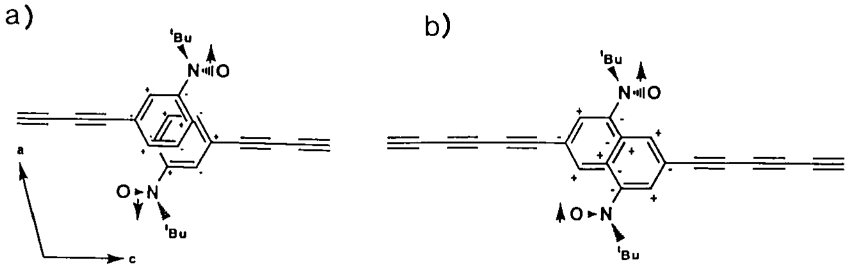


Figure 7. Schematic drawings of a) the observed and b) estimated stacking patterns responsible for the antiferromagnetic interaction in **1** and ferromagnetic interaction in **2**, respectively.

interaction between the two nitroxide units of the adjacent molecules across the column might be hindered by the linearly extruding 1,3,5-hexatriyne unit. At the same time, the stacking interaction between the neighboring spin-containing benzene rings in the column could become ferromagnetic by a slight displacement of one molecule from the other by one C-C bond length (Figure 7b).

Lastly, the crystals of **2** undergo smooth polymerization at ambient temperature. A preliminary study revealed that the H-C(≡) stretching vibration at 3310 cm^{-1} in the IR absorptions disappeared as the polymerization proceeded while the rest remained more or less intact. However, magnetic susceptibility and/or magnetization measurements revealed that the spins are mostly S = 1/2 and their concentration in the polymer sample amounted only to

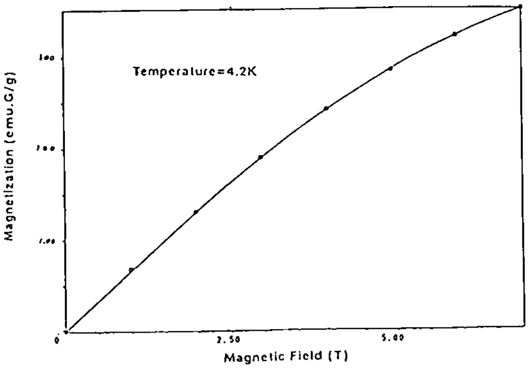


Figure 8. Magnetization curve of a polymer sample due to **2**.

ca. 10 % of the original monomer (Figure 8). Further characterization of the polymer samples is in progress.

ACKNOWLEDGMENT

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