

TEMPO radicals showing magnetic interactions. I. 4-(4-Halobenzylideneamino)TEMPO and related compounds

FUJIKO IWASAKI,* JOSEPH H. YOSHIKAWA, HAJIME YAMAMOTO, EIJI KAN-NARI, KIWAMU TAKADA, MASANORI YASUI, TAKAYUKI ISHIDA AND TAKASHI NOGAMI

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan. E-mail: fuji@pc.uec.ac.jp

(Received 12 March 1998; accepted 2 October 1998)

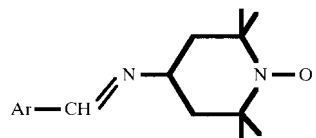
Abstract

X-ray crystal structure analyses of the 4-(4-halobenzylideneamino)TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidyl-1-oxyl) radicals 4-(4-fluorobenzylideneamino)-2,2,6,6-tetramethylpiperidyl-1-oxyl, 4-(4-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidyl-1-oxyl, 4-(4-bromobenzylideneamino)-2,2,6,6-tetramethylpiperidyl-1-oxyl and 4-(4-iodobenzylideneamino)-2,2,6,6-tetramethylpiperidyl-1-oxyl, and other 4-Ar-CH=N-TEMPO [Ar = 4-Ph-Ph, 2,2,6,6-tetramethyl-4-(4-phenylbenzylideneamino)piperidyl-1-oxyl, 4-Py, 2,2,6,6-tetramethyl-4-(4-pyridylmethylideneamino)piperidyl-1-oxyl, and 3,5-diCl-Ph, 4-(3,5-dichlorobenzylideneamino)-2,2,6,6-tetramethylpiperidyl-1-oxyl] radicals have been performed at room temperature. Some of these radicals show intermolecular ferromagnetic interactions at extremely low temperatures. X-ray analysis revealed that crystals of the 4-I-Ph derivative showed two modifications [(a) and (b)]; measurements of the magnetic properties of these crystals showed a ferromagnetic transition at an extremely low temperature for modification (a) and an antiferromagnetic interaction for modification (b). The structural features of these TEMPO radical crystals can be classified into three groups: (i) the crystal structures of the 4-Cl-Ph, 4-I-Ph(a) and 4-Ph-Ph derivatives, which show a ferromagnetic transition; (ii) the structures of the 4-Br-Ph and 4-Py derivatives, which show a ferromagnetic interaction ($\theta > 0$); (iii) miscellaneous: the antiferromagnetic 4-F-Ph and 4-I-Ph(b) derivatives ($\theta < 0$) and the ferromagnetic 3,5-diCl-Ph ($\theta > 0$) derivative. Sheet-like arrangements of O atoms and intra-sheet interactions through the CH₂ or CH₃ groups of the TEMPO rings are related to the mechanisms of the ferromagnetic interactions.

1. Introduction

Some 4-(arylmethyleneamino)TEMPO radicals (TEMPO = 2,2,6,6-tetramethylpiperidyl-1-oxyl) show intermolecular ferromagnetic interactions at extremely low temperatures (Ishida *et al.*, 1994, 1995; Nogami *et al.*,

1994, 1995; Nogami, Ishida, Yasui, Iwasaki, Iwamura *et al.* 1996; Togashi *et al.*, 1996). For the 4-(4-*X*-benzylideneamino)TEMPO radicals, an antiferromagnetic interaction ($\theta = -2.6$ K) is observed for (1) ($X = F$), a ferromagnetic transition ($T_c = 0.4$ K, $\theta = 0.7$ K) is observed for (2) ($X = Cl$) and a ferromagnetic interaction ($\theta = 0.5$ K) is observed for (3) ($X = Br$). X-ray analysis revealed that there are two modifications of crystals of the iodo derivative ($X = I$), (4a) and (4b). Measurements of the magnetic properties of these crystals showed a ferromagnetic transition ($T_c = 0.3$ K, $\theta = 0.7$ K) for (4a) and an antiferromagnetic interaction ($\theta = -0.2$ K) for (4b). X-ray crystal structure analyses were performed on these 4-(4-*X*-benzylideneamino)-TEMPO radicals and the 4-Ar-CH=N-TEMPO radicals Ar = 4-Ph-Ph [(5), $T_c = 0.4$ K, $\theta = 0.6$ K], 4-Py [(6), $\theta = 0.6$ K] and 3,5-diCl-Ph [(7), $\theta = 0.6$ K] at room temperature. Preliminary structures of some of these radicals have already been reported (Yasui *et al.*, 1996). In this paper we report the relationships between the structural features and magnetic interactions of these crystals, emphasizing the difference between the radicals showing ferromagnetic transitions and the other radicals.



- (1) Ar = 4-F-Ph
- (2) Ar = 4-Cl-Ph
- (3) Ar = 4-Br-Ph
- (4) Ar = 4-I-Ph
- (5) Ar = 4-Ph-Ph
- (6) Ar = 4-Py
- (7) Ar = 3,5-diCl-Ph

2. Experimental

Crystals of (1)–(7) for X-ray studies were grown from ethanol solutions. Crystal data and details of the data collections and structure refinements are given in Table 1. The intensity data were measured using either a

Rigaku AFC-5R or an AFC-7R diffractometer with a graphite monochromator. The positions of almost all H atoms were obtained from difference Fourier maps. The structures were refined by full-matrix least squares with anisotropic displacement factors for non-H atoms and isotropic displacement factors for H atoms.

The dihedral angle between two phenyl groups in (5), $5.1(4)^\circ$, shows that the biphenyl group is planar. The ORTEPII (Johnson, 1976) view of (5) in Fig. 1 shows that except for C(11), C(14), C(41) and C(44) the C atoms of the phenyl groups have large displacements perpendicular to the phenyl planes. With the exception

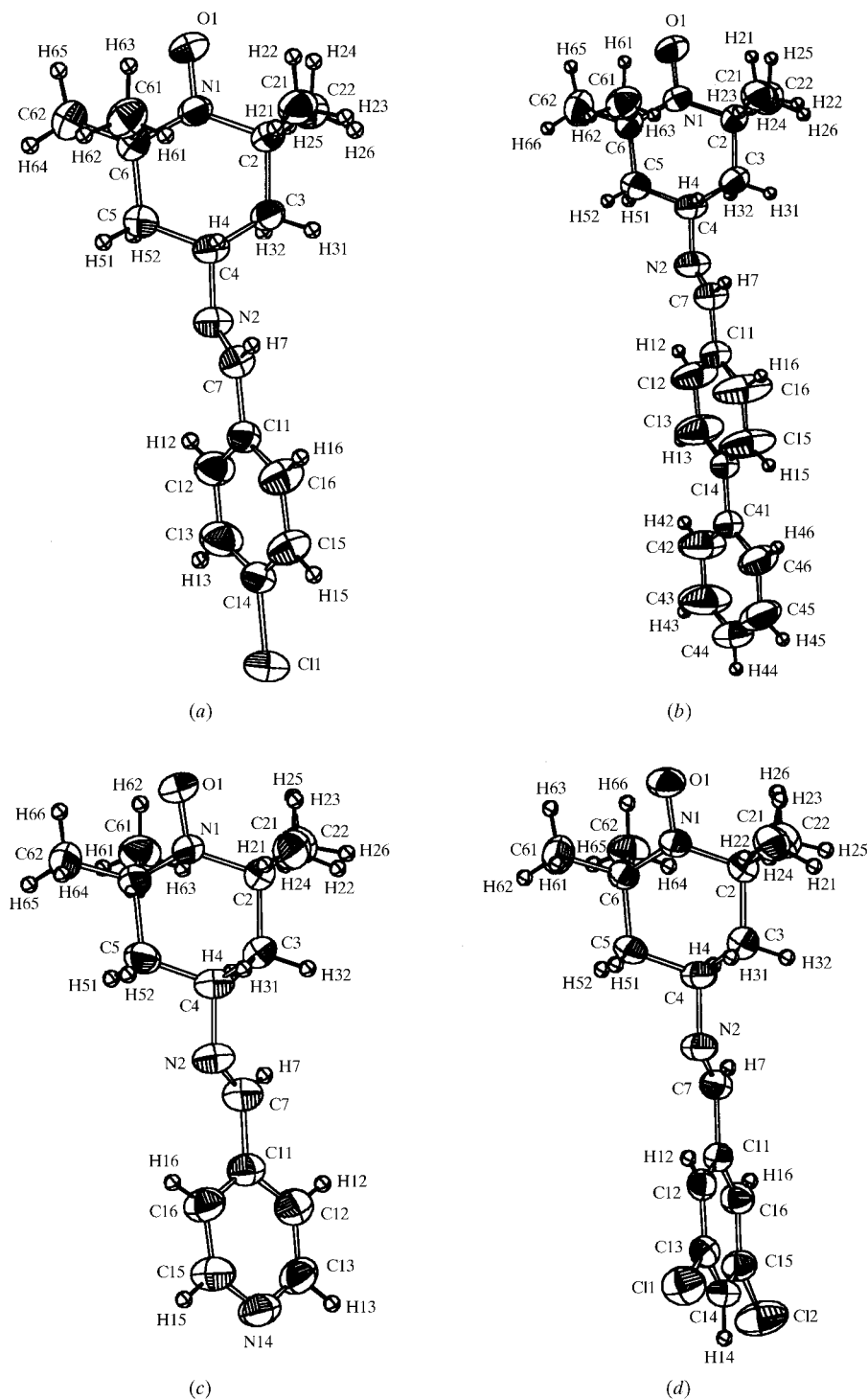


Fig. 1. ORTEPII (Johnson, 1976) drawings of the molecules with the atom-numbering schemes. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as spheres with radii of 0.1 Å. (a) (2), 4-Cl-Ph, (b) (5), 4-Ph-Ph, (c) (6), 4-Py, and (d) (7), 3,5-diCl-Ph.

