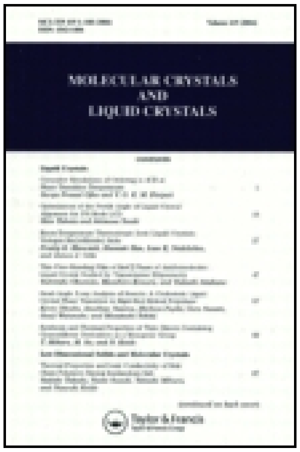

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PREPARATION AND PROPERTIES OF 2-(o-HALOPHENYL)-α-NITRONYL NITROXIDES

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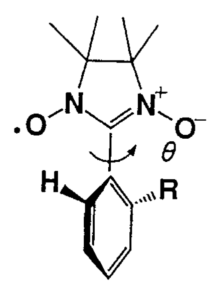
Abstract A series of nitronyl nitroxide derivatives of benzene bearing halogen atoms on ortho-position have been prepared showing remarkable substituent effect of ortho-halogen atoms on the magnetic properties; X-ray analysis for the fluorine derivative revealed the crystals being constituted of three dimensional net works of the nitroxide radicals through methyl or phenyl groups to result ferromagnetic interactions in the derivative.

INTRODUCTION

The search of new organomagnetic materials is undoubtedly one of the growing interest for scientists and fruitful advance has been achieved in recent years.[1] Since the discovery of the first organic ferromagnet, i. e., γ-phase crystal of p-nitrophenyl nitronyl nitroxide,[2] several organic free radicals have been found to show ferromagnetism in a few years.[3] The ferromagnetic p-nitrophenyl nitronyl nitroxides (β-phase and γ-phase) has been reported to have twisted dihedral angles between phenyl ring and the plane of nitronyl nitroxide[4] and the similar results were found in some other ferromagnetic radicals including 2', 5'-dihydroxy-substituted[5] and 2'-hydroxy-substituted[6] nitronyl nitroxides, which have been found to be twisted molecular structures and owing to intra- and inter-molecular hydrogen bonds to show ferromagnetic spin-spin interactions in their three dimensional structures. To see the relationship between molecular as well as crystal structures and magnetism in such molecules as that having twisted



1: R = F
2: R = Cl
3: R = Br
4: R = I

conformation between π–system and radical moiety, we have been interested in preparing nitronyl nitroxide derivatives of benzene introducing a single atomic substituent, i. e., halogen atom on ortho-position.[7] In this paper, we report the preparation of four such derivatives **1**-**4**, their magnetic properties and the crystal structure of fluorine derivative **1**.

RESULTS AND DISCUSSION

As a preliminary estimation of the distortion between phenyl ring and the radical moiety of nitronyl nitroxide in **1**-**4**, we at first calculated their dihedral angles between the plane of phenyl ring and that of O(1)-N(2)-C(7) of the radical moiety by MM2 calculation to give the result of the sequential distortion according to the van der Waals radii of halogen atoms (TABLE 1).

TABLE 1 The estimated degree of distortion (θ) by MM2 calculation[a]

compound	R=H	**1**	**2**	**3**	**4**
θ	48 (29[b])	55 (48[c])	66	71	70

[a] Optimized by using MM2 parameters in CAChe system.
[b] Found by X-ray data; Cf. W. Wang and S. F. Watkins, J. Chem. Soc., Chem. Commun., 1973, 888.
[c] Found by X-ray data; this work.

Following the result of estimation, we then have prepared the derivatives **1**-**4** from corresponding o-halobenzaldehydes in usual way[8] which were purified as relatively stable crystals. The temperature dependence of the paramagnetic susceptibility of each polycrystalline sample was measured by means of a SQUID susceptometer in the temperature range 2-300 K. It was found from the plot of the reciprocals of susceptibility against temperature for the fluorine derivative **1** to follow the Curie-Weiss law over the whole temperature range, and Curie and Weiss constants were determined to be 0.375 emu K mol^{-1} and+0.5 K, respectively. The positive Weiss constant and increase of the product $\chi_p T$ with decreasing temperature lower than ca. 20 K indicated intermolecular ferromagnetic interaction between the spins of radical **1** at low temperature (FIGURE. 1). The ferromagnetic coupling was further supported by the magnetization curve measurements at low temperature (FIGURE. 2). On the other hand, negative Weiss constants were obtained for the radicals **2**, **3**, and **4**, indicating the intermolecular spin-spin interactions were antiferromagnetic in those three radicals

