Chinese Chemical Letters Vol. 10, No. 8, pp. 685–688, 1999

Bis-radicals (nitronyl nitroxide and imino nitroxide) Substituted Benzene with Long Alkyl Chain: Synthesis, Magnetic Study and Formation of LB film

De Qing ZHANG, Liang DING, Yu XU, Dao Ben ZHU*

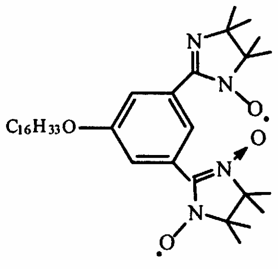
Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: The titled compound **1** as well as compounds **2** and **3** with similar chemical structures were prepared and characterized. The magnetic properties of **1** were investigated with SQUID (MPMS, quantum design) magnetometer. Studies with Langmuir-Blodgett (LB) technique indicated that stable condensed film of **1** could be formed at air-water interface and could be transferred onto various solid substrate under suitable conditions.

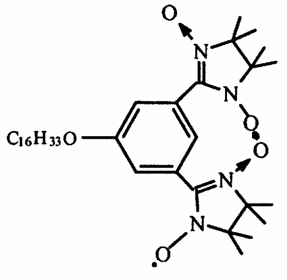
Keywords: Nitroxide radical; organic ferromagnetism; magnetic properties; LB film.

Since the discovery of the first genuine organic ferromagnet, *p*-nitronylphenyl nitronyl nitroxide (*p*-NPNN) in 1991[1], great progress has been achieved in the field of organic ferromagnetism. By now, more than twenty purely organic ferromagnets have been reported successively[2]. However, the ferromagnetic transition temperature (*T*c) of these purely organic ferromagnets are still very low with the highest being only 1.48 K[3] except for the charge-transfer complexes based on tetracyanoquinodimethane (TCNQ) and C60[4]. At present stage of research in this field, on one hand, efforts are devoted to the design and synthesis of new purely organic ferromagnets with high *T*c. On the other hand, research focuses on the relationship between the spin-spin interaction and intermolecular arrangements in the solid state. Langmuir-Blodgett (LB) technique is powerful in fabricating molecules in molecular level and controlling molecular arrangements in the solid state. Therefore, it is possible and worthwhile to study the dependence of intermolecular spin-spin interaction on the intermolecular orientations through the formation of LB films. With this aim in mind, we designed several organic compounds containing stable radicals with long alkyl chain[5] such as compound **1** with two radical substituents (nitronyl nitroxide and imino nitroxide) at the *meta* positions of benzene. In this communication, the synthesis, magnetic study and the formation of LB film of **1** will be reported.

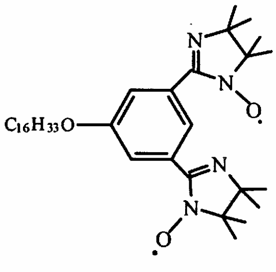
The synthesis of **1** started from dimethyl 5-hydroxyisophthalate as showed in **Scheme 1**. Compound **4**, obtained by alkylation (yield: 90%), was reduced to **5** with diisobutyl aluminum hydride (DIBAH) (yield: 83%). The above reduction was also performed with lithium aluminum hydride under different conditions, but in each



