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CRYSTAL STRUCTURES OF TEMPO RADICALS SHOWING FERROMAGNETIC INTERACTION

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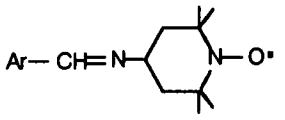
Abstract Some of the 4-arylmethyleneamino-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) radical crystals showed an intermolecular ferromagnetic interaction. The X-ray structure analyses were performed on 4-arylmethyleneamino-TEMPO crystals (aryl = phenyl, p-chlorophenyl, p-biphenyl, p-phenoxyphenyl, p-bromophenyl, 3,5-dichlorophenyl, 3-pyridyl, naphthyl and p-fluorophenyl) at room temperature to investigate whether any systematic intermolecular interactions were demonstrated among these crystals. No special interactions except van der Waals interaction were observed in these crystals. As for the arrangements of N-O radicals in the crystals, two-dimensional O···O networks are constructed, of which forms are various. A sheet-like arrangement of the N-O radicals is considered to be essentially important for the magnetic interactions, although the O···O distances are long for the direct interaction between radicals.

INTRODUCTION



Ar = **1** Ph **2** p-Cl-Ph **3** p-bi-Ph
4 p-PhO-Ph **5** p-Br-Ph **6** 3,5-di-Cl-Ph
7 3-Pyridyl **8** Naphthyl **9** p-F-Ph

Recently some 4-arylmethyleneamino-TEMPO radicals (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) were revealed to show an intermolecular ferromagnetic interaction, of which **1** ~ **4** exhibit a ferromagnetic transition (Tc) at an extremely low temperature .[1,2] Crystals of **5** ~ **8** showed only a ferromagnetic interaction ($\theta > 0$), while **9** showed an anti ferromagnetic interaction ($\theta < 0$). The X-ray structure analysis were performed on these crystals at room temperature to investigate whether any systematic intermolecular interactions were demonstrated among these crystals.

EXPERIMENTAL

Crystal data are listed in Table 1. Intensity data were collected using Rigaku AFC-4 and AFC-5R diffractometers with graphite monochromators at room temperature. The structures were solved by the direct method with the program MULTAN78. Structures were refined using block-diagonal 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.

TABLE I Crystal Data

	Tc/K	θ/K	Sp. gr.	a/Å	b/Å	c/Å	β/°	V/Å^3	Z	No. refs.	R
1	0.18	0.7	$P2_1/c$	12.684	11.740	11.024	111.40	1528	4	2245	0.056
2	0.4	0.7	$P2_1/c$	5.909	24.475	11.421	103.84	1604	4	1734	0.085
3	0.4	0.6	$P2_1/c$	5.955	28.486	11.795	106.72	1916	4	2661	0.068
4	0.2	0.4	$Pbc2_1$	5.993	30.565	22.032	90.0	4035	8	2696	0.061
5	—	0.5	$P2_1/c$	7.541	20.847	10.590	91.56	1664	4	2041	0.054
6	—	0.7	Pbca	14.035	22.964	10.710	90.0	3452	8	1734	0.062
7	—	0.4	$P2_1/c$	12.426	11.598	11.038	109.52	1499	4	2230	0.069
8	—	0.3	$Pna2_1$	20.084	5.697	15.107	90.0	1728	4	1549	0.051
9	—	-2.6	Pbca	20.010	15.249	10.417	90.0	3178	8	1870	0.041

RESULTS AND DISCUSSIONS

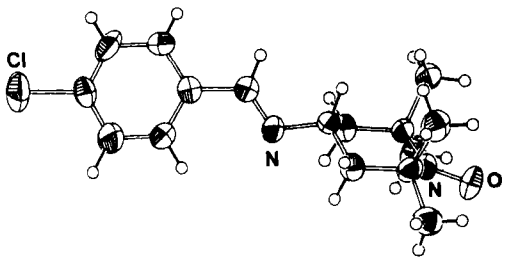


FIGURE1 Molecular sructure of **2**

Figure 1 shows the molecular structure of **2**. The arylmethyleneamino moiety is planar and almost perpendicular to the piperidine ring of which conformation is a chair form.

The molecular structures of the other radicals are very similar with that of **2**. The dihedral angles between the phenyl ring and the four C atoms of the chair-sheet plane of the piperidine ring are 82, 68, 68, 69, 77, 87, 73, 41 and 78° for **1** ~ **9**, respectively.

