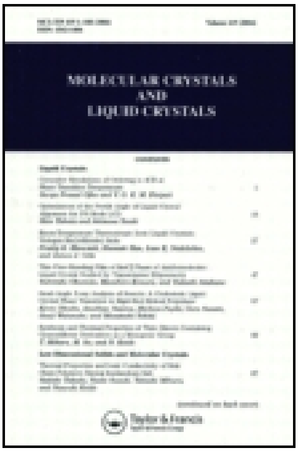


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation of Tetrathiafulvaleno-Nitronylnitroxide and Magnetic Properties of Its DDQ Complex

Reiji Kumai [a] , Akira Izuoka [a] & Tadashi Sugawara [a]
[a] Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153, Japan

To cite this article: Reiji Kumai , Akira Izuoka & Tadashi Sugawara (1993): Preparation of Tetrathiafulvaleno-Nitronylnitroxide and Magnetic Properties of Its DDQ Complex, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 151-154

To link to this article: http://dx.doi.org/10.1080/10587259308035709

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 151–154
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PREPARATION OF TETRATHIAFULVALENO-NITRONYLNITROXIDE AND MAGNETIC PROPERTIES OF ITS DDQ COMPLEX

REIJI KUMAI, AKIRA IZUOKA, TADASHI SUGAWARA
Department of Pure and Applied Sciences, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153 Japan

Abstract Tetrathiafulvalenonitronylnitroxide (**1**) which consists of a donor site and a stable radical site was prepared in order to construct organic ferromagnets. The electronic feature of the donor is that two sites becomes cross-conjugated through trimethylenemethane-type conjugation upon one-electron oxidation of the donor unit. The complex of donor molecule **1** with DDQ shows unusual magnetic behavior.

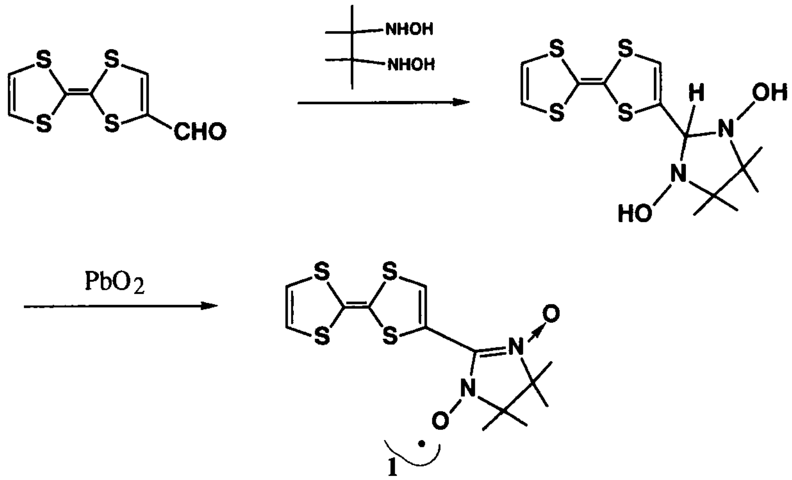
INTRODUCTION

Ferromagnetic intermolecular interaction among open-shell organic molecules have been discussed by McConnell and others[1]. After a close examination on the condition for intermolecular spin-alignment by using cyclophanedicarbenes as model compounds[2], we have succeeded in preparing clusters of diarylcarbenes with ferromagnetic intermolecular interaction[3].

Recently Yamaguchi et al. calculated intermolecular effective exchange integrals for molecular ferromagnets and ferrimagnets based CT complexes with radical substituents[4]. We have designed a TTF derivative substituted with nitronylnitroxide(**1**) as an appropriate model compound for the above system. If oxidation occurs at the donor unit, the distributed spin on the olefinic carbon atoms of the oxidized TTF skeleton[5] should be cross-conjugated with the unpaired electron on the NN group through the trimethylenemethane-type conjugation (Figure 1)[6]. Therefore the designed molecule **1** will be promising for constructing organic ferromagnets or ferromagnetic metal.

PREPARATION OF TETRATHIAFULVALENONITRONYLNITROXIDE 1

Tetrathiafulvalenonitronylnitroxide (**1**) was synthesized as shown in Scheme 1. Formyl-TTF[7], which was prepared from lithiated TTF and DMF, was reacted with bishydroxylamine. The adduct was oxidized to give reddish orange powder of **1** (FAB-MS: $(M^{+}+1)_{obs} = 360.06$, $M^{+}_{calc} = 359.00$).



SCHEME 1.

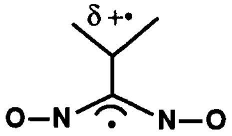


FIGURE 1 Cross-conjugation between the oxidized donor unit and nitronylnitroxide group in **1**.

An ESR spectrum of **1** in benzene shows double quintets at g = 2.0063, which was reasonably reproduced by hyperfine constants of $a_N = 7.57G$ (2N), $a_H = 0.6G$ (1H) (Figure 2). The spectrum is consistent with the structure of **1**. A cyclic voltammograms of **1** in dichloromethane shows the oxidation waves at 0.32, 0.77 V (vs. Ag/AgCl), indicating that oxidation potentials are not significantly different from those of TTF itself.

