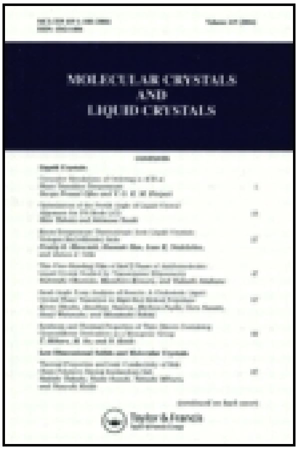

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Characterization of the Crystalline Nature of the Racemates of Novel Chiral Five-Membered Cyclic Nitroxides

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Characterization of the Crystalline Nature of the Racemates of Novel Chiral Five-Membered Cyclic Nitroxides

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Racemic samples of chiral five-membered cyclic nitroxides, 2,2,5,5-tetrasubstituted pyrrolidine-1-oxyls bearing one or two 4-hydroxyphenyl groups on the stereogenic centers [C(2) or C(2) & C(5)] adjacent to the NO radical moiety, exist as a racemic conglomerate in the crystalline state, whereas those having one or two 3-hydroxyphenyl groups at the same positions belong to a racemic compound. The key intermolecular interactions in controlling whether these racemates crystallize in a homochiral way or a heterochiral manner have been investigated by X-ray crystallographic analysis and magnetic susceptibility measurements.

Keywords: chiral nitroxide radical; electron paramagnetic resonance spectroscopy; magnetic susceptibility; racemic compound; racemic conglomerate; X-ray crystallographic analysis

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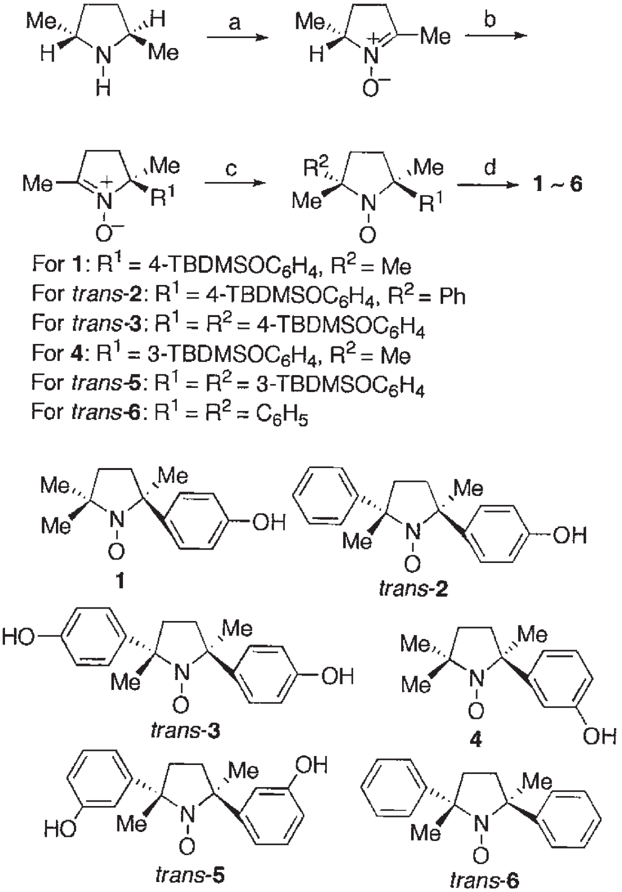
INTRODUCTION

With a view to utilizing a chiral five-membered cyclic nitroxide framework as a spin source in its core portion for the elaboration of chiral paramagnetic liquid crystals, as well as providing a new chiral spin-labeling reagent for EPR spectroscopic studies, we have synthesized racemic and enantiomerically enriched nitroxides **1**∼**5** with one or two hydroxyphenyl groups on the stereogenic centers as synthetic intermediates (Scheme 1). Among them, (±)-**1**, *trans*-(±)-**2** and *trans*-(±)-**3** having 4-hydroxyphenyl groups were found to exist as a racemic



For **1**: R^1 = 4-TBDMSOC$_6$H$_4$, R^2 = Me
For *trans*-**2**: R^1 = 4-TBDMSOC$_6$H$_4$, R^2 = Ph
For *trans*-**3**: R^1 = R^2 = 4-TBDMSOC$_6$H$_4$
For **4**: R^1 = 3-TBDMSOC$_6$H$_4$, R^2 = Me
For *trans*-**5**: R^1 = R^2 = 3-TBDMSOC$_6$H$_4$
For *trans*-**6**: R^1 = R^2 = C$_6$H$_5$

