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Preparation and Properties of Biphenyl and Cholesterol Derivatives with Nitroxide Radicals

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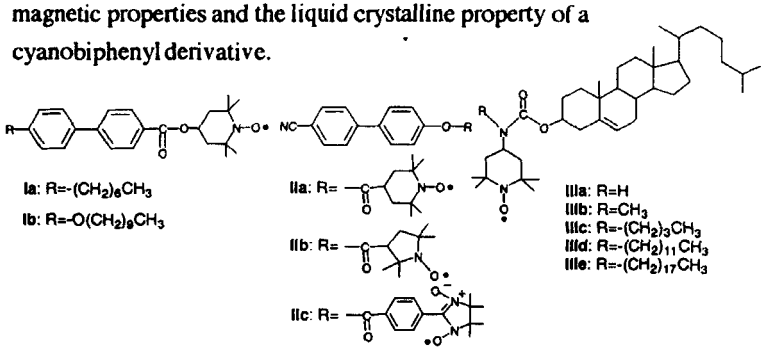
Series of biphenyl as well as cholesterol derivatives with nitroxide radicals have been prepared to investigate their magnetic/liquid crystalline characters. Weak antiferromagnetic interactions in the low temperature region with no liquid crystalline character have been observed in all cholesterol and several biphenyl derivatives prepared while a cyanobiphenyl derivative with TEMPO substituent have been found to show ferromagnetic interactions in the low temperature region on the one hand and smectic liquid crystalline behavior at elevated temperatures on the other hand.

Keywords: Biphenyl; Cholesterol; TEMPO radical; Magnetic property; Liquid crystalline property

INTRODUCTION

The search for new molecular-based magnetic materials, especially organomagnetic materials, is continuously one of the recent interest in the field of materials chemistry and the growing interest is now focused on the intelligent magnetic materials having both interesting magnetic property and other functionality such as photochromism, thermochromism or liquid crystalline property. In the course of our study for the development of new organomagnetic materials [1], we have been interested in preparing such a compound that has ferromagnetic behavior being coupled with liquid crystalline property in expectation of the stronger spin-spin interactions. Almost twenty-five years ago, Dvolaitzky et al. first reported the preparation, the mesogenic properties and EPR studies of several paramagnetic liquid crystals with DOXYL (4,4-dimethyl-3-oxazolidinyloxy) group [2]. Since then, however, no systematic studies have been reported on organic paramagnetic liquid crystals and the field has remained largely unexplored. It is only in recent years that some research groups have again paid their attention to such interesting materials to study on their magnetic/liquid crystalline properties; Kaszynski has reviewed recently the progress toward their calamitic and discotic radicals [3] and Tamura et al. have prepared several radical compounds directing toward similar aim [4]. Besides organic radical compounds, Allgaier and Finkelmann have reported in 1994 on the synthesis and magnetic properties of mesogenic side-chain polymers containing stable radicals [5] and Griesar et al. have recently prepared a ferrimagnetic metallomesogen with a discotic mesophase [6]. Up to date, however, all attempts to prepare monomeric or polymeric mesogens using TEMPO (2,2,6,6-tetramethylpiperidinyloxy) radical as a part of the rigid core have failed probably because of the undesirable bulkiness of its tetramethyl substituents. In spite of the general notion of

the disadvantage of TEMPO radical for obtaining mesogenic properties, we have been interested in preparing the biphenyl and cholesterol derivative with TEMPO radical to see whether such substances would be available that exhibit interesting magnetic and/or liquid crystalline properties and then we have initiated our study to prepare several derivatives carrying TEMPO or PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxy) radical. We report in this paper the preparation of series of biphenyl and cholesterol derivatives, their magnetic properties and the liquid crystalline property of a cyanobiphenyl derivative.

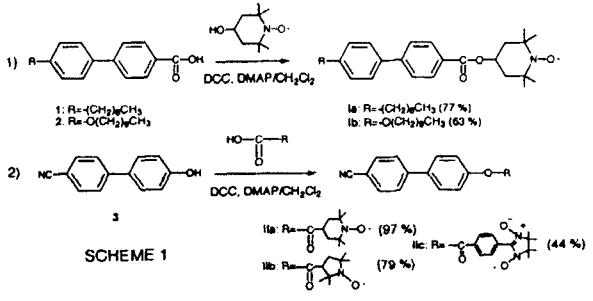


RESULTS AND DISCUSSION

Preparation of Biphenyl and Cholesterol Derivatives Carrying Nitroxide Radical

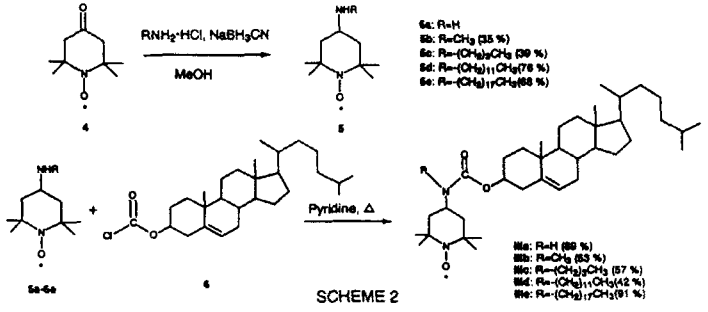
Several biphenyl derivatives with nitroxide radicals have been prepared according to the SCHEME 1. The biphenyl carboxylic acids **1**, **2** have been derivatized by 4-hydroxy-TEMPO using DCC (1,3-dicyclohexylcarbodiimide) and DMAP (4-dimethylaminopyridine) as condensation reagents to give **Ia** and **Ib** in moderate yields. Similarly, three cyanobiphenyl derivatives (**IIa-IIc**) have been prepared from 4-hydroxy-4'-cyanobiphenyl with 4-carboxy-TEMPO, 4-

carboxy-PROXYL or p-carboxyphenyl nitronyl nitroxide, although the yield of **IIc** is relatively low compared with others.