The crystal structure of **2** viewed along the a axis is shown in Fig. 2. In the crystals no special interactions except van der Waals interaction were observed. However, an arrangement of NO radicals in the crystals will attract our attention in relation to the magnetic properties. O atoms arrange to form a pleated sheet parallel to the ac plane. The nearest O···O distance in the sheet is 5.91 Å, which corresponds to the length of the a axis. The second nearest distance related by the c glide symmetry is 5.96 Å. The angle between the nearest N-O bonds is 0.0° and that of the sencond

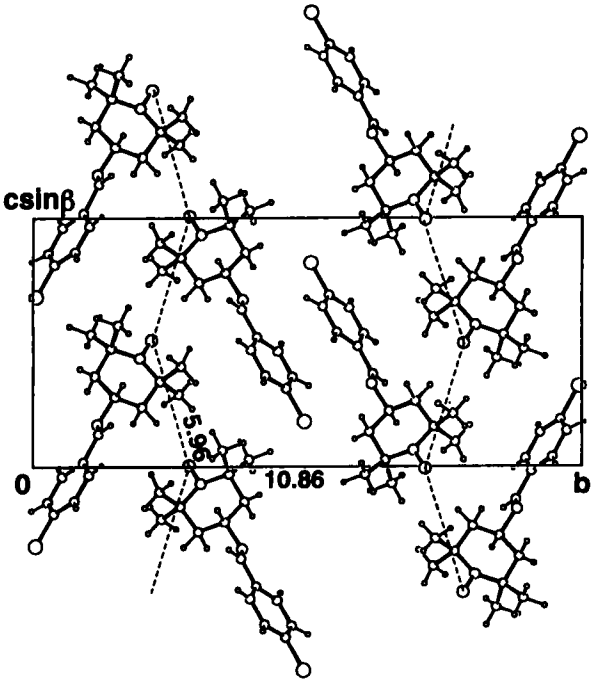


FIGURE 2 Crystal structure of **2** viewed along the a axis

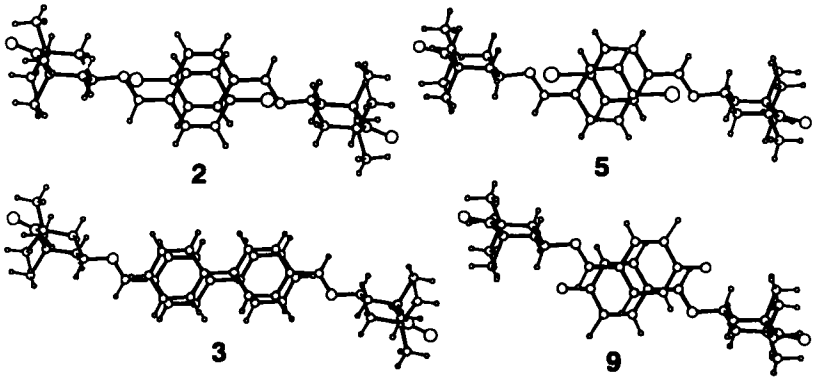


FIGURE 3 Overlappings of phenyl rings

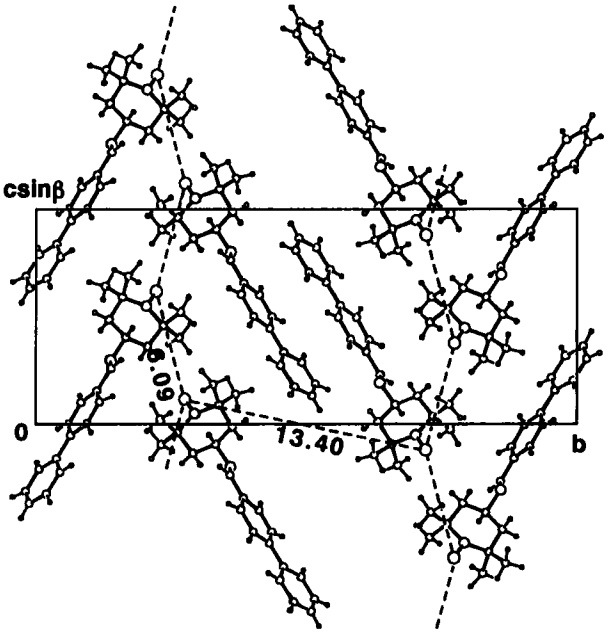


FIGURE 4 Crystal structure of **3** viewed along the a axis

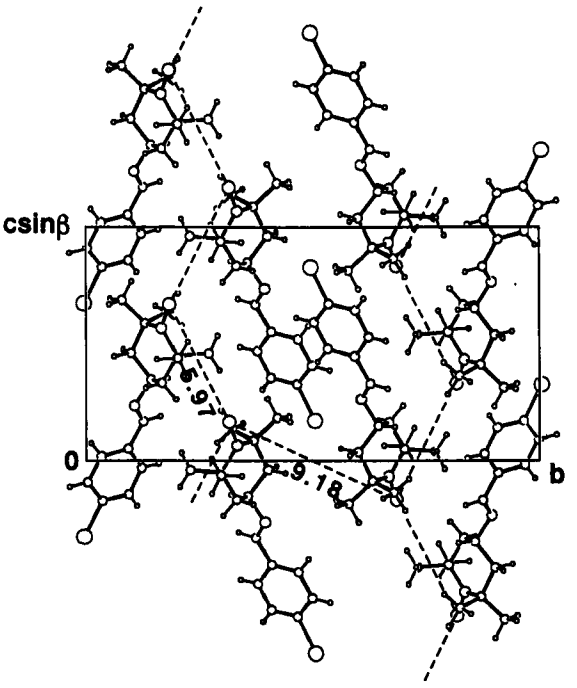


FIGURE 5 Crystal structure of **5** viewed along the a axis

nearest bonds is 47.2°. Between sheets, the aryl groups of each sheet arrange alternately with face-to-face as shown in Fig. 3. The distance between overlapping phenyl planes is 3.70 Å. The crystal structures of **3** and **5** are depicted in Fig. 4 and 5, respectively. The structures of **3** and **5** belong to the same category as **2**. However, in the case of **5**, the nearest O···O is related by the c glide symmetry and the second nearest O···O is related by the translation along the a axis. The distances between overlapping phenyl planes are 3.89 and 3.64 Å for **3** and **5**, respectively. Overlapping modes of the phenyl rings are slightly different from that of **2** as shown in Fig. 3. The O···O distances, the types of sheets and the angle between N-O bonds are summarized in Table 2 and 3, respectively.

The structure of **8** is also constructed with the O···O pleated sheets parallel to the bc plane as shown in Fig. 6. The nearest O···O distance in the sheet is 5.97 Å, which corresponds to the length of the b axis. The second nearest distance related by the 2_1 symmetry is 8.75 Å. The relationship of the aryl groups between sheets is different from those of **2**, **3** and **5**. In the case of **8**, aryl groups are arranged alternately to form a herringbone-like pattern as shown in Fig. 6.

The crystal structure of **1** viewed along the c axis is shown in Fig. 7. In **1**, the zigzag pleated sheets are arranged nearly parallel to the bc plane. The nearest O···O distance in the sheet is 5.62 Å, which corresponds to the lengths related by the c glide symmetry. The second nearest distance related by the 2_1 symmetry is 6.15 Å.