SCHEME 1 Preparation of chiral nitroxides **1**∼**6**. Reaction conditions: a) $MeReO_3$, urea · H_2O_2, MeOH, 0°C (60%); b) 1. R^1MgBr, THF, –78°C; 2. $Cu(OAc)_2$, O_2; c) 1. R^2MgBr, THF, –78°C; 2. $Cu(OAc)_2$, O_2; d) TBAF, THF, 0°C.

conglomerate (an equal mixture of *R* and *S* chiral crystals) [1], which is very rare for chiral nitroxide radicals [2]. To examine the generality of this conglomerate formation, we have characterized the crystalline nature (i.e., classification as a racemic conglomerate, a racemic compound or a racemic mixed crystal) of (±)-2-(3-hydroxyphenyl)-2,5,5-trimethylpyrrolidine-1-oxyl (**4**) and *trans*-(±)-2,5-di(3-hydroxyphenyl)-2,5-dimethylpyrrolidine-1-oxyl (**5**) by means of IR spectroscopy, X-ray crystallographic analysis and magnetic susceptibility measurements, and have compared their crystal structures and magnetic properties with those of (±)-**1**, *trans*-(±)-**3** and their parent compound, *trans*-(±)-2,5-dimethyl-2,5-diphenylpyrrolidine-1-oxyl (**6**) [3].

Origin of the Formation of a Racemic Conglomerate with Respect to (±)-1, *trans*-(±)-2 and *trans*-(±)-3

As shown in Figures 1–3 and Table 1, we reported that (±)-**1**, *trans*-(±)-**2** and *trans*-(±)-**3** exist as the racemic conglomerates (common space group $P2_12_12_1$ and $Z = 4$) in their crystalline states. Each chiral crystal commonly consists of a head-to-tail type of homochiral supramolecular 1D zigzag chains characterized by strong intermolecular hydrogen bonds between the NO radical and the phenolic OH groups [1]. At first glance, it was difficult to find out the primary interactions which must control the homochiral packing of the homochiral 1D zigzag chains. Therefore, the molar magnetic susceptibility χ_{mol} was measured for **1**, *trans*-**2** and *trans*-**3** at temperatures ranging between 2 and 300 K using a SQUID susceptometer at an applied field of 0.5 T, because the measurement of the temperature-dependence of the magnetic susceptibility of molecular magnetic materials often affords useful information on the weak intermolecular interactions present in the crystal lattice [4]. Consequently, three typical magnetic behaviors such as weak ferro- and antiferro-magnetic interactions, and isolated paramagnetic interactions were observed for **1**, *trans*-**2** and *trans*-**3**, respectively [1]. The racemic sample showed the same magnetic behaviour as the enantiomerically enriched one for each of **1**, *trans*-**2** and *trans*-**3**, because of their existence as racemic conglomerates.

Appearance of weak ferromagnetic interactions for **1** is consistent with its chiral crystal structure in which the intra- and inter-molecular spin polarization exchange coupling can be transmitted ferromagnetically in accord with the McConnell mechanism [5]. The sandwich-type weak $C(sp^3){-}H{\cdots}O{\cdots}H{-}C(sp^3)$ interactions [H···O distances: 3.380(4) and 3.541(4) Å] between the NO group of a molecule and the two methyl groups on the pyrrolidinyl C(5) of the adjacent molecule, which give a homochiral 1D zigzag chain along the *a* axis, seems responsible for