SCHEME 1

A series of cholesterol derivatives with nitroxides radicals (**IIIa-IIIe**) has been prepared as follows; reductive amination of 4-oxo-TEMPO **4** by using several primary alkylamines gave a series of mono-alkylamino-TEMPO **5a-5e**. The condensation of the latter radicals with cholesteryl chloroformate **6** in pyridine afforded the corresponding 4-alkylamino-TEMPO derivatives (**IIIa-IIIe**) in moderate isolated yields (SCHEME 2).



SCHEME 2

Magnetic Properties of Biphenyl and Cholesterol Derivatives Carrying Nitroxide Radical

In their EPR spectra, triplet absorptions based on TEMPO or PROXYL radical have been observed in each of the biphenyl and cholesterol derivatives except **IIc**, in which quintet absorption due to nitronyl nitroxide moiety has been obtained.

The measurements of the static magnetic susceptibility of the radical compounds prepared have been carried out by a SQUID susceptometer between 2-300 K and the data are summarized in TABLE 1 (biphenyls) and TABLE 2 (cholesterols). It was found from the results that the magnetic interactions between the spins of the radical compounds are usually rather weak indicating the remote distances between the spin centers because of the steric congestion around them. The temperature dependence of the χT values of **IIa** having a liquid crystalline character as mentioned below together with those of **IIb** is shown in FIGURE 1. The increase of the values in the lower temperature region (FIG. 1, left) along with the decrease of temperature indicates that the intermolecular spin-spin interactions in the radical **IIa** are ferromagnetic, whereas antiferromagnetic interactions are observed in the spins of **IIb** in the lower temperature region (FIG. 1, right). Unusual deviation from Curie-

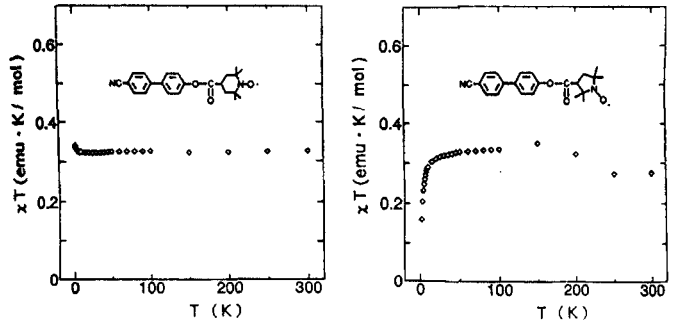


FIGURE 1 Temerature dependence of χT for **IIa** (left) and **IIb** (right).

Weiss behavior is apparent in the spins of **IIb** in the higher temperature region, although the reason is not clarified yet. As shown in TABLE 1,

ferromagnetic spin-spin interactions have been found in **Ib** and also in **IIc** beside **IIa**, while antiferromagnetic interactions have been observed

TABLE 1 Magnetic data of biphenyl derivatives **Ia**, **Ib** and **IIa-IIc**

Compound	Magnetic interaction	Weiss temperature/K[a]
Ia	antiferromagnetic	-3.89
Ib	ferromagnetic	0.30
IIa	ferromagnetic	0.13
IIb	antiferromagnetic[b]	-2.64
IIc	ferromagnetic	0.38

[a]Fitting for Curie-Weiss rule. [b]In the lower temperature region.

in **Ia** and **IIb**. Since the molecular structure of **Ia** and **Ib** as well as **IIa** and **IIb** are supposed to be similar each other, the differences of their magnetic behaviors would reflect the relatively large differences of their crystal structures.

The magnetic properties of the cholesterol derivatives **IIIa-IIIc** are summarized in TABLE 2. It is apparent from the data that weak

TABLE 2 Magnetic data of cholesterol derivatives **IIIa-IIIe**

Compound	Magnetic interaction	Weiss temperature/K[a]
IIIa (R=H)	antiferromagnetic	-0.29
IIIb ($R=CH_3$)	antiferromagnetic	-0.53
IIIc [$R=(CH_2)_3CH_3$]	antiferromagnetic	-0.31
IIId [$R=(CH_2)_{11}CH_3$]	antiferromagnetic	-1.34
IIIe [$R=(CH_2)_{17}CH_3$]	antiferromagnetic	-3.00

[a]Fitting for Curie-Weiss rule.

antiferromagnetic interactions are predominant in these radicals probably because of the large steroidal skeleton to preclude the strong spin-spin

interactions although the larger Weiss temperatures have been observed in the radicals with long alkyl chains.

Liquid Crystalline Property of a Cyanobiphenyl Derivative IIa

The liquid crystalline character for all compounds prepared has been surveyed through the investigation of their thermotropic behavior by means of melting point apparatus, DSC or optical polarizing microscopy and it was found that all the compounds except **IIa** show no liquid crystalline behaviors so far as we have examined.

In the radical **IIa**, the gradual appearance of a smectic phase, which is considered to be smectic G phase, could be observed above 80°C in a heating process through a polarizing microscope. A weak transition peak was also observed in DSC profile. The phase appeared to change to another phase at around 130°C and finally to an isotropic liquid phase above 160°C. Thus, the radical **IIa** was found to have combining solid state properties; it shows ferromagnetic spin-spin interactions at low temperatures on the one hand and an ordered liquid crystalline character at elevated temperatures on the other hand in spite of possessing bulky TEMPO radical.

Further studies on this material from the synergistic point of view are now underway and to develop other radical compounds with lower transition temperatures to a liquid crystalline phase are also in progress.

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