Table 1. *Experimental details*

	(2)	(4a) (ferro)	(5)	(3)	(6)
Aryl group	4-Cl-Ph	4-I-Ph	4-Ph-Ph	4-Br-Ph	4-Py
Crystal data					
Chemical formula	C ₁₆ H ₂₂ ClN ₂ O	C ₁₆ H ₂₂ IN ₂ O	C ₂₂ H ₂₇ N ₂ O	C ₁₆ H ₂₂ BrN ₂ O	C ₁₅ H ₂₂ N ₃ O
Chemical formula weight	293.81	385.27	335.47	338.27	260.36
Weiss constant (K)	0.7	0.7	0.6	0.5	0.6
Magnetic transition point (K)	0.4	0.3	0.4	—	—
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> (Å)	5.8845 (19)	5.889 (4)	5.955 (1)	7.541 (1)	7.977 (6)
<i>b</i> (Å)	24.417 (2)	25.851 (3)	28.488 (5)	20.848 (3)	20.158 (7)
<i>c</i> (Å)	11.397 (2)	11.322 (3)	11.796 (2)	10.591 (1)	11.383 (9)
β (°)	104.09 (2)	105.27 (3)	106.72 (2)	91.56 (1)	125.95 (6)
<i>V</i> (Å ³)	1588.3 (6)	1662.7 (13)	1916.5 (6)	1664.4 (3)	1481 (1)
<i>Z</i>	4	4	4	4	4
<i>D</i> _x (Mg m ⁻³)	1.229	1.539	1.163	1.350	1.167
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	24	25	25	25
θ range (°)	12.7–17.2	12.7–16.1	13.9–17.5	13.1–17.3	14.3–17.3
μ (mm ⁻¹)	0.238	1.925	0.071	2.468	0.075
Temperature (K)	293	293	296	295	295
Crystal form	Prism	Plate	Prism	Prism	Prism
Crystal size (mm)	0.52 × 0.15 × 0.10	0.50 × 0.19 × 0.04	0.45 × 0.35 × 0.30	0.23 × 0.20 × 0.18	0.30 × 0.30 × 0.30
Crystal color	Orange	Orange	Orange	Orange	Orange
Data collection					
Diffractometer	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-7R
Data collection method	ω -2 θ scans	ω -2 θ scans	ω -2 θ scans	ω -2 θ scans	ω -2 θ scans
Absorption correction	Integration (Coppens <i>et al.</i> , 1965)	Analytical (de Meulenaer & Tompa, 1965)	None	Integration (Coppens <i>et al.</i> , 1965)	None
<i>T</i> _{min}	0.963	0.708	—	0.521	—
<i>T</i> _{max}	0.978	0.926	—	0.701	—
No. of measured reflections	3996	4201	4774	4102	3631
No. of independent reflections	3653	3843	4372	3822	3400
No. of observed reflections	2383	2469	2488	1867	2464
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.0177	0.0195	0.0325	0.035	0.0191
θ _{max} (°)	27.5	27.5	27.5	27.54	27.5
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 7 0 → <i>k</i> → 31 -14 → <i>l</i> → 14	0 → <i>h</i> → 7 0 → <i>k</i> → 33 -14 → <i>l</i> → 14	0 → <i>h</i> → 7 0 → <i>k</i> → 36 -15 → <i>l</i> → 14	0 → <i>h</i> → 9 0 → <i>k</i> → 27 -13 → <i>l</i> → 13	-10 → <i>h</i> → 0 -26 → <i>k</i> → 0 -11 → <i>l</i> → 14
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 100 reflections	Every 100 reflections	Every 150 reflections
Intensity decay (%)	-0.085	-0.35	-0.72	-1.84	-0.08
Refinement					
Refinement on <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>F</i> ² 0.0399	<i>F</i> ² 0.0329	<i>F</i> ² 0.0624	<i>F</i> ² 0.0462	<i>F</i> ² 0.0407
<i>wR</i> (<i>F</i> ²)	0.1186	0.0945	0.1817	0.0982	0.1204
<i>S</i>	0.993	0.992	0.981	0.970	1.001
No. of reflections used in refinement	3653	3843	4372	3822	3400

Table 1 (*cont.*)

	(2)	(4a) (ferro)	(5)	(3)	(6)
No. of parameters used	269	269	335	269	260
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.3805P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.8733P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.8294P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 0.7762P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.2298P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.002	0.194	0.001	0.001
$\Delta\rho_{\max}$ (e Å ⁻³)	0.164	0.410	0.286	0.225	0.148
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.232	-0.805	-0.254	-0.294	-0.190
Extinction method	None	None	SHELXL97 (Sheldrick, 1997)	None	None
Extinction coefficient	—	—	0.013 (2)	—	—
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs					
Data collection and cell refinement	<i>AFC Control Software</i> (Rigaku, 1994)	<i>AFC Control Software</i> (Rigaku, 1994)	<i>AFC Control Software</i> (Rigaku, 1990)	<i>AFC Control Software</i> (Rigaku, 1990)	<i>AFC Control Software</i> (Rigaku, 1994)
Data reduction	TEXSAN (Molecular Structure Corporation, 1992)	TEXSAN (Molecular Structure Corporation, 1992)	TEXSAN (Molecular Structure Corporation, 1992)	TEXSAN (Molecular Structure Corporation, 1992)	TEXSAN (Molecular Structure Corporation, 1992)
Structure solution	SIR88 (Burla <i>et al.</i> , 1989)	DIRDIF92 (Beurskens <i>et al.</i> , 1992)	SIR88 (Burla <i>et al.</i> , 1989)	DIRDIF92 (Beurskens <i>et al.</i> , 1992)	SAPI91 (Fan, 1991)
Structure refinement	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)
Molecular graphics	ORTEPII (Johnson, 1976)	ORTEPII (Johnson, 1976)	SHELXL97 (Sheldrick, 1997)	ORTEPII (Johnson, 1976)	ORTEPII (Johnson, 1976)
		(7)	(1)		(4b) (antiferro)
Aryl group		3,5-diCl-Ph	4-F-Ph		4-I-Ph
Crystal data					
Chemical formula		C ₁₆ H ₂₁ Cl ₂ N ₂ O	C ₁₆ H ₂₂ FN ₂ O		C ₁₆ H ₂₂ IN ₂ O
Chemical formula weight		328.26	277.36		385.27
Weiss constant (K)		0.6	-2.6		-0.2
Magnetic transition point (K)		—	—		—
Cell setting		Orthorhombic	Orthorhombic		Monoclinic
Space group		<i>Pbca</i>	<i>Pbca</i>		<i>P2₁/c</i>
<i>a</i> (Å)		14.035 (3)	20.0097 (13)		10.980 (4)
<i>b</i> (Å)		22.964 (3)	15.249 (2)		38.914 (4)
<i>c</i> (Å)		10.710 (2)	10.4168 (18)		8.358 (4)
β (°)		90	90		103.88 (3)
<i>V</i> (Å ³)		3451.9 (9)	3178.4 (8)		3466 (1)
<i>Z</i>		8	8		8
<i>D_x</i> (Mg m ⁻³)		1.263	1.159		1.476
Radiation type		Mo <i>K</i> α	Mo <i>K</i> α		Mo <i>K</i> α
Wavelength (Å)		0.71073	0.71073		0.71073
No. of reflections for cell parameters		25	24		25
θ range (°)		14.1–17.8	12.9–17.0		17.0–17.5
μ (mm ⁻¹)		0.376	0.081		1.847
Temperature (K)		295	296 (2)		295
Crystal form		Prism	Prism		Prism
Crystal size (mm)		0.40 × 0.20 × 0.20	0.40 × 0.30 × 0.20		0.30 × 0.27 × 0.15
Crystal color		Orange	Orange		Orange

Table 1 (*cont.*)

	(7)	(1)	(4b) (antiferro)
Data collection			
Diffractionmeter	Rigaku AFC-5R	Rigaku AFC-7R	Rigaku AFC-7R
Data collection method	ω -2 θ scans	ω -2 θ scans	ω -2 θ scans
Absorption correction	Integration (Coppens <i>et al.</i> , 1965)	ψ scans (North <i>et al.</i> , 1968)	ψ scans (North <i>et al.</i> , 1968)
T_{\min}	0.927	0.993	0.828
T_{\max}	0.934	0.999	0.999
No. of measured reflections	4927	3647	8478
No. of independent reflections	3959	3647	7950
No. of observed reflections	2128	1948	5046
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0281	—	0.0215
θ_{max} (°)	27.5	27.5	27.5
Range of h, k, l	-1 \rightarrow h \rightarrow 18 -1 \rightarrow k \rightarrow 29 -1 \rightarrow l \rightarrow 13	0 \rightarrow h \rightarrow 26 0 \rightarrow k \rightarrow 19 -13 \rightarrow l \rightarrow 0	-14 \rightarrow h \rightarrow 13 -50 \rightarrow k \rightarrow 0 0 \rightarrow l \rightarrow 10
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 150 reflections	Every 150 reflections
Intensity decay (%)	-0.42	-0.3	-4.14
Refinement			
Refinement on $R[F^2 > 2\sigma(F^2)]$	F^2 0.0491	F^2 0.0425	F^2 0.0370
$wR(F^2)$	0.1233	0.1397	0.1070
S	0.996	0.989	1.029
No. of reflections used in refinement	3959	3647	7950
No. of parameters used	274	269	441
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	H atoms treated by a mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 2.0600P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.2539P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 3.3418P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.001	0.005	0.004
$\Delta\rho_{\text{max}}$ (e \AA^{-3})	0.371	0.106	0.385
$\Delta\rho_{\text{min}}$ (e \AA^{-3})	-0.276	-0.197	-0.362
Extinction method	None	None	None
Extinction coefficient	—	—	—
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection and cell refinement	<i>AFC Control Software</i> (Rigaku, 1990)	<i>AFC Control Software</i> (Rigaku, 1994)	<i>AFC Control Software</i> (Rigaku, 1994)
Data reduction	<i>TEXSAN</i> (Molecular Structure Corporation, 1992)	<i>TEXSAN</i> (Molecular Structure Corporation, 1992)	<i>TEXSAN</i> (Molecular Structure Corporation, 1992)

Table 1 (*cont.*)

	(7)	(1)	(4b) (antiferro)
Structure solution	SIR88 (Burla <i>et al.</i> , 1989)	SAPI91 (Fan, 1991)	DIRDIF92 (Beurskens <i>et al.</i> , 1992)
Structure refinement	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)
Molecular graphics	ORTEPII (Johnson, 1976)	ORTEPII (Johnson, 1976)	ORTEPII (Johnson, 1976)

of those parallel to the long axis of the biphenyl group, the C—C bond lengths are shorter than the normal C—C bond length for a phenyl group. These facts mean that the two phenyl groups show dynamical disorder around the long axis of the biphenyl group. Analysis of the disordered structure failed because of strong parameter interactions.