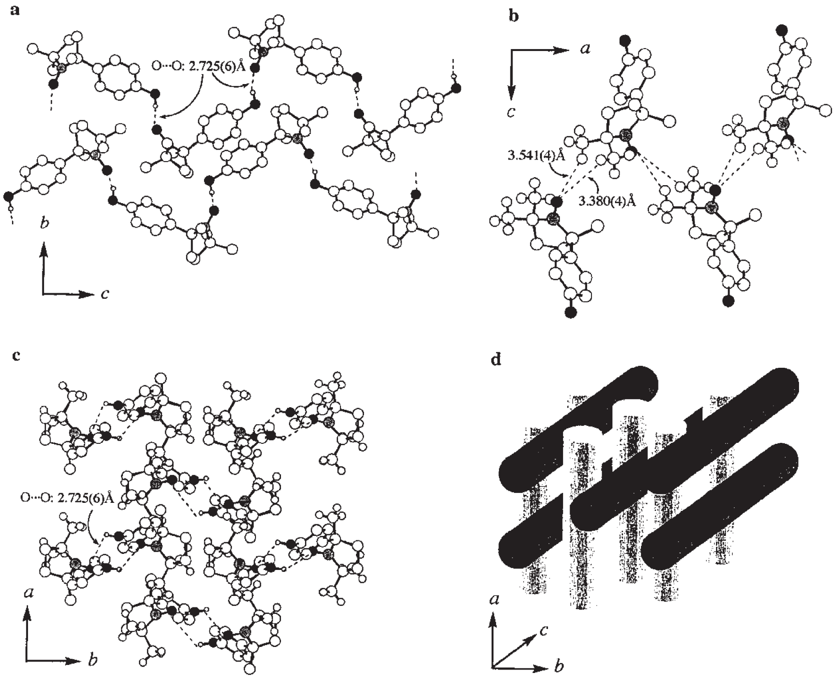


FIGURE 1 Crystal structure of (±)-**1** ($P2_12_12_1$, $Z = 4$) viewed down the (a) *a* axis, (b) *b* axis and (c) *c* axis [1] and (d) schematic representation of the homochiral 3D network structure. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively. Hydrogen atoms except the OH group and the two methyl groups on the pyrrolidinyl C(5) are omitted.

the weak ferromagnetic interactions (Fig. 1b). This zigzag chain along the *a* axis, and the foregoing homochiral 1D zigzag chain along the *c* axis formed by strong O–H···O–N hydrogen bonds [O···O distance: 2.725(6) Å] (Fig. 1a), are alternately weaved along the *b* axis into the homochiral 3D network structure (Fig. 1d).

The observed weak antiferromagnetic behavior of *trans*-**2** is explained by the through-space NO···ON interactions among the NO groups [the shortest O···O distance: 6.399(3) Å] aligned along the *c* axis (Fig. 2b). The 1D zigzag chains along the *b* axis, which were formed by O–H···O–N hydrogen bonds [O···O distance: 2.752(3) Å], were further connected with one another on the *ab* plane by C(sp^3)–H···O–N interactions [H···O distance: 2.875(2) Å] between the pyrrolidinyl C(4)Hs of a homochiral chain and the nearest N–O groups of the neighbouring chain to give a sheet structure (Fig. 2a). Thus, the above dipole–dipole

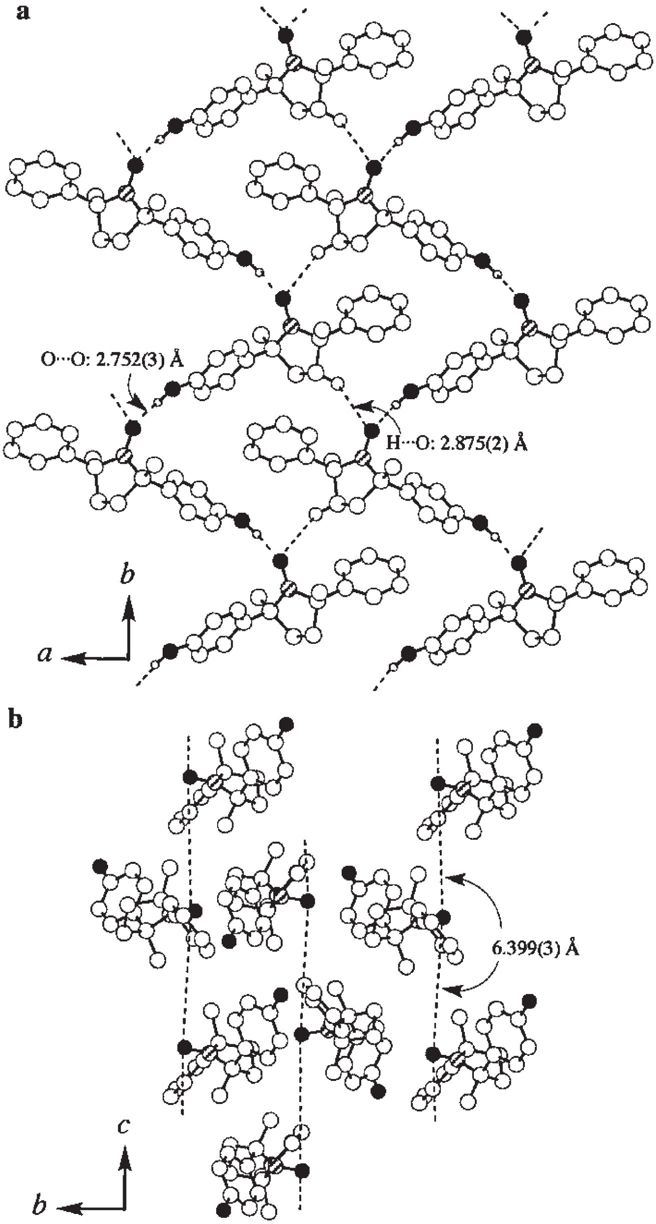


FIGURE 2 Crystal structure of *trans*-(±)-**2** ($P2_12_12_1$, $Z = 4$) viewed down the (a) *c* axis and (b) *a* axis [1]. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively. Hydrogen atoms except the OH group and one hydrogen atom on the pyrrolidinyl C(4) are omitted in (a), while all hydrogen atoms are done in (b).

