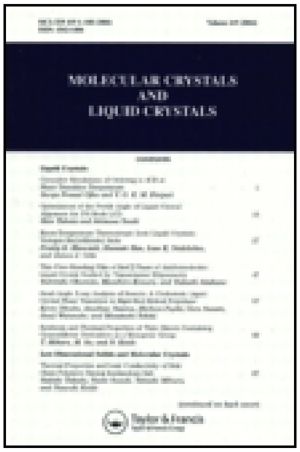


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Interactions of Organic Nitroxyl Radical and Biradical

Yuji Ishino [a] , Takahiro Ikeda [a] , Atsushi Kajiwara [a] , Yotaro Morishima [a] , Wasuke Mori [a] , Kizashi Yamaguchi [a] , Yoshihito Miyako [b] & Mikiharu Kamachi [a]

[a] Department of Macromolecular Science, Department of Chemistry

[b] Department of Earth & Space Science, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560, JAPAN

To cite this article: Yuji Ishino, Takahiro Ikeda, Atsushi Kajiwara, Yotaro Morishima, Wasuke Mori, Kizashi Yamaguchi, Yoshihito Miyako & Mikiharu Kamachi (1997): Magnetic Interactions of Organic Nitroxyl Radical and Biradical, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 203-210

To link to this article: http://dx.doi.org/10.1080/10587259708045057

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 203–210
Reprints available directly from the publisher
Photocopying permitted by license only

MAGNETIC INTERACTIONS OF ORGANIC NITROXYL RADICAL AND BIRADICAL

YUJI ISHINO, TAKAHIRO IKEDA, ATSUSHI KAJIWARA,
YOTARO MORISHIMA, WASUKE MORI,[1] KIZASHI YAMAGUCHI,[1]
YOSHIHITO MIYAKO,[2] AND MIKIHARU KAMACHI*
Department of Macromolecular Science, [1]Department of Chemistry,
[2]Department of Earth & Space Science, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560, JAPAN

Abstract

The magnetic property of 3,17-bis(4,4-dimethyl-3-oxazolidine-1-oxyl)-5α-androstane (OXZAN), in which two nitroxyl radicals were bonded to 5α-androstane, was investigated by measurements of ESR spectra and magnetic susceptibility. ESR spectrum of the OXZAN is composed of 5-line which means that intramolecular exchange interaction take place with through-bond mechanism. No dilution effect on the line shape of the 5-line spectrum and observation of half-field transition support the mechanism. The measurement of magnetic susceptibility shows that magnetic interaction is intermolecularly antiferromagnetic. 4-(2,2,6,6-Tetramethylpiperidin-1-oxyl-4-oxy)phenyl-4'-(6-acryloyloxy-hexyloxy)benzoate (TPOB) was prepared as vinyl monomer with mesogen in which the formation of liquid crystalline was confirmed by observing birefringence under a polarizing microscope (x 600). The measurement of magnetic susceptibility shows that the magnetic interaction of this monomer is ferromagnetic.

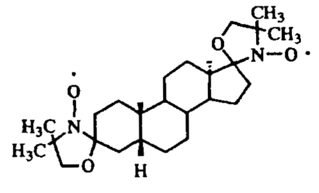
INTRODUCTION

We previously investigated magnetic properties of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MOTMP) and 4-acryloyloxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (AOTMP) and their polymers.[1-9] MOTMP has one-dimensional ferromagnetic coupling J_F ($J_F/k_B = 0.45$ K) while AOTMP shows antiferromagnetic interaction. Intermolecular magnetic coupling in these radicals changed from antiferromagnetic to ferromagnetic by substituting hydrogen at α-

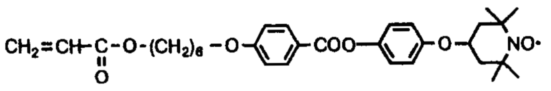
---

* To whom correspondence should be addressed.

position with a methyl group. In 1993, Chiarelli et al.[10] reported that nitroxide biradical of diazaadamantane has ferromagnetic interaction with Curie temperature at 1.48K. This result was quite impressive for us, and we paid attention to magnetic properties of 3,17-bis(4,4-dimethyl-3-oxazolidine-1-oxyl)-5α-androstane (OXZAN), which has been suggested to be intramolecularly exchanged through bond mechanism by Calvin et al.[11] This suggestion has been reported only as short communication in 1977, but, to our knowledge, no paper has been reported so far. Accordingly, we started the ESR study of this radical.

