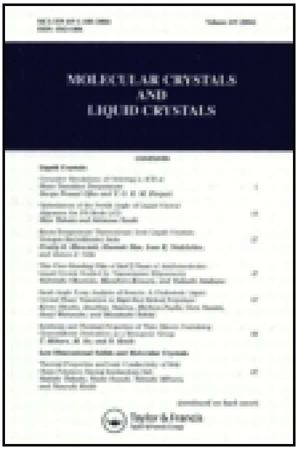

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Crystal Structures of 4-(4-Halobenzylideneamino)-TEMPO Radicals Showing Magnetic Interactions

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Crystal Structures of 4-(4-Halobenzylideneamino)-TEMPO Radicals Showing Magnetic Interactions

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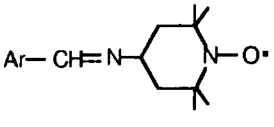
X-ray crystal structure analyses were performed on 4-(4-halo-benzylidene-amino)-TEMPO radicals, as well as other 4-Ar-CH=N-TEMPO radicals (Ar = 4-Ph-Ph, 4-Py, Ph, 4-MeS-Ph, 3-Py and 4-Me-Ph), at room temperature. Some of these crystals have been revealed to show intermolecular ferromagnetic interactions at an extremely low temperature. X-ray studies revealed that the crystals of the 4-I-Ph derivative showed two modifications; one showed a ferromagnetic transition and the other showed an antiferromagnetic interaction. Structural features of these TEMPO crystals are mainly classified to four groups: 1) structures of Cl-Ph, I-Ph and Ph-Ph derivatives which show a ferromagnetic transition, 2) Br-Ph and 4-Py derivatives with a ferromagnetic interaction, 3) Ph, 4-MeS-Ph, 3-Py, 4-Me-Ph derivatives showing different kinds of magnetic interactions, and 4) others including antiferromagnetic F-Ph and I-Ph derivatives.

Keywords: X-ray structure analysis; crystal structures; TEMPO radicals; magnetic interactions

INTRODUCTION



Some of the 4-arylmethyleneamino-TEMPO radicals (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) were revealed to show intermolecular ferromagnetic interactions at an extremely low temperature[1]. For 4-(4-X-benzylideneamino)-TEMPO, **1** (X=F) an antiferromagnetic interaction (θ=-2.6 K), **2** (X=Cl) a ferromagnetic transition (Tc=0.4K, θ=0.7K) and **3** (X=Br) a ferromagnetic interaction (θ=0.5K) were observed. The X-ray analysis revealed that crystals of the iodo derivative (X=I) showed two modifications (**4** and **4'**). The magnetic properties were measured for these crystals separately: **4**, a ferromagnetic transition (Tc=0.3K, θ=0.7K) and **4'**, an antiferromagnetic interaction (θ=-0.2K). The X-ray crystal structure analyses were performed on these radicals, as well as other 4-Ar-CH=N-TEMPO radicals, such as Ar = 3,5-diCl-Ph (**5**, Tc=0.4K, θ=0.6K), 4-Ph-Ph (**6**, Tc=0.4K, θ=0.6K), 4-Py (**7**, θ=0.6K), Ph (**8**, Tc=0.3K, θ=0.7K), 4-MeS-Ph (**9**, Tc=0.3K, θ=0.5K), 3-Py (**10**, θ=0.4K), 4-Me-Ph (**11**, θ=-1.3K) and naphthyl (**12**, θ=0.3K) at room temperature. Preliminary structures of some of these radicals have already been reported[2]. In this paper, we will report the relationships between structural features and magnetic interactions of these crystals. Structure analyses of **2**, **8** and **11** at low temperatures (100 ~ 150 K) and that of **8** at an extremely low temperature (7 K) were also carried out[3].

EXPERIMENTAL

Crystal data are listed in Table 1. Intensity data were measured using Rigaku

TABLE I Crystal data

	Ar	Sp.gr.	a/Å	b/Å	c/Å	β/°	V/Å^3	Z	Refs.	R
2	4-Cl-Ph	$P2_1/c$	5.885	24.417	11.397	104.1	1688	4	2379	0.042
	(100K)	$P2_1/c$	5.773	24.130	11.372	104.3	1535	4	2952	0.033
4	4-I-Ph	$P2_1/c$	5.889	25.851	11.322	105.3	1663	4	2462	0.032
6	4-biPh	$P2_1/c$	5.955	28.486	11.795	106.7	1916	4	2478	0.063
3	4-Br-Ph	$P2_1/c$	7.541	20.847	10.590	91.6	1664	4	1867	0.048
7	4-Py	$P2_1/c$	7.977	20.158	11.382	126.0	1481	4	2460	0.040
8	Ph	$P2_1/c$	12.684	11.740	11.024	111.4	1528	4	2107	0.048
	(150K)	$P2_1/c$	12.599	11.669	10.877	110.9	1494	4	2462	0.054
	(7 K)	$P2_1/c$	12.576	11.575	10.796	110.9	1469	4	3566	0.049
9	4-MeS-Ph	$P2_1/c$	13.574	11.880	11.163	98.8	1779	4	2978	0.048
10	3-Py	$P2_1/c$	12.425	11.598	11.038	109.5	1499	4	1867	0.073
11	4-Me-Ph	$P2_1/c$	12.490	11.597	11.280	97.1	1621	4	2581	0.051
	(100K)	$P2_1/c$	12.442	11.495	11.094	97.4	1574	4	2992	0.054
1	4-F-Ph	Pbca	20.010	15.249	10.417	90	3178	8	1870	0.043
4'	4-I-Ph	$P2_1/c$	10.980	38.914	8.358	103.9	3466	8	5040	0.038
5	di-Cl-Ph	Pbca	14.035	22.964	10.710	90	3452	8	2121	0.058
12	Naphthyl	$Pna2_1$	20.084	5.697	15.106	90	1728	4	1491	0.051