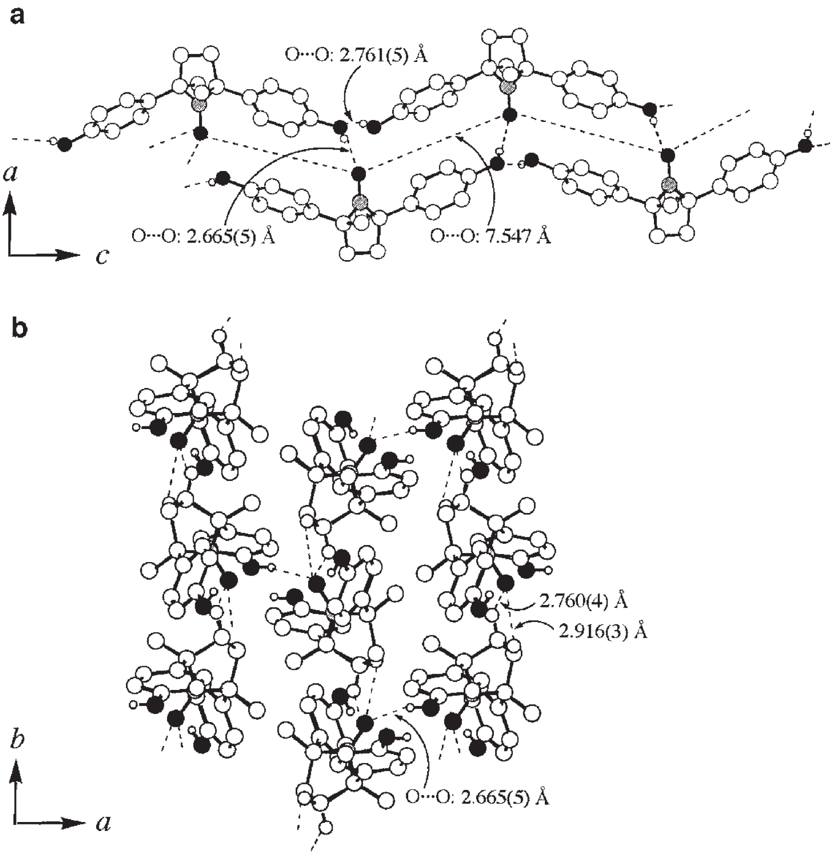


FIGURE 3 Crystal structure of *trans*-(±)-**3** ($P2_12_12_1$, $Z = 4$) viewed down the (a) *b* axis and (b) *c* axis [1]. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively. Hydrogen atoms except the OH group are omitted in (a), while those except the two OH groups and the two hydrogen atoms on the pyrrolidinyl C(3) are omitted in (b).

interactions between the NO groups along the *c* axis may be responsible for the homochiral stacking of the homochiral *ab* sheets along the *c* axis.

In the paramagnetic crystals of *trans*-**3**, in which the O···O distance (7.547 Å) between the nearest NO groups is too long to show an antiferromagnetic behavior, a combination of the hydrogen bonds between the neighboring phenolic OH groups [O···O distance: 2.761(5) Å] with the strong O–H···O–N hydrogen bonds [O···O distance: 2.665(5) Å] provides a homochiral 1D ribbon structure along the *c* axis (Fig. 3a).

TABLE 1 Melting Points, Specific Rotations, ESR g-factors and Hyperfine Coupling Constants, and Magnetic Data for Nitroxides **1**-**6**

				ESR^{d}			
Compound	mp (°C)^{a}	ee/%^{b}	$[\alpha]_{\mathrm{D}}^{25c}$	g	a_{N} (mT)	C^{e}/emu K mol^{-1}	θ^{f}/K
(S)-**1**^{g}	161.7	88	–118.7	2.0067	1.38	0.38	+0.20
(±)-**1**^{g}	151.0	–	–	2.0073	1.38	0.37	+0.15
(2S,5S)-**2**^{g}	180.8	97	–202.2	2.0070	1.33	0.38	–0.33
(±)-**2**^{g}	168.5	–	–	2.0070	1.33	0.37	–0.30
(2S,5S)-**3**^{g}	177.2	97	–187.3	2.0067	1.34	0.38	–0.01
(±)-**3**^{g}	173.8	–	–	2.0080	1.35	0.38	–0.02
(S)-**4**	160.9	98	–99.4	2.0065	1.39	0.38	–3.40
(±)-**4**	120.9	–	–	2.0064	1.38	0.38	–1.28
(2S,5S)-**5**	168.7	93	–142.0	2.0066	1.34	0.38	–1.01
(±)-**5**	191.7	–	–	2.0072	1.33	0.38	–0.70
(2S,5S)-**6**	130.5	96	–181.7	2.0070	1.34	0.38	–1.34
(±)-**6**	100.5	–	–	2.0070	1.33	0.38	–1.37

[a] Measured by DSC. All samples were decomposed at the indicated temperature.