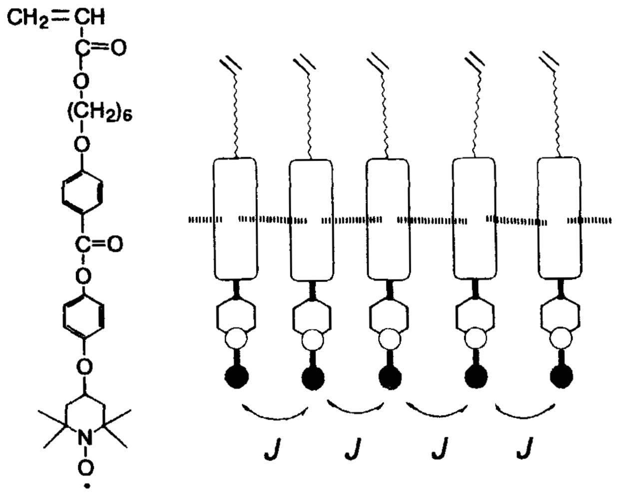


OXZAN



TPOB

We also paid attention to magnetism induced by liquid crystal as shown in the scheme 1. Accordingly, magnetic behavior of 4-(2,2,6,6-tetramethyl-piperidynyl-1-oxyl-4-oxy)phenyl-4'-(6-acryloyloxy-hexyloxy)benzoate (TPOB), which shows liquid crystal, was investigated.[12]



Scheme 1 Schematic drawing of liquid crystalline magnetic monomer (TPOB).

EXPERIMENTAL SECTION

3,17-Bis(4,4-dimethyl-3-oxazolidine-1-oxyl)-5α-androstane (OXZAN)

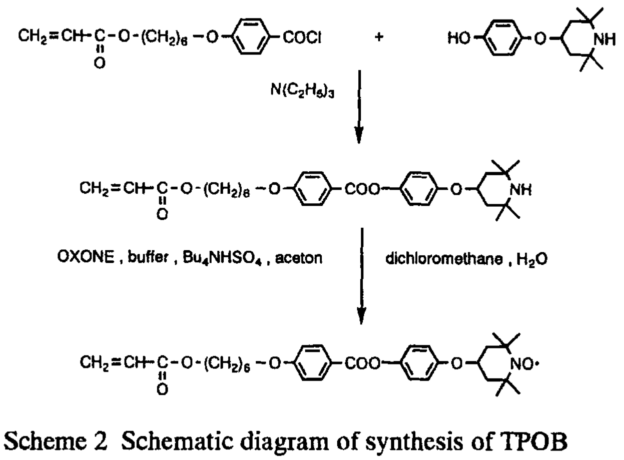
Mixed solution of acetone (400 ml), dichloromethane (300 ml), tetra-*n*-butylammonium hydrogen sulfate (0.50 g, 1.47 x 10^{-3} mol), phosphate buffer (300 ml) and 3,17-bis(4,4-dimethyl-3-oxazolidine)-5α-androstane[13] (10.0 g, 2.33 x 10^{-2} mol) was stirred vigorously at 0 °C and a solution of oxone[14] (90 g, 1.47 x 10^{-1} mol) in water (500 ml) was added dropwise over a period of 1 h. The apparent pH of the mixture was monitored and kept constant at pH 7.5-8.0 by adding an aqueous solution of KOH (2N). The reaction mixture became deep yellow colored gradually. Upon completion of the addition, the reaction mixture was allowed to proceed at 0-6 °C for 4 h with stirring. This reaction was monitored by ESR spectroscopy. Then products were purified by flash column chromatography on silica gel column (Wako C-40, the diameter 5 cm x the height 11 cm) using hexane/dichloromethane/acetonitrile (85/10/5 (v/v/v)) as an eluent. The separated product was purified by recrystallization from diethyl ether to yield 180 mg of OXZAN as pale yellow microcrystals (mp. 184-185 °C). Anal Calcd for $C_{27}H_{44}N_2O_4$: C, 70.40; H, 9.63; N, 6.08. Found: C, 70.29; H, 9.73; N, 6.07.

4-(6-Acryloyloxyhexyloxy)benzoyloxy-4'-benzoylamine-4"-(2,2,6,6-tetramethylpiperidine-1-oxyl) (TPOB)

4-(6-Acryloyloxyhexyloxy)benzoyloxy-4'-benzoylamine-4"-(2,2,6,6-tetramethylpiperidine-1-oxyl) (TPOB) was prepared by the scheme 2 as shown below (ref. 12). Monomer was characterized by elementary analysis and formation of liquid crystalline was confirmed to be a mesogenic monomer by observing birefringence under a polarizing microscope(x 600).