Final atomic parameters are given in Table 2.†

3. Results and discussion

3.1. Crystal structures

The molecular structures of (2), (5), (6) and (7) with the atomic numbering are shown in Fig. 1. Structural features of these crystals can be classified into three groups as shown from the crystal data (Table 1): (i) the crystal structures of (2) (Ar = 4-Cl-Ph), (4a) (Ar = 4-I-Ph) and (5) (Ar = 4-Ph-Ph), which are isostructural with each other and show a ferromagnetic transition; (ii) the crystal structures of (3) (Ar = 4-Br-Ph) and (6) (Ar = 4-Py) showing a ferromagnetic interaction ($\theta > 0$); (iii) others including antiferromagnetic (1) (Ar = 4-F-Ph, $\theta < 0$) and (4b) (Ar = 4-I-Ph, $\theta < 0$) and ferromagnetic (7) (Ar = 3,5-diCl-Ph, $\theta > 0$).

The crystal structure of (2) is shown in Fig. 2. (4a) and (5) are isostructural with (2). All these crystals show a ferromagnetic transition at extremely low temperatures. The O atoms in these crystals are arranged to form a pleated sheet parallel to the *ac* plane. The nearest O···O distance in a sheet in (2) is 5.8845 (19) Å for O(1)···O(1)($x - 1, y, z$), which corresponds to the length of the *a* axis. The second nearest O···O distance is 5.9437 (13) Å for O(1)···O(1)($x, \frac{1}{2} - y, \frac{1}{2} + z$). These O···O distances are too long for a direct spin-spin interaction. Within the sheet, O atoms show contacts with the H atoms of the CH₂ or CH₃ groups of the neighboring TEMPO rings with van der Waals distances as shown in Table 3. The ferromagnetic interactions are considered to be transferred through O···H van der Waals interactions with these β -H atoms (Nogami *et al.*, 1995; Nogami, Ishida, Yasui, Iwasaki, Iwamura *et al.*, 1996; Nogami, Ishida, Yasui, Iwasaki, Takeda *et al.*, 1996). Between sheets, the aryl groups of each sheet

stack alternately face-to-face as shown in Fig. 3. The distance between the phenyl planes is 3.673 (3) Å. The corresponding dimensions for (4a) and (5) are listed in Table 3. In these crystals, two-dimensional O···O interactions through the β -H atoms of CH₂ or CH₃ groups and overlap of the aryl groups may be essential for the ferromagnetic interaction.

The crystal structure of (3) (X = Br) is shown in Fig. 4. The crystals of (3) have the same space group as (2), although the *a* axis is longer than that of (2) and *vice versa* for the *b* axis. A characteristic sheet structure and overlap of the aryl groups are also observed in (3). The O···O distances within the sheet are 7.541 (1) and 5.996 (2) Å for O(1)···O(1)($x - 1, y, z$) and O(1)···O(1)($x, \frac{1}{2} - y, \frac{1}{2} + z$), respectively, which are longer than those of (2). The distance between the phenyl planes is 3.638 (5) Å. Fig. 5 shows a comparison of the intra-sheet relationships of (2) and (3). The interactions within the sheet *via* the β -H atoms are weaker than those of (2) as shown in Fig. 5 and Table 3. This is considered to be the reason why (2) and (4a) show ferromagnetic transitions, while (3) shows only a ferromagnetic interaction. However, an important question remains as to why the crystal structure of the 4-Br-Ph derivative (3) is so different from those of the 4-Cl-Ph (2) and 4-I-Ph (4) derivatives. In (3), an intermolecular Br(1)···Br(1)($-x, -y, -z - 1$) contact

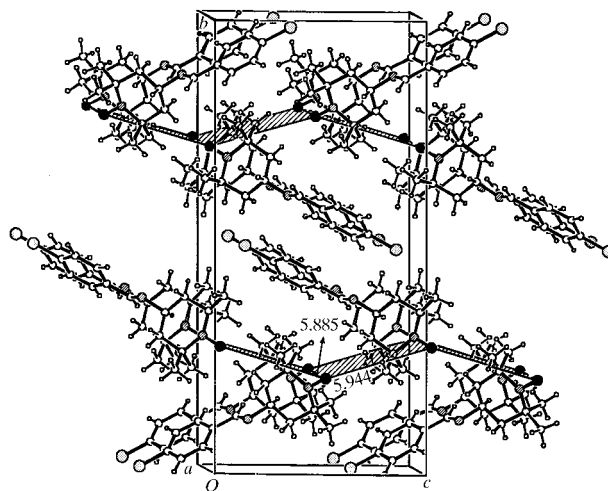


Fig. 2. A perspective view of the crystal structure of (2), 4-Cl-Ph.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA0019). Services for accessing these data are described at the back of the journal.

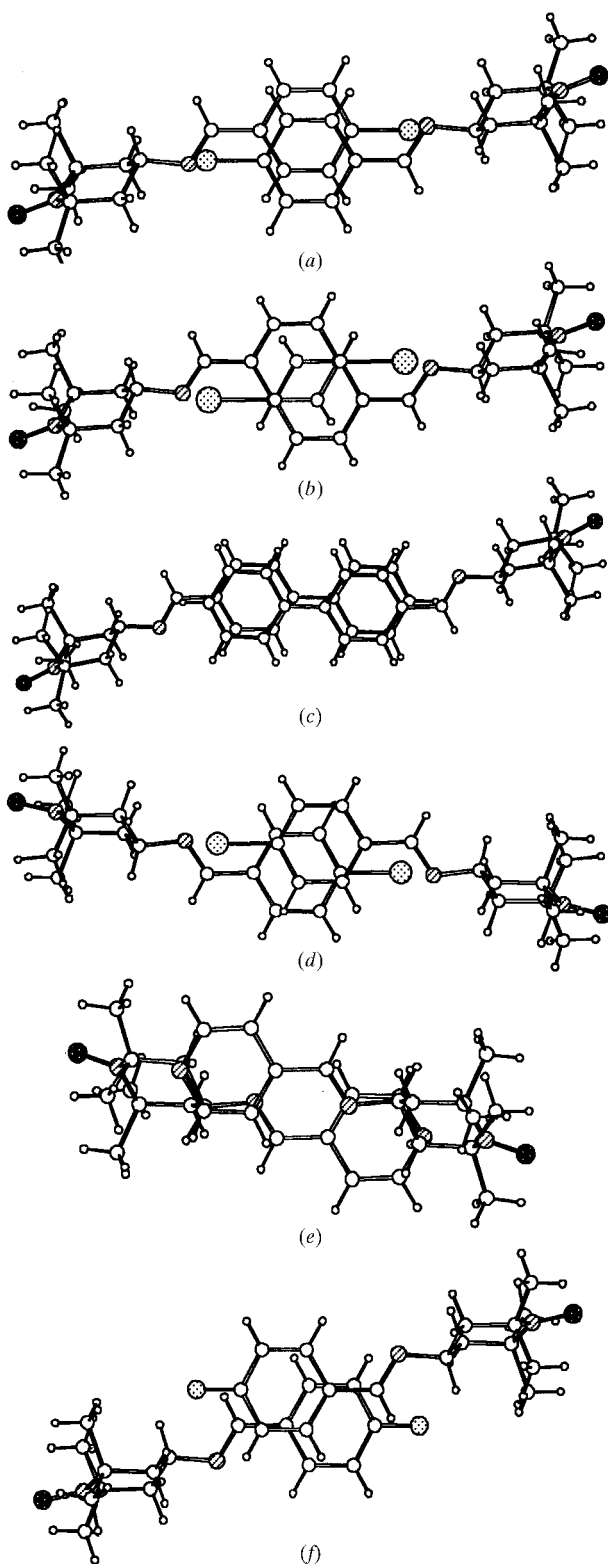


Fig. 3. Overlap of the molecules of (a) (2), 4-Cl-Ph, (b) (4a), 4-I-Ph, (c) (5), 4-Ph-Ph, (d) (3), 4-Br-Ph, (e) (6), 4-Py, and (f) (1), 4-F-Ph.

[3.684 (1) Å], shorter than the van der Waals contact (3.9 Å), is observed. For (2) and (4a), intermolecular Cl···Cl and I···I distances are 4.303 (1) and 4.052 (1) Å, respectively. The I···I contact is also shorter than the van der Waals contact (4.3 Å). The overlapping modes of the parallel phenyl groups of (2), (3) and (4a) are slightly different from each other, so as to avoid close contacts between the halogen atoms and the —CH=N— groups. The halogen···N(2) distances are 3.893 (2), 4.119 (3) and 4.115 (3) Å for (2), (3) and (4a), respectively, and the halogen···C(7) distances are 3.777 (2), 3.900 (4) and 3.966 (4) Å for (2), (3) and (4a), respectively. These relationships between the halogen atoms and the —CH=N— groups may correspond to the structural modes of these crystals, although it is very difficult to treat the construction of crystal structures quantitatively.