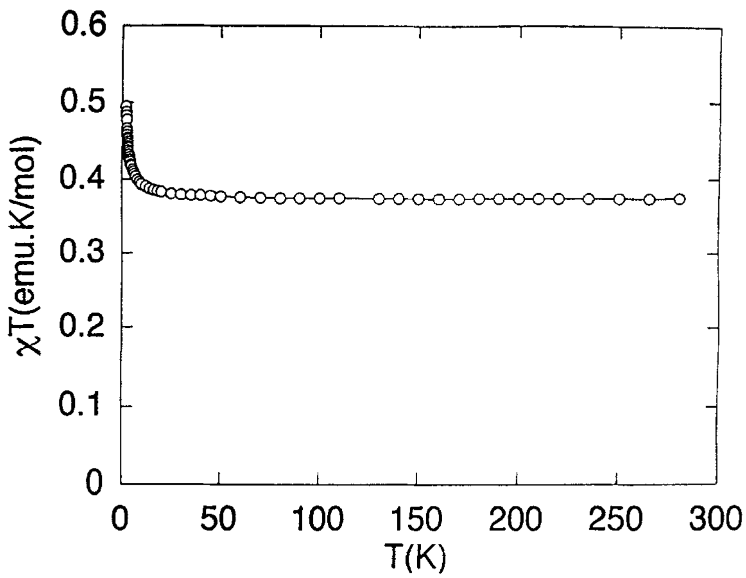


FIGURE 1 Temperature dependence of products of paramagnetic susceptibility χ and temperature T for **1**.

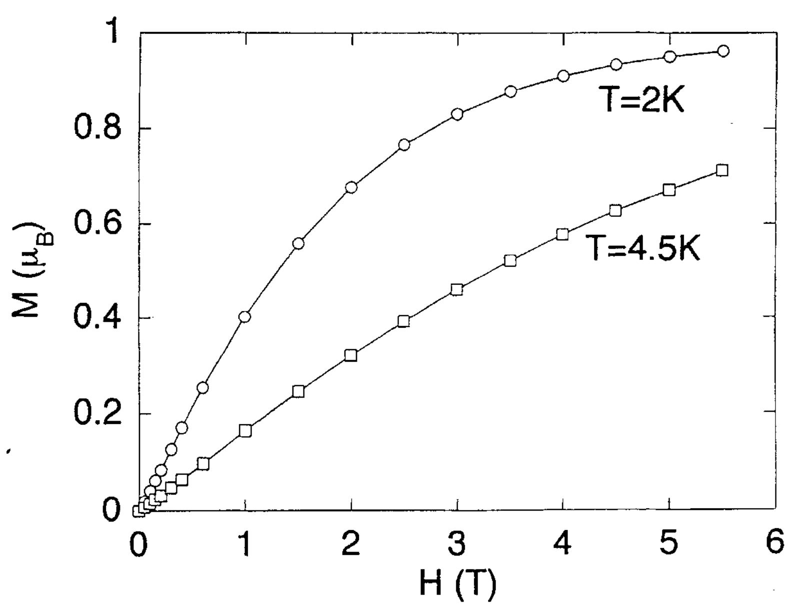


FIGURE 2 Magnetization Curve for **1** at 2 K and 4.5 K.

and stronger interactions were observed in the latter two (**3** and **4**) than chlorine derivative **2** or unsubstituted derivative (R=H)[9] (TABLE 2). It is also notable that **3** and **4** showed almost the same order of magnitude.