[b] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OD-H, 0.4 × 25 cm) and a mixture of hexane and 2-propanol (9:1) as the mobile phase.

[c] Measured in THF. *c* 1.00.

[d] Measured in THF at 25°C.

[e] Curie constants.

[f] Weiss temperature.

[g] Data quoted from Ref. 1.

The homochiral ribbons further interact with one another along the *b* axis by two C(sp^3)−H···O−N interactions [H···O distances: 2.760(4) and 2.916(3) Å] between the two pyrrolidinyl C(3)Hs of a homochiral ribbon and the nearest NO groups of the neighbouring ribbons to give the homochiral 3D network structure (Fig. 3b).

Thus, the origin of the conglomerate formation with respect to **1**, *trans*-**2** and *trans*-**3** can be interpreted in terms of the formation of homochiral 1D zigzag chains by the strong intermolecular O−H···O−N O−N hydrogen bonds, together with weak attractive forces such as dipole–dipole interactions between the NO groups and C(sp^n)–H···O−N interactions [1].

Preparation of 4 and *trans*-5

Racemic and enantiomerically enriched nitroxides **4** and *trans*-**5** were prepared analogously to the preparation of *trans*-(±)- and *trans*-(2*S*,5*S*)-**6**

[3,6] from *trans*-(±)- and *trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidine, respectively (Scheme 1) [7]. The phenolic hydroxy group was protected by a *tert*-butyldimethylsilyl (TBDMS) group prior to the Grignard reaction and then was deprotected in the final step using tetrabutylammonium fluoride (TBAF) to give phenolic nitroxides **4** and *trans*-**5**. These were purified by flash column chromatography on silica gel eluting with CH_2Cl_2/Et_2O, followed by recrystallization from CH_2Cl_2 or MeOH, respectively. The single crystals of (±)-**4**, *trans*-(±)-**5** and *trans*-(±)-**6** for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2, MeOH or hexane, respectively. Their thermal, optical and magnetic properties are summarized in Table 1, together with those of nitroxides **1**, *trans*-**2** and *trans*-**3** [1].

Origin of the Formation of a Racemic Compound with Respect to (±)-4, *trans*-(±)-5 and *trans*-(±)-6

As expected from the comparison of IR spectra between the enantiomerically enriched material and the racemate (Fig. 4), all of the racemic samples of **4**, *trans*-**5** and *trans*-**6** have been found to exist as a racemic compound consisting of a pair of *R* and *S* molecules by X-ray crystallographic analysis.

The temperature-dependence of the molar magnetic susceptibility χ_{mol} measured for the polycrystalline samples of (±)-**4**, *trans*-(±)-**5** and *trans*-(±)-**6** is shown in the χT vs. T plot in Figure 5. These solid materials uniformly show weak antiferromagnetic interactions below 20 K. The χT value at 300 K for each compound corresponds to the free $S = 1/2$ spin with a *g*-factor of 2.0, indicating that the radical purity of the obtained nitroxides is satisfactory.

The crystal structure of (±)-**4** (space group $P2_1/c$, $Z = 4$) is characterized by a centrosymmetric head-to-head cyclic dimer which is formed by hydrogen bonds between the NO and the OH groups [O···O distance: 2.720(2) Å] in a pair of *R* and *S* molecules. The cyclic dimers interact with each other in a cyclic manner around an inversion center by means of weak $C(sp^3)-H\cdots O-N$ interactions [H···O distance: 3.1479(13) Å] between one of the two methyl groups on the pyrrolidinyl C(5) of one dimer and the NO group of the neighboring dimer, eventually forming heterochiral 1D chains along the *c* axis (Fig. 6). The O···O distances among the NO groups in the 1D chain are alternately 4.282(2) and 5.554(2) Å. No appreciable interchain interaction other than van der Waals forces is seen in the crystal lattice. Accordingly, the observed weak antiferromagnetic behavior of (±)-**4** below 20 K is explained by the through-space NO···ON interactions among the NO groups which form an alternating linear chain.