Crystals of (6), which also show a ferromagnetic interaction, are pseudo-isomorphous with those of (3). The sheet-like arrangement of the O atoms and the stacking of the aryl groups are also observed in (6). The O···O distances within the sheet are 7.977 (6) and 5.963 (4) Å for O(1)···O(1)(x - 1, y, z) and O(1)···O(1)(x, $\frac{1}{2} - y, \frac{1}{2} + z$), respectively. In the sheet, the arrangement of the molecules related by the *c* glide plane is very similar to that of (3), although the network is distorted from a rectangle, reflecting the difference of the β angles as shown in Fig. 6. The overlapping mode of the aryl groups between sheets is different from that of (3) as shown in Fig. 3. The molecular conformation of (6) is slightly different from that of (3) as presented in §3.2.

The crystal structure of (1) (X = F) shown in Fig. 7 is quite different from those of the other 4-halo-aryl derivatives, while the O atoms are also arranged to form a two-dimensional zigzag network. The shortest O···O

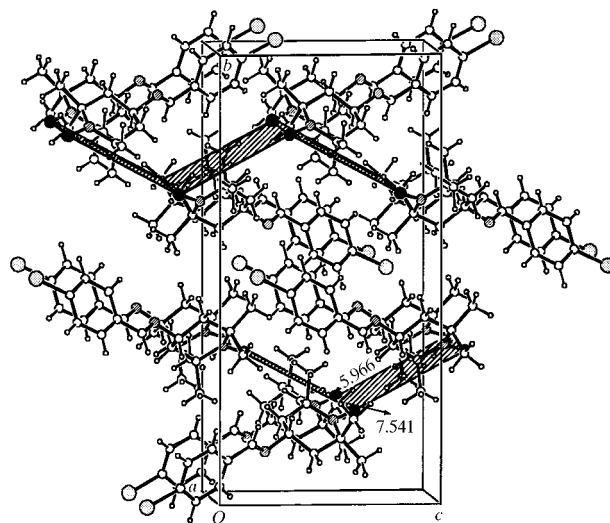


Fig. 4. A perspective view of the crystal structure of (3), 4-Br-Ph.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
(1) (Ar = 4-F-Ph)				
F(1)	-0.07687 (7)	0.18277 (9)	-0.22964 (12)	0.0977 (4)
O(1)	0.21003 (8)	0.01944 (10)	0.73277 (13)	0.0896 (5)
N(1)	0.18047 (7)	0.03940 (9)	0.62714 (13)	0.0592 (4)
N(2)	0.08721 (7)	0.10207 (11)	0.27581 (14)	0.0661 (4)
C(2)	0.20017 (9)	0.12437 (11)	0.56772 (16)	0.0590 (4)
C(3)	0.15145 (11)	0.14760 (12)	0.46079 (18)	0.0625 (5)
C(4)	0.13569 (9)	0.07210 (12)	0.37212 (16)	0.0583 (4)
C(5)	0.10388 (10)	0.00026 (13)	0.45138 (18)	0.0612 (5)
C(6)	0.14878 (9)	-0.03535 (10)	0.55699 (15)	0.0571 (4)
C(7)	0.09967 (9)	0.08762 (12)	0.15986 (17)	0.0598 (4)
C(11)	0.05404 (9)	0.11417 (11)	0.05609 (16)	0.0568 (4)
C(12)	-0.00342 (9)	0.16124 (12)	0.08352 (19)	0.0641 (5)
C(13)	-0.04745 (10)	0.18428 (14)	-0.0121 (2)	0.0709 (5)
C(14)	-0.03296 (10)	0.16035 (13)	-0.13430 (19)	0.0689 (5)
C(15)	0.02302 (13)	0.11541 (16)	-0.1664 (2)	0.0851 (6)
C(16)	0.06681 (11)	0.09242 (16)	-0.06965 (19)	0.0778 (6)
C(21)	0.19703 (17)	0.19394 (16)	0.6735 (3)	0.0841 (7)
C(22)	0.27175 (11)	0.11717 (18)	0.5171 (3)	0.0800 (6)
C(61)	0.20363 (13)	-0.09445 (15)	0.5031 (3)	0.0755 (6)
C(62)	0.10709 (15)	-0.08643 (17)	0.6540 (2)	0.0819 (6)
(2) (Ar = 4-Cl-Ph)				
Cl(1)	0.44430 (12)	0.00565 (2)	-0.32069 (5)	0.0765 (2)
O(1)	-0.2174 (3)	0.21540 (6)	0.50610 (12)	0.0602 (4)
N(1)	-0.1091 (2)	0.19397 (6)	0.43244 (12)	0.0425 (3)
N(2)	0.1741 (3)	0.11743 (6)	0.16952 (13)	0.0472 (4)
C(2)	-0.0536 (3)	0.23162 (7)	0.33992 (15)	0.0437 (4)
C(3)	0.0055 (3)	0.19770 (7)	0.23834 (15)	0.0437 (4)
C(4)	0.1674 (3)	0.14925 (7)	0.27834 (15)	0.0425 (4)
C(5)	0.0656 (4)	0.11284 (8)	0.36107 (17)	0.0477 (4)
C(6)	0.0208 (3)	0.14195 (8)	0.47216 (15)	0.0461 (4)
C(7)	0.3553 (3)	0.11993 (8)	0.13015 (15)	0.0440 (4)
C(11)	0.3763 (3)	0.09147 (7)	0.01895 (15)	0.0421 (4)
C(12)	0.2109 (4)	0.05370 (8)	-0.03742 (19)	0.0559 (5)
C(13)	0.2299 (4)	0.02727 (9)	-0.1417 (2)	0.0634 (6)
C(14)	0.4162 (4)	0.03928 (7)	-0.18984 (16)	0.0496 (4)
C(15)	0.5824 (4)	0.07696 (10)	-0.13745 (18)	0.0592 (5)
C(16)	0.5622 (4)	0.10271 (10)	-0.03214 (18)	0.0582 (5)
C(21)	0.1489 (4)	0.26969 (10)	0.4004 (2)	0.0601 (6)
C(22)	-0.2722 (4)	0.26557 (10)	0.2880 (2)	0.0593 (5)
C(61)	0.2493 (4)	0.15481 (11)	0.56646 (19)	0.0615 (6)
C(62)	-0.1350 (5)	0.10608 (10)	0.5300 (2)	0.0615 (6)
(3) (Ar = 4-Br-Ph)				
Br(1)	0.04002 (6)	-0.00432 (3)	-0.32787 (4)	0.07052 (18)
O(1)	0.7671 (3)	0.18407 (12)	0.6672 (2)	0.0582 (7)
N(1)	0.6809 (4)	0.16653 (13)	0.5667 (2)	0.0420 (7)
N(2)	0.4062 (4)	0.10603 (15)	0.2352 (3)	0.0528 (9)
C(2)	0.7232 (5)	0.20214 (17)	0.4497 (3)	0.0429 (9)
C(3)	0.6424 (6)	0.1681 (2)	0.3340 (4)	0.0499 (11)
C(4)	0.4557 (6)	0.14357 (19)	0.3488 (3)	0.0464 (10)
C(5)	0.4533 (6)	0.0993 (2)	0.4618 (4)	0.0498 (10)
C(6)	0.5125 (5)	0.13049 (18)	0.5865 (3)	0.0445 (9)
C(7)	0.2773 (5)	0.1257 (2)	0.1683 (3)	0.0478 (10)
C(11)	0.2172 (4)	0.09224 (18)	0.0517 (3)	0.0416 (9)
C(12)	0.0957 (6)	0.1218 (2)	-0.0298 (4)	0.0564 (11)
C(13)	0.0412 (6)	0.0932 (2)	-0.1429 (4)	0.0558 (11)
C(14)	0.1084 (5)	0.03442 (19)	-0.1713 (3)	0.0450 (9)
C(15)	0.2255 (5)	0.0026 (2)	-0.0916 (3)	0.0502 (9)
C(16)	0.2797 (5)	0.03280 (19)	0.0195 (3)	0.0466 (10)
C(21)	0.9252 (7)	0.2028 (3)	0.4394 (5)	0.0660 (13)
C(22)	0.6520 (7)	0.2709 (2)	0.4599 (4)	0.0580 (12)
C(61)	0.3741 (7)	0.1770 (3)	0.6343 (5)	0.0616 (12)
C(62)	0.5501 (8)	0.0791 (2)	0.6850 (5)	0.0636 (13)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
<i>(4a)</i> (Ar = 4-I-Ph)				
I(1)	0.45126 (7)	0.004363 (10)	−0.32970 (2)	0.07079 (13)
O(1)	−0.2183 (5)	0.21731 (10)	0.5145 (2)	0.0585 (7)
N(1)	−0.1104 (5)	0.19722 (10)	0.4410 (2)	0.0396 (6)
N(2)	0.1662 (5)	0.12361 (12)	0.1779 (3)	0.0497 (7)
C(2)	−0.0545 (6)	0.23247 (13)	0.3482 (3)	0.0430 (7)
C(3)	−0.0005 (7)	0.20025 (14)	0.2456 (3)	0.0446 (8)
C(4)	0.1610 (7)	0.15434 (14)	0.2874 (3)	0.0436 (8)
C(5)	0.0622 (7)	0.12052 (14)	0.3706 (3)	0.0465 (8)
C(6)	0.0205 (6)	0.14798 (13)	0.4821 (3)	0.0437 (8)
C(7)	0.3460 (7)	0.12450 (15)	0.1413 (3)	0.0483 (8)
C(11)	0.3692 (6)	0.09610 (14)	0.0320 (3)	0.0448 (8)
C(12)	0.2093 (8)	0.05855 (17)	−0.0219 (4)	0.0594 (10)
C(13)	0.2309 (8)	0.03243 (18)	−0.1257 (4)	0.0627 (11)
C(14)	0.4139 (7)	0.04436 (13)	−0.1744 (3)	0.0477 (8)
C(15)	0.5738 (8)	0.08174 (18)	−0.1235 (4)	0.0603 (10)
C(16)	0.5511 (8)	0.10713 (18)	−0.0197 (4)	0.0620 (11)
C(21)	0.1498 (10)	0.26798 (18)	0.4090 (4)	0.0606 (11)
C(22)	−0.2755 (9)	0.26510 (18)	0.2949 (4)	0.0619 (11)
C(61)	0.2487 (8)	0.1601 (2)	0.5784 (4)	0.0597 (10)
C(62)	−0.1361 (9)	0.11420 (17)	0.5396 (4)	0.0593 (11)
<i>(4b)</i> (Ar = 4-I-Ph)				
I(1A)	1.07330 (3)	0.188609 (8)	−0.17483 (4)	0.06813 (11)
O(1A)	0.2750 (3)	0.16431 (10)	0.6753 (4)	0.0859 (11)
N(1A)	0.3581 (3)	0.17027 (9)	0.5950 (4)	0.0582 (9)
N(2A)	0.6328 (4)	0.18288 (9)	0.3200 (5)	0.0643 (10)
C(2A)	0.3137 (4)	0.18603 (12)	0.4301 (6)	0.0621 (11)
C(3A)	0.4137 (5)	0.18174 (15)	0.3346 (7)	0.0637 (12)
C(4A)	0.5473 (4)	0.19049 (12)	0.4285 (6)	0.0613 (11)
C(5A)	0.5791 (4)	0.16798 (13)	0.5798 (7)	0.0619 (12)
C(6A)	0.4911 (4)	0.17099 (12)	0.6956 (6)	0.0609 (11)
C(7A)	0.6988 (5)	0.20582 (14)	0.2923 (6)	0.0609 (12)
C(11A)	0.7877 (4)	0.20194 (11)	0.1866 (5)	0.0525 (9)
C(12A)	0.8089 (4)	0.16985 (11)	0.1240 (6)	0.0595 (11)
C(13A)	0.8872 (4)	0.16612 (11)	0.0185 (6)	0.0581 (10)
C(14A)	0.9484 (4)	0.19496 (11)	−0.0216 (5)	0.0554 (10)
C(15A)	0.9309 (5)	0.22697 (12)	0.0408 (6)	0.0589 (11)
C(16A)	0.8507 (4)	0.23044 (12)	0.1434 (6)	0.0588 (11)
C(21A)	0.2818 (6)	0.22373 (15)	0.4509 (8)	0.0918 (18)
C(22A)	0.1961 (5)	0.16612 (18)	0.3428 (7)	0.0934 (18)
C(61A)	0.5130 (6)	0.20386 (15)	0.7975 (7)	0.0906 (17)
C(62A)	0.5095 (5)	0.13973 (15)	0.8101 (7)	0.0827 (15)
<i>(4c)</i> (Ar = 4-I-Ph)				
I(1B)	0.73229 (3)	0.063140 (8)	0.04373 (4)	0.07281 (11)
O(1B)	−0.0794 (3)	0.08687 (10)	0.8680 (5)	0.0879 (11)
N(1B)	0.0055 (3)	0.08162 (9)	0.7883 (5)	0.0584 (9)
N(2B)	0.2829 (4)	0.06509 (10)	0.5236 (6)	0.0712 (11)
C(2B)	0.1309 (5)	0.06987 (11)	0.8887 (6)	0.0650 (12)
C(3B)	0.2267 (4)	0.07301 (13)	0.7885 (7)	0.0662 (12)
C(4B)	0.1847 (4)	0.05903 (12)	0.6126 (7)	0.0661 (12)
C(5B)	0.0688 (5)	0.07902 (14)	0.5272 (7)	0.0673 (12)
C(6B)	−0.0401 (4)	0.07675 (12)	0.6080 (6)	0.0624 (11)
C(7B)	0.3240 (4)	0.04092 (13)	0.4585 (6)	0.0622 (11)
C(11B)	0.4205 (4)	0.04540 (11)	0.3647 (6)	0.0566 (10)
C(12B)	0.4691 (4)	0.07771 (12)	0.3499 (6)	0.0640 (12)
C(13B)	0.5574 (4)	0.08276 (13)	0.2593 (7)	0.0646 (12)
C(14B)	0.5987 (4)	0.05483 (11)	0.1824 (5)	0.0580 (10)
C(15B)	0.5514 (5)	0.02231 (12)	0.1987 (6)	0.0642 (12)
C(16B)	0.4638 (5)	0.01787 (12)	0.2890 (6)	0.0634 (12)
C(21B)	0.1176 (6)	0.03273 (14)	0.9472 (8)	0.0942 (18)
C(22B)	0.1651 (6)	0.09340 (15)	1.0399 (7)	0.0870 (16)
C(61B)	−0.1091 (5)	0.04208 (14)	0.5752 (8)	0.0871 (17)
C(62B)	−0.1329 (5)	0.10603 (15)	0.5407 (8)	0.0918 (17)