Thus, sharp difference was observed in their magnetic properties between **1** and other derivatives reflecting possibly the degree of their molecular deformation estimated from the van der Waals radii of halogen atom and the resulting crystal structural

TABLE 2 The Weiss constants of the radicals[a]

compound	**1**	**2**	**3**	**4**
Θ/K	+0.48	-2.00	-3.32	-3.36

[a] The value of unsubstituted derivative is reported in Ref. 9 as Θ/K = −1.4

difference in three dimension. In order to elucidate the magnetostructural correlation, we then have carried out the X-ray structural analysis on the fluorine derivative **1**. As shown in FIGURE 3, the dihedral angle between the plane of phenyl ring and that of O(1)-N(2)-C(7) of the radical **1** was found to be 48° being somewhat smaller value than the estimated one from MM calculation. FIGURE 4 shows the crystal structure of **1** viewed along the a axis. As

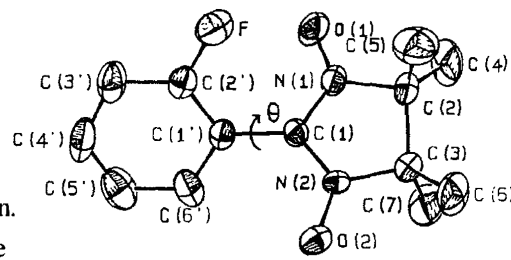


FIGURE 3 Molecular Structure of **1**.

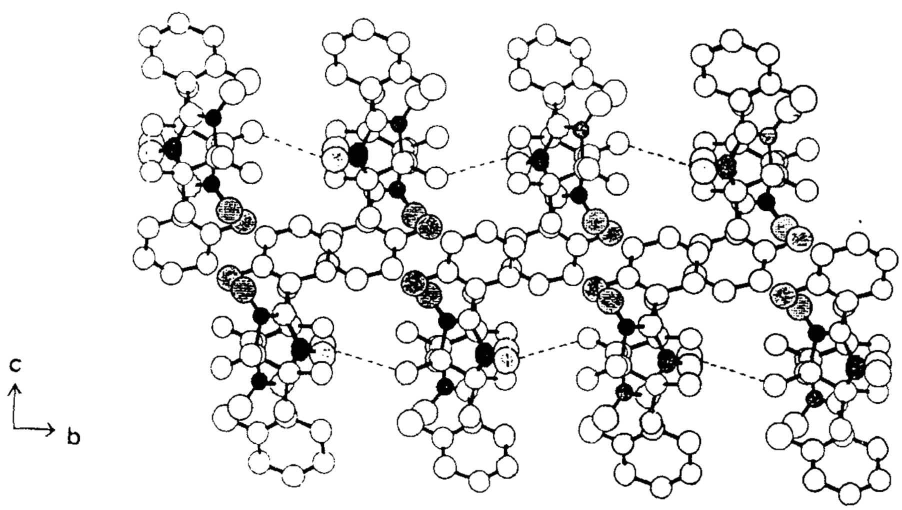


FIGURE 4 Crystal structure of **1** viewed along the a axis.

seen from the FIGURE, the molecules stack along b axis with head-to-tail arrangement and b column corrugates each other along with c axis. The O-O distance along the direction of b axis is amounted to be 4.39 Å and the distances are larger in other directions. The straight lines connected between the molecules are depicted to show the short O-C distances with the values of around 3.5-3.8 Å. The shortest distances *in* each b column are those between O atoms and methyl group (O(2)-C(5) = 3.53 Å) and those between O atoms and phenyl groups are the shortest *between* b columns. Following tendency is apparent from the data, i. e., the direct interaction between O-O is very small and hence the overlap between SOMOs between the molecules is estimated to be very small, which is relevant to ferromagnetic interaction. Moreover, the interactions between the radicals work through methyl groups or phenyl groups by weak hydrogen bonds of the C-H···O-N type to build up three dimensional net work system and then to give efficient spin polarization effect for the ferromagnetic interactions between the radicals.[10] Thus, ferromagnetic behaviour of the fluorine derivative **1** could be rationally interpreted from its crystal structural analysis and it is apparent from the results obtained above that the ferromagnetic behavior of radical crystals depends subtly upon their molecule/crystal structures as no ferromagnetic but antiferromagnetic behavior was found for the radicals **2**, **3** and **4**, which have possibly more distorted molecular structures than **1**. Further studies including X-ray analysis of **2** are in progress.

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