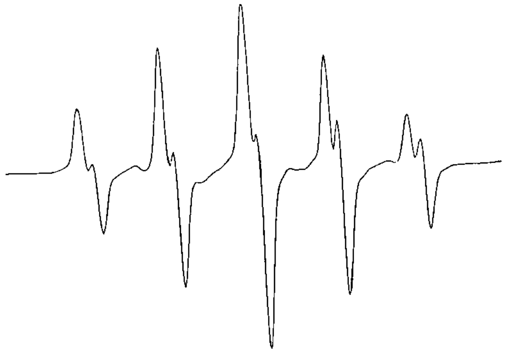


FIGURE 2 ESR spectrum of **1** in benzene solution at room temperature.

MAGNETIC PROPERTIES OF **1**•DDQ COMPLEX

In order to obtain CT complex with **1** we chose dichlorodicyano-p-benzoquinone (DDQ) as an acceptor. Addition of a benzene solution of DDQ to a benzene solution of **1** afforded black micro crystals. A UV spectrum of the solid sample shows a broad maximum at ca. 700nm. The absorption seems to be a CT band between donor moiety of **1** and DDQ. The tendency is consistent with the low frequency-shift of $\nu_{C\equiv N}$ observed in the IR spectrum ($\nu_{C\equiv N} = 2215\ \mathrm{cm}^{-1}$ in the complex and $\nu_{C\equiv N} = 2233\ \mathrm{cm}^{-1}$ in neutral DDQ)[8] .

Magnetic susceptibility of the complex was measured by the Faraday method at temperatures higher than 2 K. The susceptibility of the sample was kept constant in the temperature range between 250 and 100 K (Figure 3). Although the values of susceptibility are plotted in the arbitrary scale due to the uncertainty of sample composition, the temperature dependence can not be explained by simple paramagnetism.

An ESR spectrum of the complex shows a singlet signal with line width of 13G at g=2.0068. The temperature dependence of the signal intensity was measured in the temperature range from 10 K to 270 K. The line width of the signal did not change at temperatures of the measurement. The intensity was kept constant in the temperature range between 100 K and 270 K. The result is qualitatively consistent with the magnetic behavior revealed by the measurement of the magnetic balance. Since the g-value of the signal is close to that of **1** in benzene solution, the signal can definitely be assigned to the charge-transfer complex. These results indicate that the unusual magnetic behavior does not come from magnetic impulities but is intrinsic to the radical species. The accurate characterization of the sample is in progress in these laboratories.

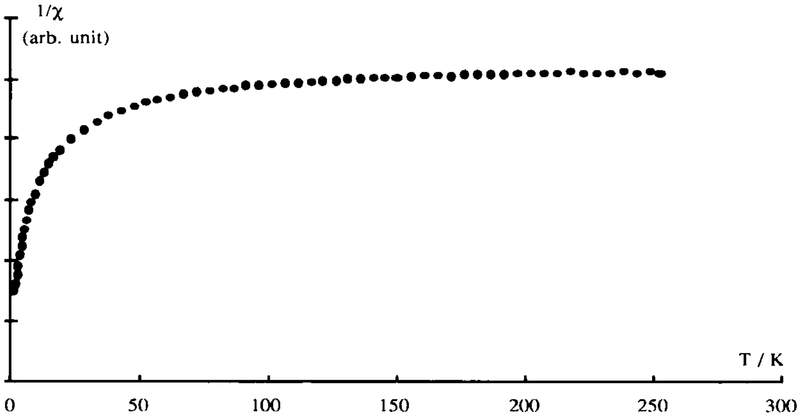


FIGURE 3 Temperature dependence of magnetic susceptibility of **1**•DDQ complex.

This work was supported by Grants-in Aid for Science Research on Priority Area, "Molecular Magnetism" (Area No.228/04 242 104) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1 H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963); R. Bleslow, B. Jaun, R. Q. Kluttz, C. Z. Xia, *Tetrahedron*, **38**, 863 (1982); H. Iwamura, *Pure Appl. Chem.*, **58**, 187 (1986); E. Dormann, M. J. Nowak, K. A. Williams, R. O. Augus, Jr., F. Wudl, *J. Am. Chem. Soc.*, **109**, 2549 (1987); M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, Y. Maruyama, *Chem. Lett.*, **1991**, 1225.

2 A. Izuoka, S. Murata, T. Sugawara, H. Iwamura, *J. Am. Chem. Soc.*, **107**, 1786 (1985); A. Izuoka, S. Murata, T. Sugawara, H. Iwamura, *ibid.*, **109**, 2631 (1987).

3 T. Sugawara, H. Tukada, A. Izuoka, S. Murata, H. Iwamura, *ibid.*, **108**, 4272 (1986); T. Sugawara, S. Murata, K. Kimura, H. Iwamura, Y. Sugawara, H. Iwasaki, *ibid.*, **107**, 5293 (1985).

4 K. Yamaguchi, H. Namimoto, T. Fueno, T. Nogami, Y. Shirota, *Chem. Phys. Lett.*, **166**, 408 (1990).

5 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, T. Enoki, H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57** 627 (1984); R. Zahradnik, P. Cársky, S. Hünig, G. Kiesslich, D. Scheutzow, *Theor. Chim. Acta*, **17**, 316 (1970); D. B. Hibbert, A. E. Hamedelniel, L. H. Sutcliffe, *Magnetic Resonance in Chemistry*, **25**, 648 (1987); H. Bock, B. Roth, R. Schumaker, *Phosphorus and Sulfur*, **21**, 79 (1984).

6 W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977).

7 D. C. Green, *J. Org. Chem.*, **44**, 1476 (1979).

8 J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. C. Anderson, A. J. Epstein, *J. Am. Chem. Soc.*, **108**, 4459 (1986).