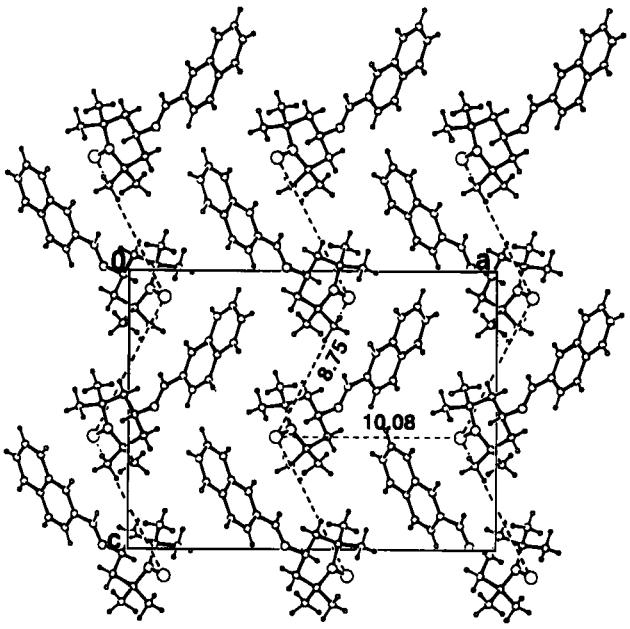


FIGURE 6 Crystal structure of **8** viewed along the b axis

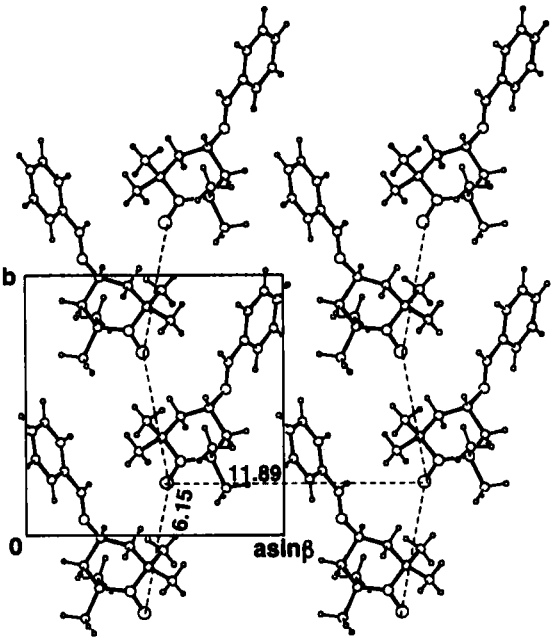


FIGURE 7 Crystal structure of **1** viewed along the c axis within the range from z=0.0 to 0.5