Table 2 (cont.)

	x	y	z	U_{eq}
(5) (Ar = 4-Ph-Ph)				
O(1)	-0.2026 (3)	0.22330 (7)	0.61910 (15)	0.0714 (6)
N(1)	-0.0943 (3)	0.20482 (7)	0.55047 (15)	0.0492 (5)
N(2)	0.1857 (4)	0.13859 (8)	0.30386 (17)	0.0607 (6)
C(2)	-0.0380 (4)	0.23685 (8)	0.46225 (19)	0.0526 (6)
C(3)	0.0168 (5)	0.20741 (9)	0.3655 (2)	0.0536 (6)
C(4)	0.1819 (4)	0.16641 (8)	0.4082 (2)	0.0516 (6)
C(5)	0.0833 (5)	0.13554 (9)	0.4874 (2)	0.0569 (6)
C(6)	0.0346 (4)	0.16040 (8)	0.59225 (19)	0.0522 (6)
C(7)	0.3585 (5)	0.13943 (9)	0.2654 (2)	0.0568 (6)
C(11)	0.3634 (4)	0.11384 (8)	0.1576 (2)	0.0518 (6)
C(12)	0.1862 (6)	0.08486 (13)	0.1029 (3)	0.0941 (12)
C(13)	0.1850 (7)	0.06131 (14)	0.0009 (3)	0.1019 (13)
C(14)	0.3603 (4)	0.06534 (8)	-0.05117 (19)	0.0517 (6)
C(15)	0.5345 (6)	0.09551 (16)	0.0024 (3)	0.1100 (15)
C(16)	0.5377 (6)	0.11921 (17)	0.1053 (3)	0.1160 (17)
C(21)	0.1670 (6)	0.26881 (11)	0.5243 (3)	0.0734 (9)
C(22)	-0.2572 (7)	0.26630 (13)	0.4070 (3)	0.0764 (9)
C(41)	0.3546 (5)	0.03879 (8)	-0.1609 (2)	0.0564 (6)
C(42)	0.1828 (7)	0.00671 (14)	-0.2074 (3)	0.1034 (13)
C(43)	0.1731 (9)	-0.01843 (17)	-0.3096 (4)	0.1279 (18)
C(44)	0.3387 (8)	-0.01204 (14)	-0.3654 (3)	0.0967 (12)
C(45)	0.5088 (8)	0.02003 (15)	-0.3224 (3)	0.0996 (12)
C(46)	0.5178 (6)	0.04565 (12)	-0.2207 (3)	0.0829 (9)
C(61)	0.2610 (6)	0.17127 (14)	0.6900 (3)	0.0719 (8)
C(62)	-0.1236 (7)	0.12947 (12)	0.6428 (3)	0.0755 (8)
(6) (Ar = 4-Py)				
O(1)	0.66692 (17)	0.20588 (5)	0.68638 (10)	0.0614 (3)
N(1)	0.57579 (17)	0.18079 (5)	0.55966 (10)	0.0426 (2)
N(2)	0.32248 (19)	0.08646 (6)	0.15827 (12)	0.0556 (3)
N(14)	0.1225 (2)	-0.02359 (7)	-0.30557 (13)	0.0618 (3)
C(2)	0.5925 (2)	0.21876 (6)	0.45395 (13)	0.0449 (3)
C(3)	0.5402 (2)	0.17283 (7)	0.32952 (14)	0.0486 (3)
C(4)	0.3435 (2)	0.13250 (7)	0.26638 (14)	0.0494 (3)
C(5)	0.3671 (3)	0.09152 (7)	0.38637 (17)	0.0533 (3)
C(6)	0.4072 (2)	0.13205 (6)	0.51462 (14)	0.0476 (3)
C(7)	0.1824 (2)	0.09644 (8)	0.02753 (16)	0.0546 (3)
C(11)	0.1579 (2)	0.05324 (7)	-0.08720 (14)	0.0500 (3)
C(12)	0.0459 (2)	0.07502 (8)	-0.22893 (16)	0.0596 (4)
C(13)	0.0340 (3)	0.03546 (9)	-0.33276 (16)	0.0623 (4)
C(15)	0.2279 (3)	-0.04471 (9)	-0.16901 (17)	0.0645 (4)
C(16)	0.2495 (2)	-0.00854 (8)	-0.05737 (16)	0.0594 (4)
C(21)	0.8150 (3)	0.24249 (10)	0.5323 (2)	0.0655 (4)
C(22)	0.4489 (3)	0.27924 (8)	0.40051 (19)	0.0627 (4)
C(61)	0.2127 (3)	0.16838 (9)	0.4769 (2)	0.0613 (4)
C(62)	0.4821 (4)	0.08522 (8)	0.6422 (2)	0.0661 (4)
(7) (Ar = 3,5-diCl-Ph)				
Cl(1)	0.12604 (6)	-0.04521 (4)	-0.28124 (8)	0.0682 (3)
Cl(2)	0.43007 (6)	0.08783 (4)	-0.37751 (9)	0.0791 (3)
O(1)	-0.03302 (16)	0.19379 (9)	0.49966 (17)	0.0579 (6)
N(1)	0.01245 (16)	0.17800 (10)	0.40146 (19)	0.0418 (6)
N(2)	0.14398 (17)	0.11600 (11)	0.0744 (2)	0.0487 (6)
C(2)	0.09738 (19)	0.14025 (13)	0.4217 (2)	0.0463 (7)
C(3)	0.1249 (3)	0.11150 (15)	0.2979 (3)	0.0499 (8)
C(4)	0.1265 (2)	0.15156 (13)	0.1858 (3)	0.0454 (7)
C(5)	0.0294 (2)	0.17977 (14)	0.1728 (3)	0.0428 (7)
C(6)	-0.00257 (19)	0.21422 (12)	0.2875 (2)	0.0416 (7)
C(7)	0.2145 (2)	0.12751 (13)	0.0064 (3)	0.0435 (7)
C(11)	0.23550 (18)	0.09205 (12)	-0.1052 (2)	0.0386 (6)
C(12)	0.1775 (2)	0.04533 (12)	-0.1372 (3)	0.0402 (6)
C(13)	0.19897 (19)	0.01287 (12)	-0.2410 (2)	0.0417 (6)
C(14)	0.2769 (2)	0.02516 (13)	-0.3152 (3)	0.0446 (7)
C(15)	0.3332 (2)	0.07152 (13)	-0.2828 (3)	0.0457 (7)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(16)	0.3141 (2)	0.10468 (14)	-0.1787 (3)	0.0454 (7)
C(21)	0.0687 (3)	0.09282 (18)	0.5143 (3)	0.0652 (10)
C(22)	0.1794 (3)	0.1764 (2)	0.4747 (4)	0.0669 (11)
C(61)	-0.1084 (2)	0.22702 (19)	0.2764 (4)	0.0610 (9)
C(62)	0.0523 (3)	0.27139 (15)	0.2998 (3)	0.0580 (9)