Measurements

Infra-red (IR) spectra were recorded with a JASCO FT/IR-3 infrared spectrometer. Absorption spectra were measured with a Shimadzu UV-2100 spectrometer. ^{1}H-NMR spectra were obtained by JEOL JNM GSX-400 NMR spectrometer at 30 °C. Mass spectra were acquired by JEOL JMS SX-102 mass spectrometer by fast atom bombardment (FAB) method. ESR spectra were taken by a JEOL JES RE-2X ESR spectrometer under 100 kHz modulation. HPLC analysis was carried out in hexane/dichloromethane/acetonitrile (85/10/5 (v/v/v)) by using TSK gel Silica-150. CCPS, TOSOH UV-8020 (254 nm), CO-8020, SD-8022/23, FX-8020 and Chromatocorder 21 were used.



Scheme 2 Schematic diagram of synthesis of TPOB

RESULTS AND DISCUSSION

Characterization of biradical

Before reaction products were separated by HPLC, smaller several peaks were found around a predominant peak in the chromatogram. The compound corresponding to the predominant peak was isolated by HPLC, and was characterized to be OXZAN by their elementary analysis, mass spectroscopy, and UV-visible spectroscopy. Compounds corresponding to other peaks were isolated and characterized by the same method. Some of them were assigned to be at least four isomers, which are possible in the cyclic reactions, by their elementary analysis, mass spectroscopy, and UV-visible spectroscopy. ESR spectra of the isomers are different in the line-shape, respectively, as mentioned later.

ESR study of biradicals

ESR spectrum of OXZAN was measured in toluene solution. 5-line spectrum was observed as shown in Figure 1.

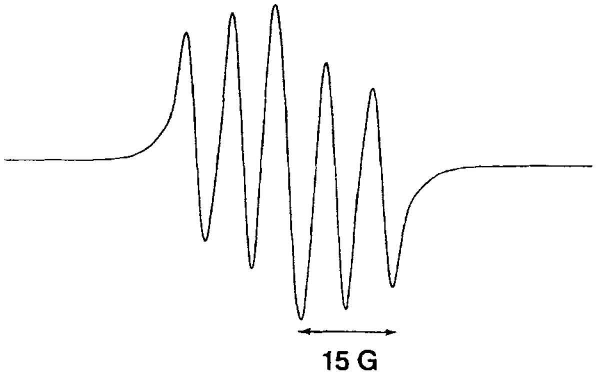


Figure 1 ESR spectra of OXZAN in toluene at 293 K (2 mM).

Usually, 3-line spectrum is observed in isolated nitroxyl radical such as 2,2,6,6-tetramethylpiperidin-1-oxyl. Accordingly, the observation of the 5-line spectrum indicates the presence of intramolecular magnetic exchange interaction between radicals.

In order to confirm the intramolecular magnetic exchange interaction between radicals, concentration dependence of the spectrum was also investigated. No change was observed in the line-shape of the spectra (Fig. 2), indicating that no influence of the concentration of the spectra was observed in these spectra and that intramolecular exchange through bond took place.

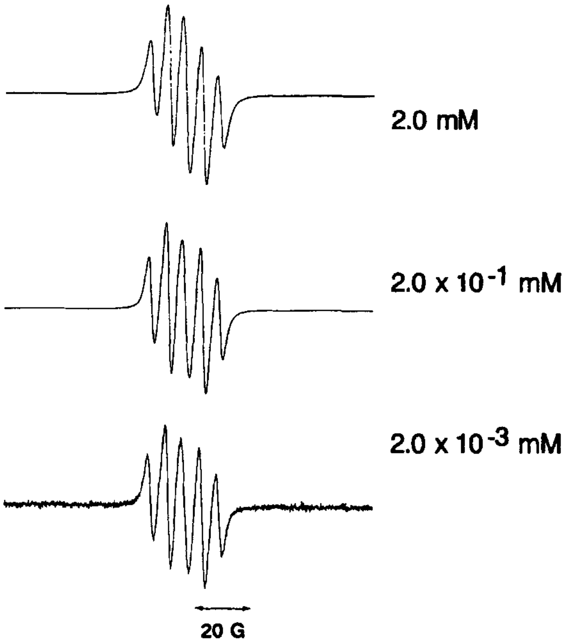


Figure 2 Concentration dependence of ESR spectra of OXZAN in toluene at 293 K.