1



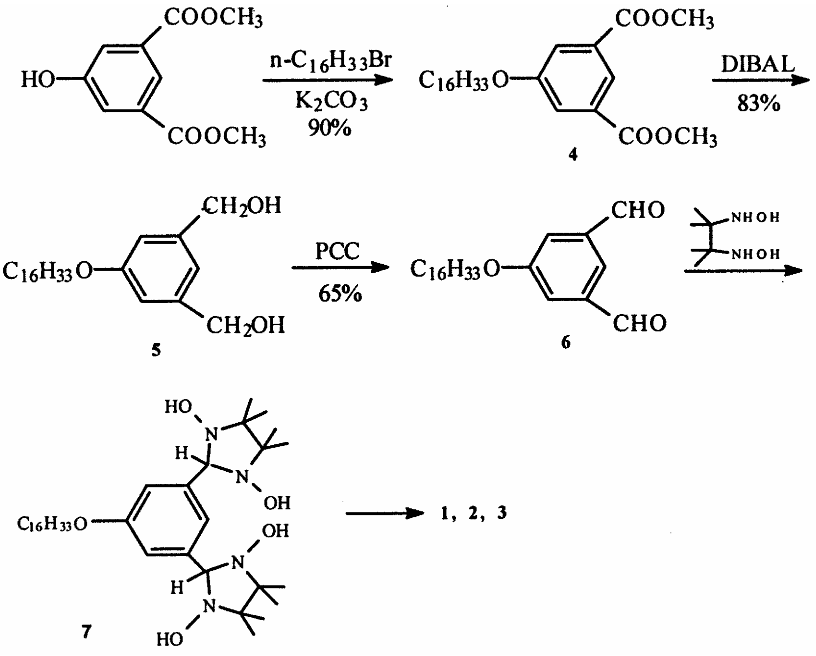
2



3

case no identified product was obtained. Oxidation of **5** with pyridinium chlorochromate (PCC) afforded **6** in the yield of 65%. The condensation between **6** and 2,3-dimethyl–2,3-dihydroxyamino butane[6] was much more complicated than expected. The above condensation product was not purified further and was oxidized directly with sodium periodate in the presence of water and tetrabutylammonium bromide yielding **1** together with compounds **2** and **3** with very similar chemical structures. It was originally expected that only compound **2** was produced by the above synthesis sequences. The formation of **1** and **3** was most probably due to loss one and two molecules of water respectively from the intermediate compound **7**. The individual yields of **1**, **2** and **3** were strongly dependent on the condensation reaction conditions: time, temperature, solvent, and the molar ratio of **6** to 2,3-dimethyl-2,3-dihydroxyaminobutane as well. The overall yield for **1**, **2** and **3** could reach 20% based on dimethyl–5-hydroxyisophthalate

Scheme 1. Synthesis of compounds **1**, **2** and **3**.



when the condensation reaction was carried out in benzene at 80°C for 16 hrs under nitrogen atmosphere with 2,3-dimethyl-2,3-dihydroxyaminobutane in large excess as compared to **6**. Surprisingly, under each condition compound **1** was produced in relatively high yield by comparing with compounds **2** and **3**. Analytically pure compounds **1**, **2** and **3** were obtained by purification with chromatography on silica gel with the mixture of ethyl acetate and petroleum. Their chemical structures were confirmed by spectroscopic data and elemental analysis[7].

As an example, the magnetic properties of polycrystals of **1** were investigated with SQUID as showed in **Figure 1**, where the plot of the product of magnetic susceptibility (χ) with temperature *versus* temperature was given. Above 84 K, the product $\chi{\cdot}T$ remains almost constant (≈ 0.732 emu. K. mol^{-1}), then it increases with decreasing temperature, reaching maximum (0.763 emu. K. mol^{-1}) at 24 K and again decreasing with lowering temperature below 24 K. This magnetic behavior can be well explained by S-T (singlet – triplet) model. For compound **1**, the two radical units occupy *meta* positions of benzene, accordingly, intra-molecular spin-spin ferromagnetic interaction is expected[8]. Hence, for the polycrystals of **1** inter-molecular spins should