Table 3. Selected intermolecular distances (Å) to the O radical atoms

	(2)	(4a)	(5)	(3)	(6)
Ar	4-Cl-Ph	4-I-Ph	4-Ph-Ph	4-Br-Ph	4-Py
O(1)···O(1 ⁱ)	5.8845 (19)	5.889 (4)	5.955 (1)	7.541 (1)	7.977 (6)
O(1)···O(1 ⁱⁱ)	5.9437 (13)	5.908 (2)	6.0910 (13)	5.966 (2)	5.963 (4)
O(1)···O(1 ⁱⁱⁱ)					6.774 (7)
O(1)···C(22 ⁱⁱ)	3.339 (3)	3.310 (5)	3.516 (4)	3.376 (5)	
O(1)···C(3 ⁱⁱ)	3.397 (2)	3.356 (5)	3.445 (3)	3.687 (5)	3.404 (2)
O(1)···C(21 ⁱⁱ)					3.539 (4)
O(1)···H(61 ⁱ)	2.72 (2)	2.81 (4)	2.85 (3)		
O(1)···H(21 ⁱ)	2.87 (3)	2.89 (6)	2.81 (3)		
O(1)···H(26 ⁱⁱ)	2.54 (3)	2.44 (5)	2.70 (3)	2.49 (4)	
O(1)···H(22 ⁱⁱ)					2.67 (2)
O(1)···H(31 ⁱⁱⁱ)	2.83 (2)	2.71 (4)	2.83 (3)		
O(1)···H(32 ⁱⁱⁱ)				2.78 (3)	2.51 (2)
Ph···Ph ^{iv}	3.673 (3)	3.789 (6)	3.869 (6)	3.638 (5)	3.854 (5)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x + 1, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, -y, -z$ for (2), (4a) and (5), $-x, -y, -z$ for (3) and (6).

	(1)	(7)
Ar	4-F-Ph	3,5-diCl-Ph
O(1)···O(1 ⁱ)	5.4806 (14)	5.945 (2)
O(1)···O(1 ⁱⁱ)	7.7904 (14)	7.477 (2)
O(1)···C(61 ⁱ)	3.496 (3)	3.522 (5)
O(1)···H(61 ⁱ)	2.53 (3)	3.554 (4)
O(1)···H(24 ⁱ)	2.69 (3)	2.72 (3)
O(1)···H(4 ⁱ)	2.70 (2)	2.71 (3)
		O(1)···O(1 ⁱⁱⁱ)
		O(1)···O(1 ^{iv})
		O(1)···C(62 ⁱⁱⁱ)
		O(1)···C(5 ⁱⁱⁱ)
		O(1)···H(65 ⁱⁱⁱ)
		O(1)···H(52 ⁱⁱⁱ)

Symmetry codes: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

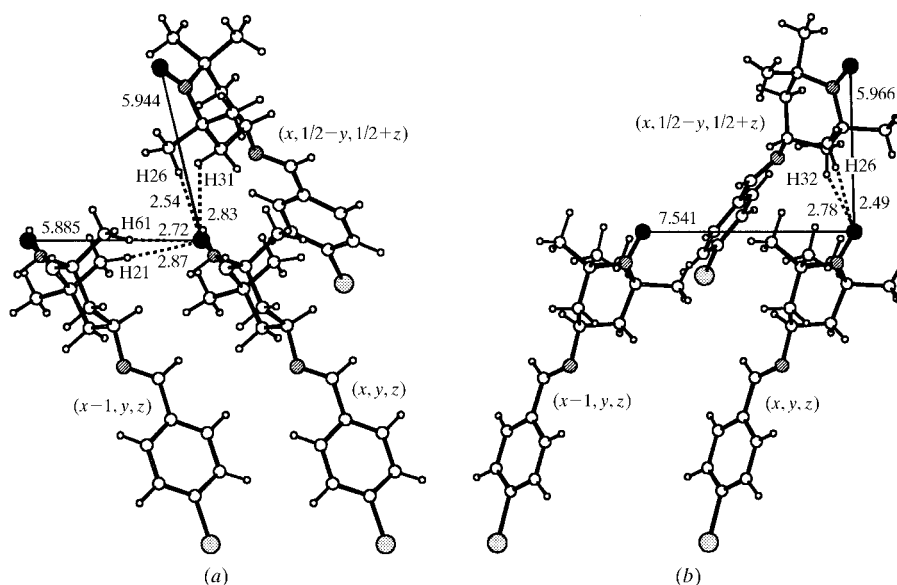


Fig. 5. Comparison of the intermolecular O···O and O···H contacts in (a) (2), 4-Cl-Ph, and (b) (3), 4-Br-Ph.

Table 4. Selected bond lengths (\AA), angles ($^\circ$) and torsion angles ($^\circ$)