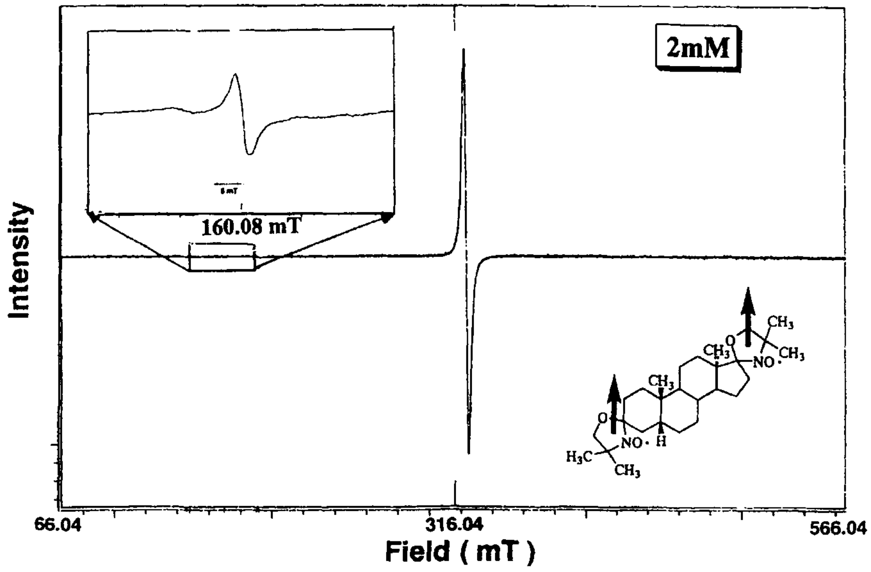


Figure 3 Observation of half-field transition of OXZAN at 20 K in toluene (2 mM).

Moreover, we paid attention to the ESR spectra in a frozen state. Half-field transition was clearly observed even in dilute solution (Figure 3), indicating that this biradical is in triplet state through the intramolecular exchange interaction. There are two possibilities as the mechanism for the intramolecular exchange interaction: through-bond exchange interaction or through-space exchange interaction. Since no concentration dependence of the line-shape of the spectrum was observed, we can conclude that the intramolecular exchange interaction was due to through-bond mechanism.

When other isomer was separately isolated by chromatography, intensity distribution were different with the isomer (Figure 4). This suggests that the intramolecular exchange interaction was influenced by the configuration.[15]

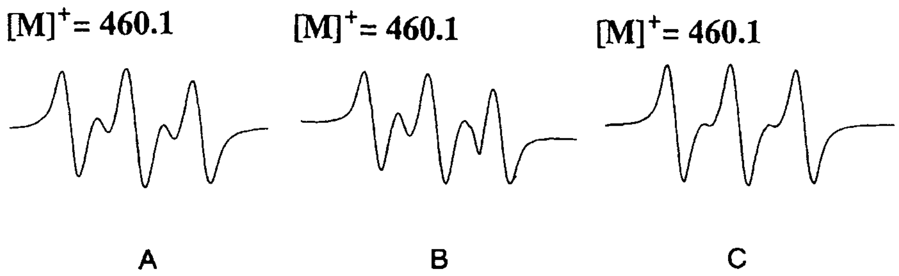


Figure 4 ESR spectra of some isolated isomers of OXZAN (A, B, and C are isomers isolated by HPLC).

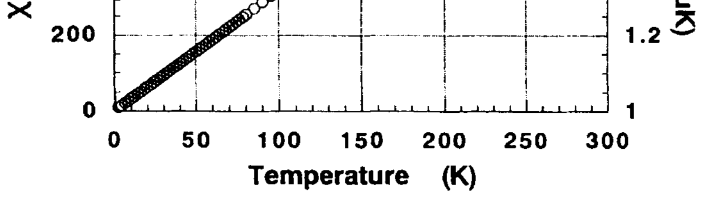


Figure 5 Temperature dependence of magnetic susceptibility (○) and magnetic moment (●) of OXZAN in powder state.

Magnetic behavior of biradical was investigated by temperature dependence of the reciprocal magnetic susceptibility of main isomer. Results are shown in Figure 5. Below 100K, ferromagnetic ordering seems to take place, but antiferromagnetic ordering took place below 20K.
The details will remain as future work.

Magnetic behavior of acrylate with mesogen and nitroxyl radical

4-(2,2,6,6-Tetramethylpiperidynyl-1-oxyl-4-oxy)phenyl-4'-(6-acryloyloxy-hexyloxy)benzoate (TPOB) was prepared and the formation of liquid crystalline was confirmed to be a mesogenic monomer by observing a mosaic texture due to birefringence under a polarizing microscope (x 600) (Fig. 6). This finding means that TPOB forms smectic phase. The temperature dependence of reciprocal magnetic susceptibility and magnetic moments of monomer are shown in Figure 7.