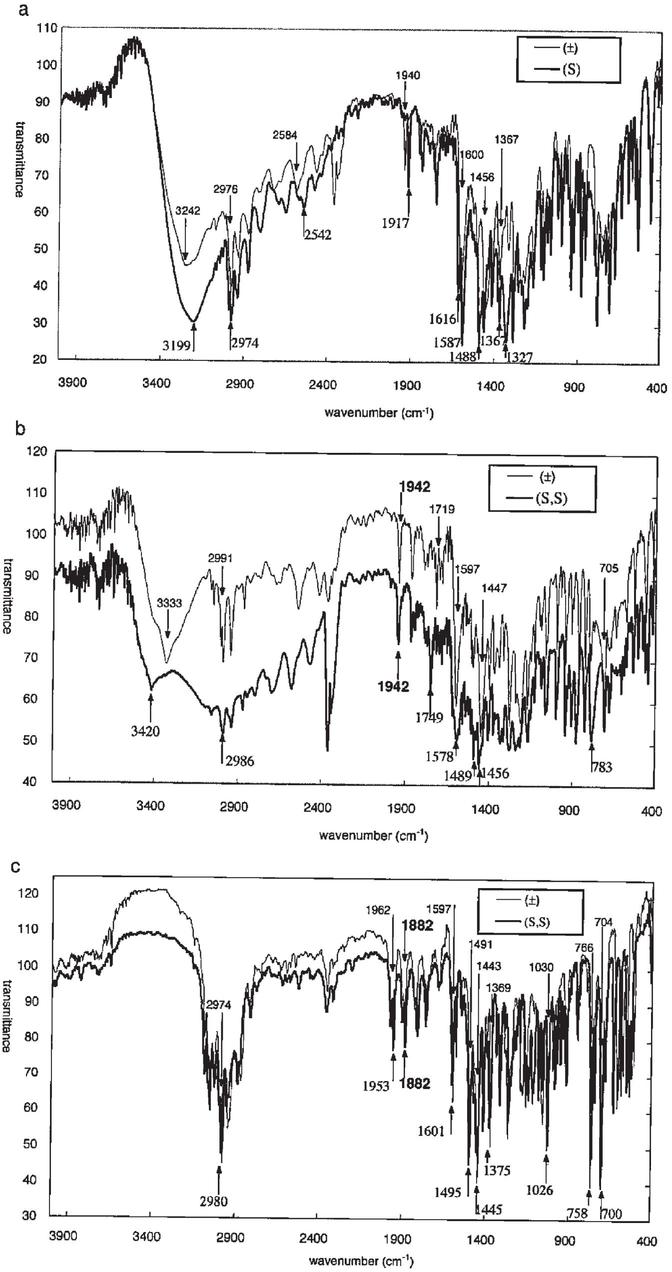


FIGURE 4 Comparison of the diffuse reflectance IR spectra between the enantiomerically enriched material and the racemate with respect to (a) **4**, (b) *trans*-**5** and (c) *trans*-**6**.

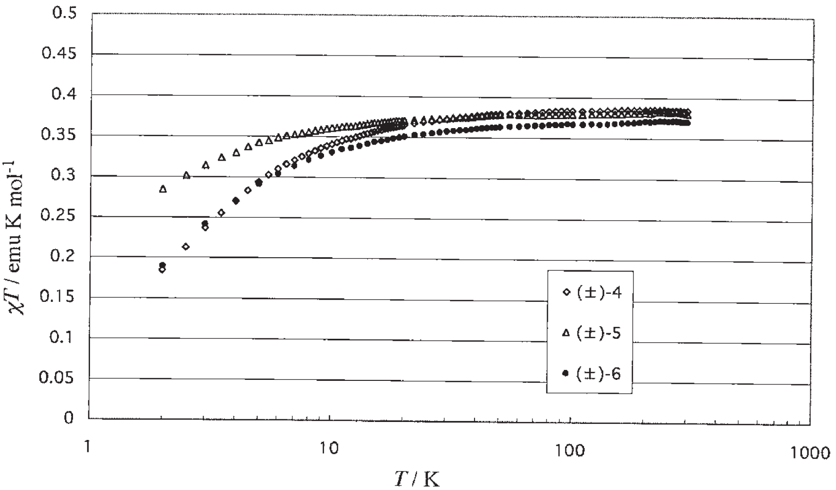


FIGURE 5 Temperature dependence of the magnetic susceptibility for (±)-**4** (represented by squares), *trans*-(±)-**5** (triangles) and *trans*-(±)-**6** (circles).