AFC-5R or AFC-7R diffractometers with graphite monochromators. The structures were solved by the direct method and were refined using full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. The final R values were also listed in Table 1. Intensities at 150 Kfor **8** and at 100 K for **2** and **11** were measured on an AFC-7R diffractometer equipped a N_2 gas-flow device. For **8**, intensities at 7 K were also measured on a MacScience Weissenberg-type diffractometer with an imaging plate equipped a He gas-flow device in Institute for Molecular Science. In the range from room temperature to these low temperatures, no structural transition were observed.

RESULTS AND DISCUSSIONS

Structural features of these crystals are mainly classified to four groups: 1) structures of **2**, **4** and **6** which show a ferromagnetic transition, 2) structures of **3** and **7** with a ferromagnetic interaction ($\theta > 0$), 3) structures of **8** ~ **11**, and 4) others including antiferromagnetic **1** and **4'**.

Figure 1 shows the crystal structure of **4**. In this crystal, oxygen atoms arrange to form a pleated sheet parallel to the ac plane. The nearest O···O distance in the sheet is 5.889 Å, which corresponds to the length of the a axis. The second nearest O···O distance is 5.908 Å. These O···O distances are too long for a direct spin-spin interaction. Within the sheet, O atoms contact to the H atoms of the CH_2 or CH_3 groups of the neighboring TEMPO rings with van der Waals' distances. The ferromagnetic interactions are considered to be transferred via O···H van der Waals' interactions of these β-H atoms[11]. Between sheets, the aryl groups of each sheet arrange alternately with face-to-face. The distance between the phenyl planes is 3.79 Å. Crystal structures of **2** (X = Cl) and **6** (Ar = biphenyl) are isomorphous with that of **4**. All these crystals show the ferromagnetic transition at extremely low temperature. In these crystals, two-dimensional O···O interactions via H atoms of CH_2 or CH_3 groups and overlap of aryl groups may be essential for the ferromagnetic interaction.

The crystals of **3** (X = Br) have the same space group as that of **4**, although the length of the a axis is longer than that of **4** and vice versa for the b

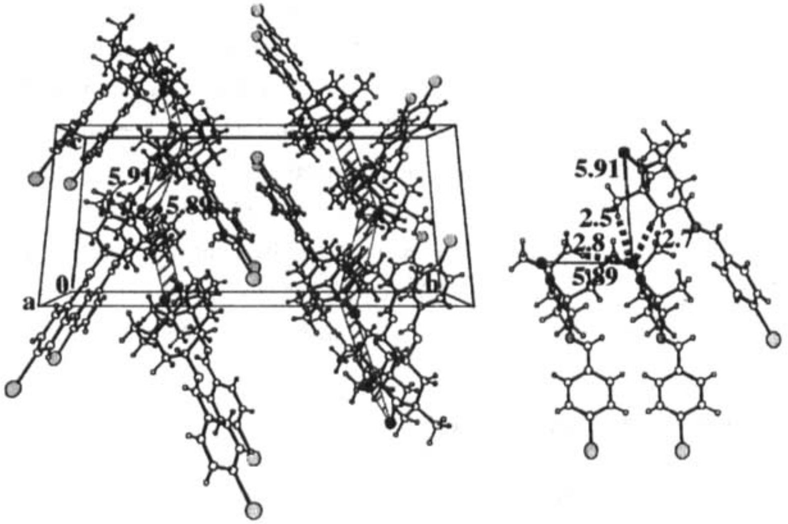


FIGURE 1 Crystal structure of **4** (X=I) and O···H contacts (broken lines) within the O···O sheet.