Figure 1. The plot of χT *versus* temperature for polycrystals of 1

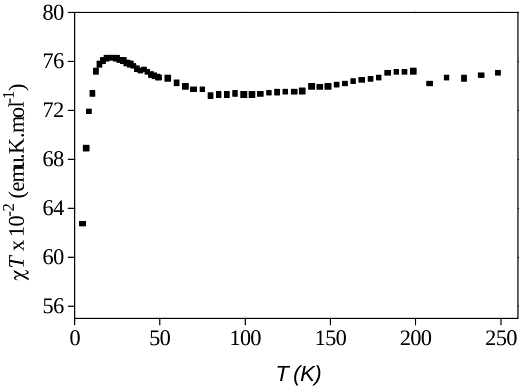
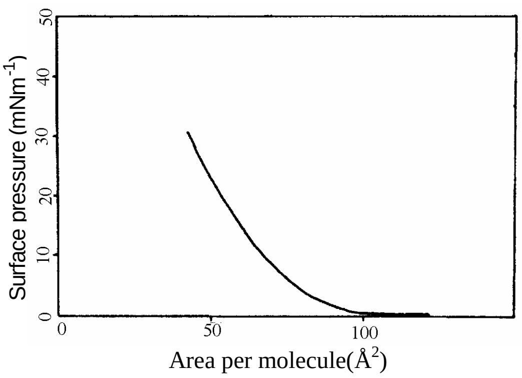


Figure 2. Surface pressure-area isotherm of **1**



interact anti-ferromagnetically. Therefore, the magnetic properties of polycrystals of **1** should be due to intra-molecular spin-spin ferromagnetic interaction and inter-molecular spin-spin antiferromagnetic interaction.

The formation process of LB film of **1** was studied. **Figure 2** showed the surface pressure-area isotherm of **1** on pure water, which indicated that stable condensed film of **1** could be formed at air-water interface and did not collapse until 30 mNm^{-1}. The limiting molecular area of **1** was determined to be 73 Å^{2}. At a pressure of approximate 25 mNm^{-1} the monolayer of **1** could be transferred onto various solid substrate in Z or Y type by the vertical dipping method with transfer ratio greater than 0.9. Multi-layer LB films of **1** could be prepared similarly.

Further investigations are in progress. These include crystal structural analysis of **1**, characterization of the prepared LB film with AFM, MFM, and magnetic studies of the LB film. Studies on the LB films of **2** and **3** will be also conducted.

Acknowledgment

The present research work is supported by NNSFC and Chinese Academy of Sciences.

References and Notes

1. M. Kinoshita *et al*, *Chem. Lett*, **1991**, 1225.
2. S. Nakatsuji, H. Anzai, *J. Mater. Chem.*, **1997**, *7*, 2161.
3. R. Chiarelli, M. A. Novak, A. Rassat, J. L. Tholence, *Nature* **1993**, *363*, 147.
4. a) P. Allemand *et al*, *Sciences*, **1991**, *253*, 301.
   b) K. Ueda et al, *Chem. Phys. Lett.*, **1996**, *261*, 295.
5. Y. Xu, D. Zhang, P. Zhang, Y. Liu, M. Han, D. Zhu, *Thin Solid Film*, **1996**, *284*, 537.
6. E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, and R. Darcy, *J. Am. Chem. Soc.*, **1972**, *94*, 7049.
7. **1**: greylish-blue powder; m.p. 75-76^{o}C; IR 1366 cm^{-1} (typical absorption of nitronyl nitroxide); FAB-MS 615 (M + 2e +3H); Anal. Calc. C 70.50, H 9.96, N 9.14; Found C 70.03, H 9.73, N 8.80. **2**: dark-blue powder; m.p. 90-91^{o}C; IR 1358cm^{-1}; FAB-MS 631 (M + 2e+ 3H); Anal. Calc. C 68.76, H 9.61; N 8.91; Found C 68.45, H 9.69, N 8.80. **3**: orange powder; m.p. 60-61^{o}C; IR 1371cm^{-1}; FAB-MS 599 (M + 2e + 3H); ESR: broad signal with small shoulders in dichloromethane (~10^{-5} M) was observed for each compound.
8. See for example, T. Ishida, H. Iwamura, *J. Am. Chem. Soc.*, **1991**, *113*, 4238.

Received 15 February 1999