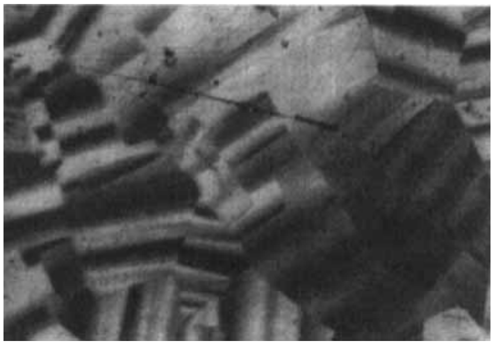


Figure 6 Mosaic texture of TPOB at 293 K after annealing. (See Color Plate I).

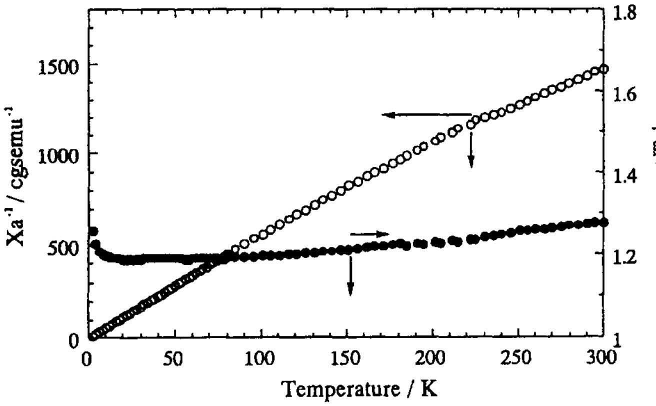


Figure 7 Temperature dependence of magnetic susceptibility (○) and magnetic moment (●) of TPOB in powder state.

Magnetic susceptibility follows the Curie-Weiss law with 0.42 K, indicating the ferromagnetic interaction took place. Magnetic moments also increased with lowering the temperature and indicating that the ferromagnetic interaction took place. Saturation of magnetization was observed in the magnetic field dependence of magnetization, although hysterysis was not observed. Accordingly, we can conclude that liquid crystalline monomer have ferromagnetic interaction.

ACKNOWLEDGMENT

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/04242104) from the Ministry of Education, Science, and Culture, Japan.

REFERENCES

1) M. Kamachi, M. Tamaki, Y. Morishima, S. Nozakura, W. Mori, and M. Kishita, Polym. J., 12, 362 (1982).
2) S. Nozakura and M. Kamachi, Makromol. Chem. Suppl., 12, 255 (1985).
3) H. Sugimoto, H. Aota, A. Harada, Y. Morishima, M. Kamachi, W. Mori, M. Kishita, N. Ohmae, M. Nakano, and M. Sorai, Chem. Lett., 1991, 2095.
4) M. Kamachi, H. Sugimoto, A. Kajiwara, A. Harada, Y. Morishima, W. Mori, N. Ohmae, M. Nakano, M Sorai, T. Kobayashi, and K. Amaya, Mol. Cryst. Liq. Cryst., 232, 53 (1993).
5) T. Kobayashi, M. Takiguchi, K. Amaya, H. Sugimoto, A. Kajiwara, A. Harada, and M. Kamachi, J. Phys. Soc. Jpn., 62, 3239 (1993).
6) A. Kajiwara, H. Sugimoto, and M. Kamachi, Bull. Chem. Soc. Jpn., 67, 2373 (1994).
7) A. Kajiwara, W. Mori, M. Sorai, K. Yamaguchi, and M. Kamachi, Mol. Cryst. Liq. Cryst., 272, 67 (1995).
8) N. Ohmae, A. Kajiwara, Y. Miyazaki, M. Kamachi, and M. Sorai Thermochimica Acta, 267, 435 (1995).
9) T. C. Kobayashi, M. Takiguchi, C. Hong, A. Okada, K. Amaya, A. Kajiwara, A. Harada, and M. Kamachi, J. Phys. Soc. Jpn., 65, 1427 (1996)
10) R. Chiarelli, M. A. Novak, A. Rassart, and J. L. Tholence, Nature, 363, 147 (1993).
11) E. K. Metzner, L. J. Libertini, and M. Calvin, J. Am. Chem. Soc., 99, 4500 (1977).
12) Y. Morishima, J. Fujita, T. Ikeda, and M. Kamachi, Chem. Lett., 1994, 557.
13) J. F. W. Keana, S. B. Keana, and D. Beetham, J Am. Chem. Soc., 89, 3055 (1967)
14) M. E. Brik, Tetrahedron Lett., 36, 5519 (1995).
15) A. Nakajima and J. Yamauchi, Bull. Inst. Chem. Res. Kyoto Univ., 54, 234 (1976).