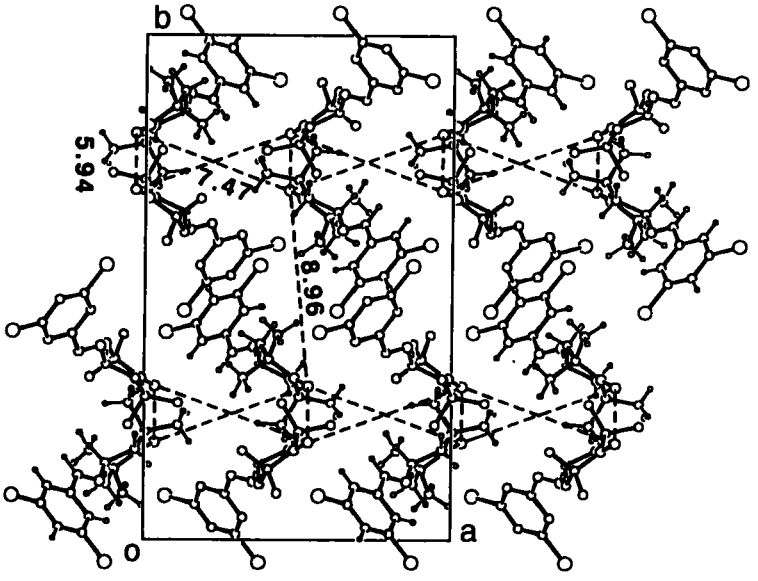


FIGURE 8 Crystal structure of **6** viewed along the c axis

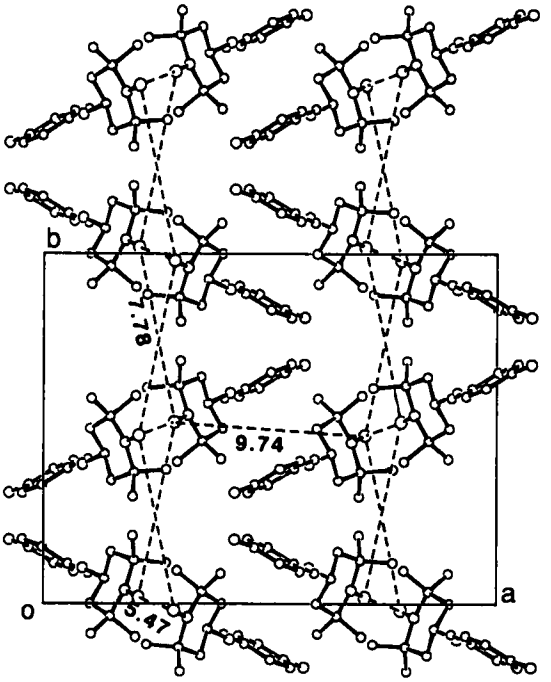


FIGURE 9 Crystal structure of **9** viewed along the c axis

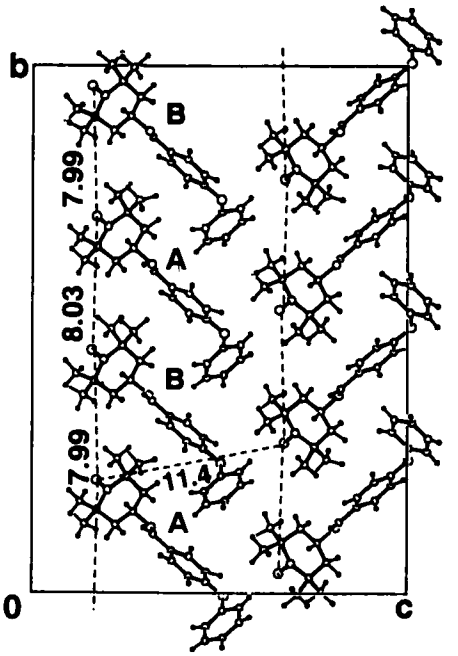


FIGURE 10 Crystal structure of **4** viewed along the a axis

The crystals of **7** are isomorphous with those of **1**. The corresponding lengths of **7** are 5.59 and 6.18 Å, respectively. Between sheets, the nearest aryl groups belonging to the neighboring sheets arrange herringbone-like.

The networks of **6** are constructed with complicated double-zigzag sheets as shown in Fig. 8, so that the surface of the sheet is rough in all directions. The arrangement of the aryl groups between sheets is a herringbone-like. The crystal structure of **9** (Fig. 9) is also formed with complicated double-zigzag sheets like **6**, although the arrangements of intersheet aryl groups and intrasheet TEMPO radicals are different from those of **6**. Between sheets, the aryl groups of each sheet arrange alternately with face-to-face as in the crystal structure of **2**.

TABLE II O···O distances and the types of sheets

	Ar	Sheet	O···O nearest	O···O second	O···O intersheet	Ar···Ar interaction
1	Ph	pleated (zigzag)	5.62	6.15	11.89	herring-bone
2	p-Cl-Ph	pleated	5.91	5.96	10.86	parallel overlapped
3	p-bi-Ph	pleated	5.96	6.09	13.40	parallel overlapped
4	p-phenoxy-Ph	planar	5.99	7.99 8.03	11.42	----
5	p-Br-Ph	pleated	5.97	7.54	9.18	parallel overlapped
6	3,5-di-Cl-Ph	double zigzag	5.94	7.47	8.96	herring-bone
7	3-pyridyl	pleated (zigzag)	5.59	6.18	12.42	herring-bone
8	naphthyl	pleated	5.70	8.75	10.08	herring-bone
9	p-F-Ph	double zigzag	5.47	7.78	9.74	parallel overlapped

TABLE III Relationships between the nearlest O···O atoms, angles between N-O bonds and dihedral angles between COC planes