The crystal structure of *trans*-(±)-**5** (space group *Pbcn*, $Z = 4$) is characterized by a bifurcated hydrogen bond formed by the two facing phenolic hydroxy groups and the NO groups [O···O distance: 2.810(2) Å] to give a heterochiral 1D ribbon structure composed of

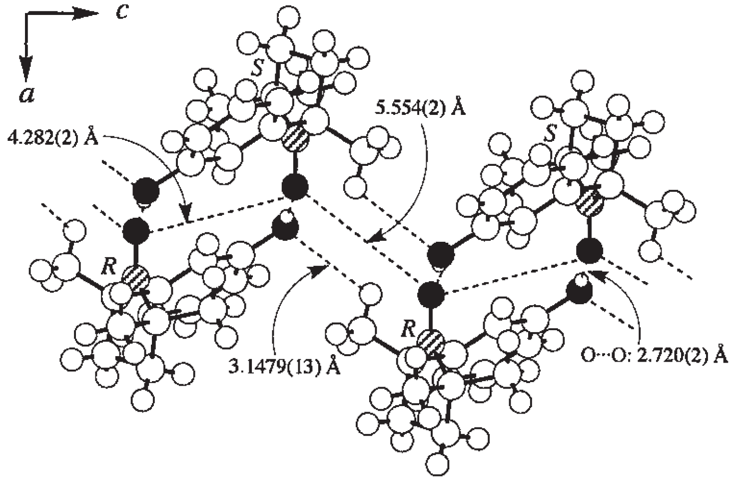


FIGURE 6 Crystal structure of (±)-**4** ($P2_1/c$, $Z = 4$) viewed down the b axis. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively.

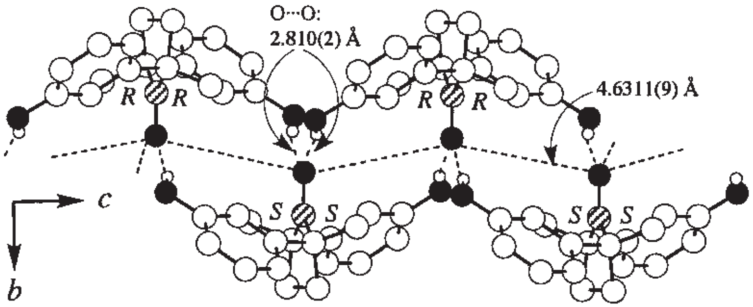


FIGURE 7 Crystal structure of *trans*-(±)-**5** (*Pbcn*, $Z = 4$) viewed down the *a* axis. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively. Hydrogen atoms except the two OH group are omitted.

centrosymmetric cyclic dimers along the *c* axis (Fig. 7). The O···O distance among the NO groups in the 1D ribbon is uniformly 4.6311(9) Å. No appreciable inter-ribbon interaction other than van der Waals forces is seen in the crystal lattice. Accordingly, the observed weak antiferromagnetic behavior is also interpreted in terms of the through-space NO···ON interactions among the NO groups which form a regular linear chain.

The crystal structure of *trans*-(±)-**6** (space group *Pbcn*, $Z = 4$) is isomorphous with that of *trans*-(±)-**5** (Fig. 8). In this case, each NO group

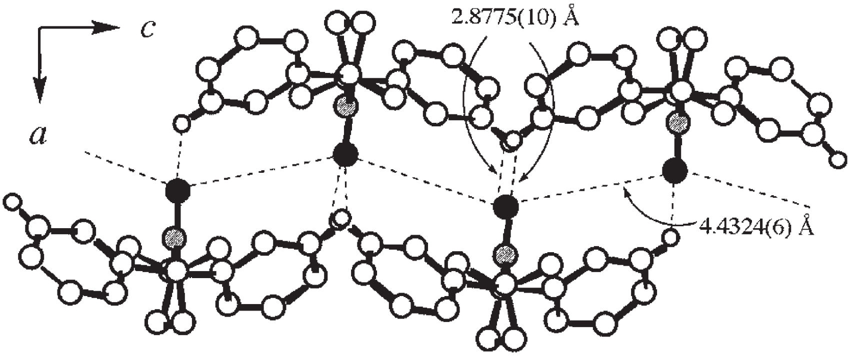


FIGURE 8 Crystal structure of *trans*-(±)-**6** (*Pbcn*, $Z = 4$) viewed down the *b* axis. The carbon, hydrogen, nitrogen, and oxygen atoms are represented by large open, small open, crosshatched, and closed circles, respectively. Hydrogen atoms except one of the two meta hydrogen atoms for each phenyl group are omitted.

interacts with two meta hydrogen atoms on the two facing phenyl groups [O···H−C(sp^2) distances: 2.8775(10) Å], giving a heterochiral 1D ribbon structure along the *c* axis (Fig. 8). No appreciable inter-ribbon interaction other than van der Waals forces is observed in the crystal lattice. The O···O distance among the NO groups in the 1D ribbon is uniformly 4.4324(6) Å, which is shorter than that [4.6311(9) Å] present in *trans*-(±)-**5**. For this reason, the antiferromagnetic interactions ($\theta = -1.37$ K) observed for *trans*-(±)-**6**, which are relevant to the through-space NO···ON interactions, are stronger than those ($\theta = -0.70$ K) for *trans*-(±)-**5**.