	(2)	(4a)	(5)	(3)	(6)	(7)	(1)	(4b) molecule A	(4b) molecule B
Aryl groups	4-Cl-Ph	4-I-Ph	4-Ph-Ph	4-Br-Ph	4-Py	3,5-diCl-Ph	4-F-Ph	4-I-Ph	4-I-Ph
Weiss constant (K)	0.7	0.6	0.6	0.5	0.6	0.6	-2.6	-0.2	-0.2
Magnetic transition point (K)	0.4	0.3	0.4	—	—	—	—	—	—
O(1)—N(1)	1.2829 (17)	1.282 (3)	1.284 (2)	1.286 (3)	1.2782 (17)	1.283 (3)	1.2858 (18)	1.277 (4)	1.286 (4)
N(1)—C(2)	1.494 (2)	1.492 (4)	1.493 (3)	1.486 (4)	1.4963 (17)	1.490 (3)	1.489 (2)	1.480 (6)	1.501 (6)
N(1)—C(6)	1.495 (2)	1.497 (4)	1.489 (3)	1.495 (4)	1.4926 (19)	1.492 (3)	1.495 (2)	1.500 (6)	1.482 (6)
N(2)—C(4)	1.472 (2)	1.479 (4)	1.470 (3)	1.474 (4)	1.4701 (17)	1.467 (3)	1.468 (2)	1.484 (5)	1.468 (6)
N(2)—C(7)	1.255 (2)	1.235 (5)	1.238 (3)	1.256 (4)	1.246 (2)	1.257 (3)	1.253 (2)	1.206 (6)	1.225 (6)
C(2)—C(3)	1.531 (2)	1.529 (4)	1.525 (3)	1.529 (5)	1.5308 (19)	1.531 (4)	1.522 (2)	1.514 (6)	1.499 (7)
C(3)—C(4)	1.517 (2)	1.517 (5)	1.516 (3)	1.510 (5)	1.521 (2)	1.513 (4)	1.509 (3)	1.526 (7)	1.531 (7)
C(4)—C(5)	1.521 (2)	1.509 (5)	1.519 (3)	1.512 (5)	1.510 (2)	1.515 (4)	1.512 (2)	1.509 (7)	1.516 (7)
C(5)—C(6)	1.530 (2)	1.523 (5)	1.524 (3)	1.527 (5)	1.534 (2)	1.528 (4)	1.521 (2)	1.527 (6)	1.510 (6)
C(7)—C(11)	1.477 (2)	1.476 (5)	1.474 (3)	1.479 (5)	1.484 (2)	1.476 (4)	1.472 (2)	1.473 (6)	1.472 (6)
X(1)—C(14)†	1.7452 (18)	2.101 (3)	—	1.903 (3)	—	1.736 (3)	1.369 (2)	2.103 (4)	2.101 (4)
X(2)—C(15)	—	—	—	—	—	1.736 (3)	—	—	—
O(1)—N(1)—C(2)	116.09 (14)	116.7 (3)	116.32 (18)	115.7 (3)	116.42 (11)	116.3 (2)	116.10 (14)	116.5 (3)	116.1 (4)
O(1)—N(1)—C(6)	116.58 (13)	116.5 (2)	116.39 (17)	116.0 (3)	116.67 (11)	116.3 (2)	115.65 (14)	115.6 (4)	115.9 (4)
C(2)—N(1)—C(6)	123.59 (13)	123.1 (3)	123.52 (17)	124.8 (3)	123.23 (11)	123.8 (2)	124.92 (13)	125.0 (3)	124.8 (3)
C(4)—N(2)—C(7)	118.37 (15)	118.7 (3)	120.7 (2)	117.5 (3)	118.66 (13)	119.1 (3)	118.20 (15)	117.8 (4)	119.6 (4)
N(1)—C(2)—C(3)	109.26 (14)	109.3 (3)	108.95 (18)	110.3 (3)	109.28 (11)	109.1 (2)	109.71 (14)	109.1 (4)	109.5 (4)
C(2)—C(3)—C(4)	115.86 (14)	115.3 (3)	115.67 (19)	115.3 (3)	113.93 (12)	115.4 (2)	113.83 (15)	115.7 (4)	114.7 (4)
N(2)—C(4)—C(3)	107.58 (14)	107.9 (3)	107.59 (19)	108.1 (3)	108.19 (12)	108.0 (2)	108.58 (15)	108.2 (4)	109.9 (4)
N(2)—C(4)—C(5)	108.01 (14)	108.0 (3)	107.72 (19)	108.3 (3)	107.70 (12)	108.3 (2)	108.69 (15)	110.0 (4)	108.4 (4)
C(3)—C(4)—C(5)	109.21 (15)	109.6 (3)	108.8 (2)	108.7 (3)	108.57 (13)	108.7 (2)	107.84 (15)	107.6 (4)	107.1 (4)
C(4)—C(5)—C(6)	114.50 (15)	114.8 (3)	115.3 (2)	114.5 (3)	114.53 (12)	114.3 (2)	113.89 (15)	115.6 (4)	115.2 (4)
N(1)—C(6)—C(5)	108.83 (14)	108.8 (3)	109.08 (18)	108.8 (3)	108.64 (11)	109.1 (2)	109.39 (14)	108.8 (4)	109.7 (4)
N(2)—C(7)—C(11)	122.68 (17)	123.3 (4)	122.1 (2)	122.1 (4)	121.26 (15)	120.7 (3)	122.43 (17)	123.6 (5)	122.3 (4)
O(1)—N(1)—C(2)—C(3)	-163.09 (15)	-162.1 (3)	-162.3 (2)	168.2 (3)	161.59 (11)	163.7 (2)	-168.24 (16)	-163.6 (4)	-166.5 (4)
O(1)—N(1)—C(6)—C(5)	160.93 (15)	160.4 (3)	161.9 (2)	-165.9 (3)	-161.72 (11)	-162.2 (2)	168.00 (15)	163.9 (4)	167.1 (4)
C(3)—C(2)—N(1)—C(6)	39.5 (2)	40.4 (4)	40.4 (3)	-33.8 (5)	-40.77 (16)	-38.5 (4)	33.3 (2)	36.7 (6)	34.5 (5)
C(2)—N(1)—C(6)—C(5)	-41.8 (2)	-42.1 (4)	-40.9 (3)	36.3 (5)	40.69 (16)	40.0 (3)	-33.5 (2)	-36.2 (6)	-33.9 (6)
N(1)—C(2)—C(3)—C(4)	-44.4 (2)	-45.0 (4)	-46.4 (3)	42.5 (5)	47.67 (16)	45.5 (4)	-45.7 (2)	-46.3 (6)	-46.2 (5)
N(1)—C(6)—C(5)—C(4)	48.7 (2)	48.5 (4)	47.1 (3)	-47.7 (5)	-48.31 (17)	-48.1 (3)	46.1 (2)	45.7 (5)	45.6 (6)
C(2)—C(3)—C(4)—C(5)	54.6 (2)	54.6 (4)	55.4 (3)	-56.3 (5)	-58.19 (16)	-56.8 (4)	61.0 (2)	57.9 (5)	59.5 (5)
C(3)—C(4)—N(2)—C(7)	-56.7 (2)	-56.6 (4)	-55.7 (3)	59.4 (5)	58.76 (16)	57.9 (3)	-61.3 (2)	-57.4 (5)	-59.0 (5)
N(2)—C(4)—C(3)—C(2)	171.59 (15)	172.0 (3)	171.8 (2)	-173.7 (3)	-174.81 (11)	-174.1 (3)	178.58 (15)	176.7 (4)	177.0 (4)
N(2)—C(4)—C(5)—C(6)	-173.40 (15)	-173.9 (3)	-172.0 (2)	176.6 (4)	175.69 (12)	175.0 (2)	-178.85 (15)	-175.1 (4)	-177.6 (4)
C(3)—C(4)—N(2)—C(7)	106.40 (19)	107.8 (4)	106.8 (3)	-118.0 (4)	-109.73 (17)	-122.6 (3)	129.56 (18)	123.8 (5)	125.3 (5)
C(5)—C(4)—N(2)—C(7)	-135.83 (18)	-133.8 (4)	-136.1 (3)	124.4 (4)	133.09 (15)	119.8 (3)	-113.38 (19)	-118.9 (5)	-117.9 (5)
C(4)—N(2)—C(7)—C(11)	-177.42 (15)	-178.9 (3)	-176.9 (2)	179.4 (3)	177.72 (12)	178.9 (2)	179.36 (16)	-179.8 (4)	178.7 (4)
N(2)—C(7)—C(11)—C(12)	-10.1 (3)	-13.3 (6)	-6.2 (4)	-168.8 (15)	-161.08 (15)	0.0 (4)	3.7 (3)	-6.2 (8)	0.9 (8)
N(2)—C(7)—C(11)—C(16)	169.04 (19)	165.9 (4)	171.1 (3)	10.1 (6)	16.8 (2)	-179.2 (3)	-175.68 (19)	172.4 (5)	-178.6 (5)

† C(13) for (7).

distance in the sheet is 5.481 (1) Å for $O(1) \cdots O(1)(\frac{1}{2} - x, -y, \frac{1}{2} + z)$, which is shorter than those of (2)–(4a). The aryl groups between the sheets show parallel overlapping like the other 4-halo-aryl derivatives, with a $Ph \cdots Ph$ distance of 3.925 (3) Å, which is the longest value among the 4-halo-aryl derivatives. In the crystals of (1), spin-spin interactions are transferred through the γ -H atom [$O(1) \cdots H(4)(\frac{1}{2} - x, -y, \frac{1}{2} + z) = 2.70$ (4) Å] as well as *via* β -H atoms. This is considered to be a reason for the antiferromagnetic interaction.

The crystal structure of (4b) ($X = I$), a polymorphic form of (4a), is shown in Fig. 8. It is also quite different from those of (1)–(4a). In (4b) there are two independent molecules (*A* and *B*) in the asymmetric unit. In the crystals, the molecules are linked to form a chain structure through the short intermolecular $I \cdots O$ contacts of 2.949 (3) and 2.957 (4) Å for $I(1A) \cdots O(1A^i)$ and $I(1B) \cdots O(1B^i)$, respectively [symmetry code (i): $x + 1, y, z - 1$]. Two chains are connected by a weak $CH(\text{phenyl}) \cdots O$ hydrogen bond [$O(1B) \cdots C(13A^{ii}) = 3.384$ (6), $O(1B) \cdots H(13A^{ii}) = 2.34$ (4) Å; symmetry code (ii) $x - 1, y, z + 1$]. The shortest $O \cdots O$ distance is 5.461 (5) Å for $O(1A) \cdots O(1B)$, although no sheet-like $O \cdots O$ interactions are observed.

The crystal packing of (7) is different from that of (1), although the space group is same as that of (1) and a two-dimensional zigzag $O \cdots O$ network is also formed as shown in Fig. 9. The $O \cdots O$ distances in the sheet are

5.945 (2) and 7.477 (2) for $O(1) \cdots O(1)(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $O(1) \cdots O(1)(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, respectively. Within the sheet, some $O \cdots \beta$ -H contacts are observed. In this case, no parallel overlapping of the inter-sheet aryl groups is observed.

3.2. Molecular structures

Selected bond distances, bond angles and torsion angles are listed in Table 4. The conformation of the TEMPO ring of each derivative is a shallow chair. The torsion-angle ranges within the rings are $C-C-N(1)-C \pm 33.3$ to $\pm 42.1^\circ$, $N(1)-C-C-C \pm 42.5$ to $\pm 48.7^\circ$ and $C-C-C-C \pm 54.6$ to $\pm 61.3^\circ$. These endocyclic torsion angles and the exocyclic torsion angles of (2), (4a) and (5) (belonging to the same class of crystal structures and showing a ferromagnetic transition) and (6) and (7) (showing a ferromagnetic interaction) are slightly different from those of (3) (showing a ferromagnetic interaction) and (1) and (4b) (showing an antiferromagnetic interaction). The differences of the torsion angles of the first group and the last group are about 5° for $O(1)-N(1)-C-C$, 4° for $N(2)-C(4)-C-C$ and 10° for $C-C(4)-N(2)-C(7)$. It is interesting that the torsion angles of the amino groups are so different between the ferromagnetic derivatives (2), (4a) and (5) and the antiferromagnetic derivatives (1) and (4b). However, it is difficult to state whether these torsion angles relate to the magnetic interactions directly. These differences in the conformation are considered to be related to the packing in the crystals.