	Relationships between O···O		Angle between N-O		Dihedral angles between COC	
	nearest	second	nearest	second	nearest	second
1	c glide	2_1	97.8	82.2	53.6	53.6
2	a translation	c glide	0.0	47.2	0.0	50.9
3	a translation	c glide	0.0	48.1	0.0	50.8
4	a translation	independent	0.0	3.9 89.4	0.0	3.6 76.3
5	c glide	a translation	34.9	0.0	72.9	0.0
6	c glide	2_1	32.9	60.0	84.9	76.1
7	c glide	2_1	86.7	93.3	63.6	63.6
8	b translation	2_1	0.0	37.7	0.0	39.5
9	2_1	b glide	44.0	59.6	48.7	64.3

For **4**, the planar sheet is constructed parallel to the ac plane. The nearest O···O distances in the sheet is 5.60 Å, which corresponds to the lengths of the a axis. The second nearest distances between two independent molecules are 7.99 and 8.00 Å. There are no intersheet interactions between aryl groups, because the sheet is

perpendicular to the crystallographic polar axis as shown in Fig 10. This arrangement is quite different from the other crystals.

No special interactions except van der Waals interaction were observed in crystals, **1** ~ **9**. As for arrangements of N-O radicals in the crystals, two-dimensional O···O networks are constructed, although of which forms are various as shown in Figures and Table 2. Although the O···O distances are long for the direct interaction between radicals, a sheet-like arrangement of the N-O radicals is considered to be essentially important for the magnetic interactions. A magnetic interaction will be transmitted via methyl groups of TEMPO rings and/or aryl rings, although the packing mode in the crystals is of the van der Waals interaction. To obtain the direct evidence of the systematic interaction which manifests the difference of magnetic character, more accurate structure analysis at a low temperature will be needed because the interactions are very weak.

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