Thus, the origin of the racemic compound formation with respect to (±)-**4**, *trans*-(±)-**5** and *trans*-(±)-**6** can be accounted for by the formation of a centrosymmetric cyclic dimer structure arising from the strong intermolecular O−H···O−N hydrogen bonds, along with additional weak attractive forces such as dipole–dipole interactions between the NO groups and C(sp^n)−H···O−N interactions.

CONCLUSIONS

It has been revealed that O−H···O−N hydrogen bonds play an important role in the formation of both the racemic conglomerates for **1**, *trans*-**2** and *trans*-**3** and the racemic compounds for (±)-**4**, *trans*-(±)-**5** and *trans*-(±)-**6**. Therefore, the presence of at least one 4-hydroxyphenyl group on the stereogenic centers has turned out to be essential to the formation of a racemic conglomerate with respect to the 2,2,5,5-tetrasubstituted pyrrolidine-1-oxyl system.

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[8] The X-ray data were collected at 298 K on an Enraf-Nonius Kappa CCD diffractometer. The crystal structures were solved by the direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. All of the crystallographic calculations were performed by using maXus software package. Crystal data for (±)-**4**: $C_{13}H_{18}NO_2$, $Mr = 220.29$, $0.29 \times 0.25 \times 0.20$ mm, monoclinic, space group $P2_1/c$, $a = 8.1217(5)$, $b = 20.2165(7)$, $c = 8.0943(5)$ Å, $\beta = 110.403(2)^\circ$, $V = 1245.65(12)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.175$ g cm^{-3}, $2\theta_{\mathrm{max}} = 53.5^\circ$, MoK$\alpha$ ($\lambda = 0.71073$ Å), $\mu = 0.79$ cm^{-1}, ϕ–ωscans, $T = 298$ K, 2655 independent reflections, 1605 observed reflections ($I > 2.0\sigma(I)$), 149 refined parameters, $R = 0.051$, $R_{\mathrm{w}} = 0.126$, $\Delta\rho_{\mathrm{max}} = 0.187$ eÅ^{-3}, $\Delta\rho_{\mathrm{min}} = -0.281$ eÅ^{-3}. Crystal data for *trans*-(±)-**5**: $C_{18}H_{20}NO_3$, $Mr = 298.36$, $0.26 \times 0.16 \times 0.06$ mm, orthorhombic, space group *Pbcn*, $a = 19.178(2)$, $b = 8.9422(8)$, $c = 9.0107(4)$ Å, $V = 1545.3(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.282$ g cm^{-3}, $2\theta_{\mathrm{max}} = 54.2^\circ$, MoK$\alpha$ ($\lambda = 0.71073$ Å), $\mu = 0.87$ cm^{-1}, ϕ–ωscans, $T = 298$ K, 1717 independent reflections, 887 observed reflections ($I > 2.0\sigma(I)$), 103 refined parameters, $R = 0.052$, $R_{\mathrm{w}} = 0.128$, $\Delta\rho_{\mathrm{max}} = 0.241$ eÅ^{-3}, $\Delta\rho_{\mathrm{min}} = -0.328$ eÅ^{-3}. Crystal data for *trans*-(±)-**6**: $C_{18}H_{20}NO$, $Mr = 266.36$, $0.30 \times 0.24 \times 0.20$ mm, orthorhombic, space group *Pbcn*, $a = 19.3353(6)$, $b = 9.2424(6)$, $c = 8.5632(5)$ Å, $V = 1530.3(1)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.156$ g cm^{-3}, 3, $2\theta_{\mathrm{max}} = 58.3^\circ$, MoK$\alpha$ ($\lambda = 0.71073$ Å), $\mu = 0.71$ cm^{-1}, ϕ–ωscans, $T = 298$ K, 2063 independent reflections, 1284 observed reflections ($I > 2.0\sigma(I)$), 103 refined parameters, $R = 0.055$, $R_{\mathrm{w}} = 0.156$, $\Delta\rho_{\mathrm{max}} = 0.251$ eÅ^{-3}, $\Delta\rho_{\mathrm{min}} = -0.452$ eÅ^{-3}. CCDC-217527-217529 contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).