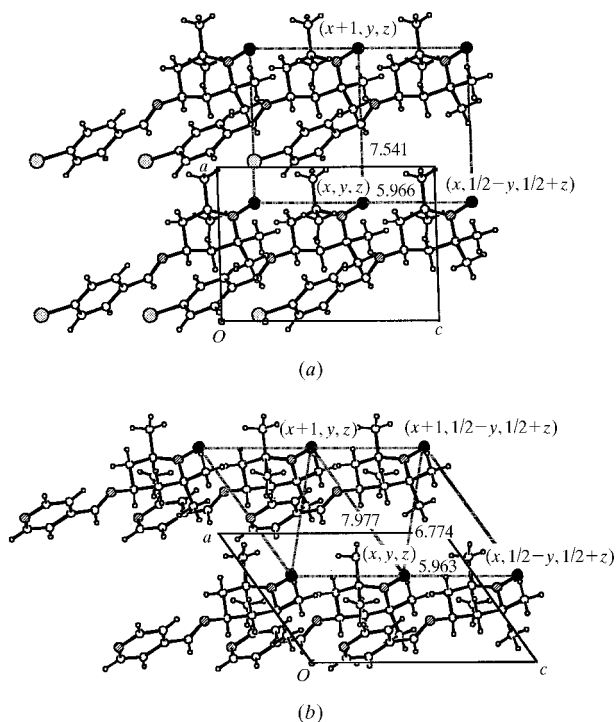


Fig. 6. Comparison of the $O \cdots O$ network viewed along the *b* axis in (a) (3), 4-Br-Ph, and (b) (6), 4-Py.

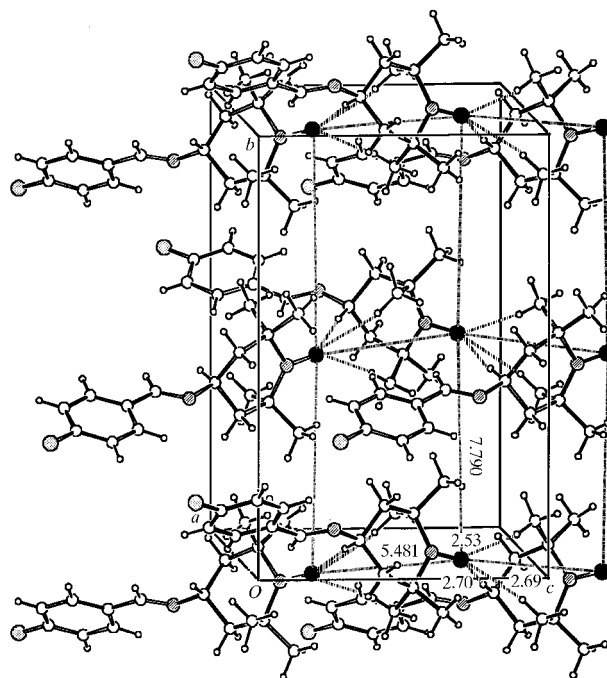


Fig. 7. A perspective view of the crystal structure of (1), 4-F-Ph. Molecules in half of the unit cell are omitted for clarity.

Recently we performed the structure analysis of mixed crystals of (2) and (3). The preliminary result showed that an approximately 1:1 ratio of disordered molecules of (2) and (3) occupied the crystal structure of (3) and that the observed conformations of both molecules are similar to those of (3) (Hashizume *et al.*, 1999).

The O(1)–N(1) distances lie in the range 1.277–1.286 Å and are between the normal single-bond

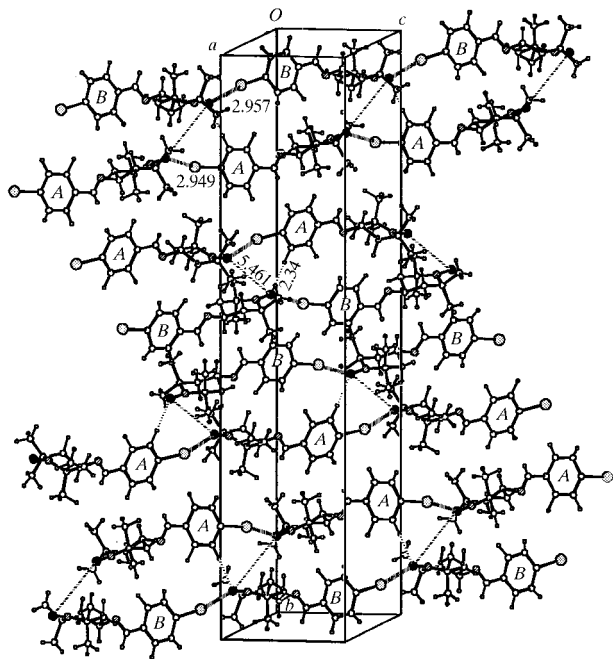


Fig. 8. A perspective view of the crystal structure of (4b), 4-I-Ph.

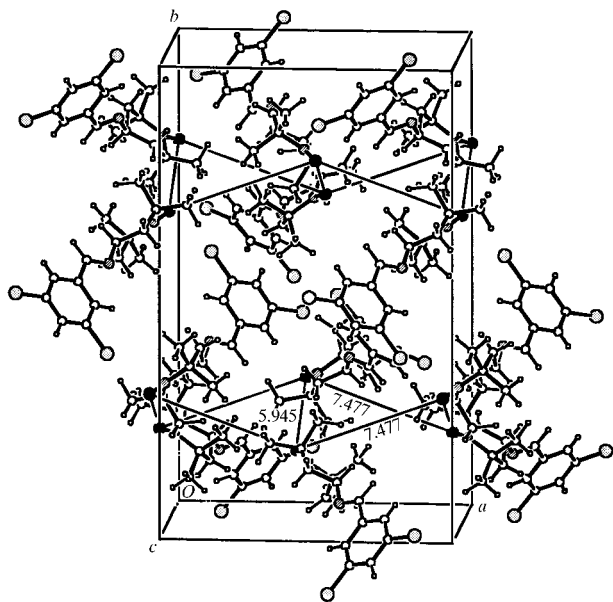


Fig. 9. A perspective view of the crystal structure of (7), 3,5-diCl-Ph. Molecules in half of the unit cell are omitted for clarity.

(1.36 Å) and double-bond lengths (1.22 Å). The lengths of the N(1)–C bonds in the TEMPO rings lie in the range 1.480–1.501 Å and are slightly longer than the normal single-bond length (1.47 Å). The sums of the bond angles O(1)–N(1)–C(2), O(1)–N(1)–C(6) and C(2)–N(1)–C(6) are 356.1–356.6°, showing the sp^2 character of the N atom. The deviations of the N(1) atom from the plane of O(1), C(2) and C(6) are about 0.150–0.163 Å. From these structural features, the differences in the magnetic characters of these radicals is considered to be independent of the molecular structures.

The magnetic interactions are very weak in the crystals of TEMPO radicals, as can be seen from the extremely low temperatures of the magnetic transition points and Weiss constants. It is difficult to pinpoint the origin of the magnetic interactions exactly. Nevertheless, the sheet-like arrangement of O atoms and intra-sheet interactions through the CH₂ or CH₃ groups of the TEMPO rings are related to the mechanisms of the ferromagnetic interactions. The parallel overlapping of the inter-sheet aryl groups may be considered to be related to the magnetic interactions of these radicals. However, different types of crystal structures of 4-Ar–CH=N–TEMPO radicals show ferromagnetic interactions, such as the Ar = Ph, 4-MeS-Ph and 3-Py derivatives (Yasui *et al.*, 1996). In these crystals no parallel stacking of the aryl groups is observed. Details of these structures will be reported in another paper (Iwasaki *et al.*, 1999).

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 08454180) from the Ministry of Education, Science and Culture, Japan.

References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *DIRDIF92. The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Fan, H.-F. (1991). *SAP91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Hashizume, D., Takashima, N., Yasui, M. & Iwasaki, F. (1999). In preparation.
- Ishida, T., Mitsubori, S., Nogami, T., Ishikawa, Y., Yasui, M., Iwasaki, F., Iwamura, H., Takeda, N. & Ishikawa, M. (1995). *Synth. Met.* **71**, 1791–1792.
- Ishida, T., Tsuboi, H., Nogami, T., Yoshikawa, H., Yasui, M., Iwasaki, F., Iwamura, H., Takeda, N. & Ishikawa, M. (1994). *Chem. Lett.* pp. 919–922.

- Iwasaki, F., Yoshikawa, J. H., Yamamoto, H., Takada, K., Kan-nari, E., Yasui, M., Ishida, T. & Nogami, T. (1999). In preparation.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nogami, T., Ishida, T., Tsuboi, H., Yoshikawa, H., Yamamoto, H., Yasui, M., Iwasaki, F., Iwamura, H., Takeda, N. & Ishikawa, M. (1995). *Chem. Lett.* pp. 635–636.
- Nogami, T., Ishida, T., Yasui, M., Iwasaki, F., Iwamura, H., Takeda, N. & Ishikawa, M. (1996). *Mol. Cryst. Liq. Cryst.* **279**, 97–106.
- Nogami, T., Ishida, T., Yasui, M., Iwasaki, F., Takeda, N., Ishikawa, M., Kawakami, T. & Yamaguchi, K. (1996). *Bull. Chem. Soc. Jpn.* **69**, 1841–1848.
- Nogami, T., Tomioka, K., Ishida, T., Yoshikawa, H., Yasui, M., Iwasaki, F., Iwamura, H., Takeda, N. & Ishikawa, M. (1994). *Chem. Lett.* pp. 29–32.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku (1990). *AFC Control Software*. Version 4.5-PC. Rigaku Corporation, Tokyo, Japan.
- Rigaku (1994). *AFC Control Software*. Version 5.3.1. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Togashi, K., Imachi, R., Tomioka, K., Tsuboi, H., Ishida, T., Nogami, T., Takeda, N. & Ishikawa, M. (1996). *Bull. Chem. Soc. Jpn.* **69**, 2821–2830.
- Yasui, M., Yoshikawa, H., Yamamoto, H., Ishida, T., Nogami, T. & Iwasaki, F. (1996). *Mol. Cryst. Liq. Cryst.* **279**, 77–85.