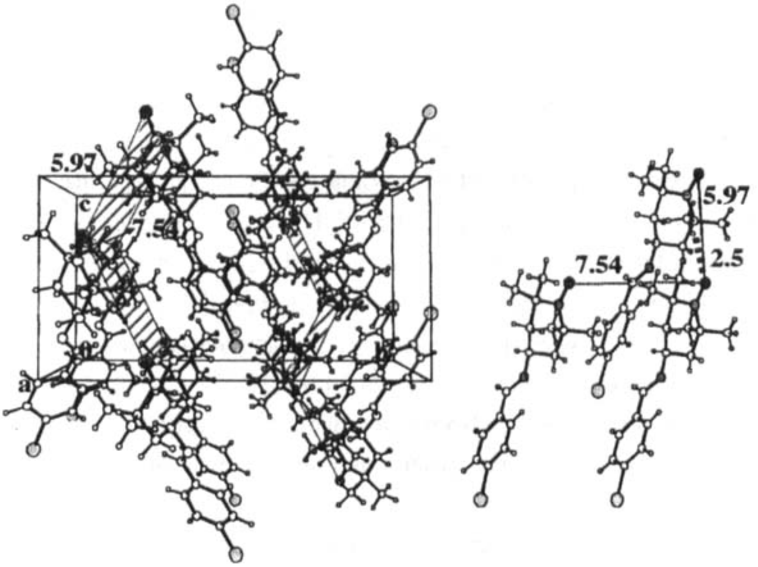


FIGURE 2 Crystal structure of **3** (X=Br) and O···H contacts (broken lines) within the O···O sheet.

axis. A characteristic sheet-structure and overlap of the aryl groups are also observed in **3** as shown in Fig. 2. The O···O distances within the sheet are 7.541 and 5.996 Å, which are longer than those of **4**. The interactions within the sheet via β-H atoms are weaker than those of **4** as shown in Figures 1 and 2. This is considered to be a reason that **2** and **4** show the ferromagnetic transitions, while **3** shows only a ferromagnetic interaction. The crystals of **7**, which show only the ferromagnetic interaction, are isomorphous with those of **3**. However, an important question is remained why the crystal structure of the 4-Br-Ph derivative (**3**) is so different from those of 4-Cl-Ph and 4-I-Ph derivatives (**2** and **4**).

The structure of **1** (X = F) is different from those of the other 4-halo-Ph derivatives, while O atoms also arrange to form two-dimensional zigzag networks[2]. The shortest distance of O···O lengths in the sheet is 5.477 Å, which is shorter than those of **2** ~ **4**. In this crystals, O···O interaction are transferred via γ-H atoms as well as via β-H atoms. This is considered to be the origin of the anti-ferromagnetic interaction at extremely low temperature.

The crystal structure of **4 '** (X = I), a polymorphic form of **4**, is shown in Fig. 3, which is also quite different from those of **1** ~ **4**. In this case, the molecules are linked to form a chain structure through the short intermolecular I···O contacts of 2.947 and 2.951 Å. Two chains are connected with a weak

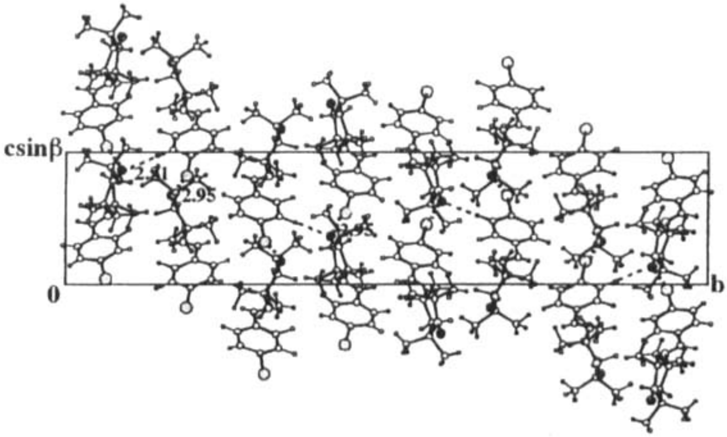


FIGURE 3 Crystal structure of 4' (X = I)

$CH_{phenyl}\cdots O$ hydrogen bond ($H\cdots O$ = 2.31 Å) and the $O\cdots O$ distance between two chains is 5.468 Å. No sheet-like $O\cdots O$ interactions are observed.

The mode of the crystal structures of **8** ~ **11** are very similar with each other, although they show different magnetic behaviors at low temperature. The two-dimensional $O\cdots O$ sheets are also constructed for these crystals like 4-halo-phenyl derivatives. Within the sheet, O atoms contact to the β-H atoms of the neighboring TEMPO rings with van der Waals' distances. The packing mode of the aryl groups between sheets is a herringbone-type, which is different from a parallel overlapping of 4-halo-phenyl derivatives. While the intermolecular relationships within a sheet are very similar in **8** ~ **11**, the relationships between aryl groups seem to be different from each other. The structures of **8** and **9**, both of which show the ferromagnetic transition, are very similar with each other. The structure of **10**, showing a ferromagnetic interaction, slightly changes from those of **8** and **9**, and the packing mode of the aryl groups of **11** showing an anti-ferromagnetic interaction is considerably different from those of **8** ~ **9**.

In the crystals of TEMPO radicals, the magnetic interactions are very weak as can been seen from the extremely low values of magnetic transition points and Weiss constants. It is difficult to point out the origin of the magnetic interactions exactly. In spite of that, the sheet-like arrangement of O atoms, intra-sheet interactions via CH_2 or CH_3 groups of TEMPO rings, and arrangements of aryl groups are related to the mechanisms of the magnetic interactions.

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