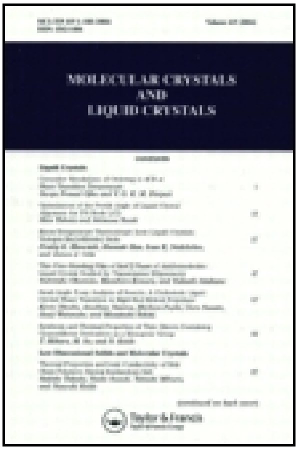

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Use of Cyclotriphosphazene as a Molecular Scaffold for Building Chiral Multispin Systems

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Chiral mononitroxide-, dinitroxide-, tetranitroxide- and hexanitroxide- cyclotriphosphazene hybrid compounds, along with a chiral 2,2′-bridged trinitroxide-bis (cyclotriphosphazene) hybrid compound, have been prepared to examine the potential use of the cyclotriphosphazene framework as a molecular scaffold for elaborating chiral multispin systems. EPR spectroscopic studies in solution and in frozen solvent matrixes indicate that strong intramolecular through-space electron-exchange interactions are observed for the tetranitroxide and hexanitroxide hybrid compounds, while magnetic susceptibility measurements show that weak antiferromagnetic interactions are uniformly recognized in the solid states for all of them. The X-ray crystallographic analysis of the dinitroxide hybrid compound ascribes the latter antiferromagnetic behavior to an intermolecular origin.

Keywords: chiral multispin system; chiral nitroxide-cyclotriphosphazene hybrid; chiral nitroxide radical; electron paramagnetic resonance spectroscopy; magnetic susceptibility measurement; X-ray crystallographic analysis

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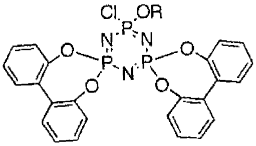
INTRODUCTION

Cyclotriphosphazene is a unique inorganic compound which can serve as a molecular scaffold by incorporating various organic functional groups into the cyclic –P=N– backbone, making possible the preparation of organic-inorganic hybrid materials [1]. Although thus far four examples have been documented for the preparation and characterization of radical-cyclotriphosphazene hybrid compounds, they are limited to a monoradical or an 2,2-diradical and their magnetic properties in the solid states have not been studied [2–5].

With a view to examining the possibility of building chiral multispin systems on the cyclotriphosphazene scaffold, we have prepared chiral nitroxide-cyclotriphosphazene hybrid compounds such as mononitroxide (S)-**1**, 2,2-dinitroxide (S)-**2**, 2,2,4,4-tetranitroxide (S)-**3**, 2,2,4,4,6,6-hexanitroxide (S)-**4** and 2,2′-bridged 2,2,2′,2′-trinitroxide (S)-**5**, evaluated the magnitude of the intramolecular through-space electron-exchange interactions by means of X-band EPR spectroscopy in solution and in frozen solvent matrixes, and have investigated their magnetic properties in the solid state by means of magnetic susceptibility measurements and X-ray crystallographic analysis.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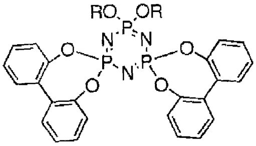
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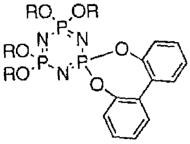
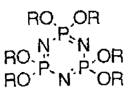
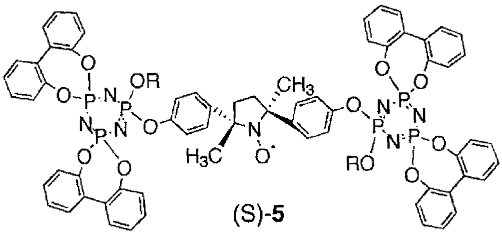
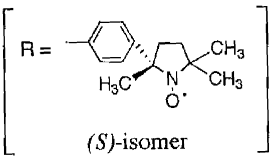

(S)-**3**


(S)-**4**


(S)-**5**


(*S*)-isomer

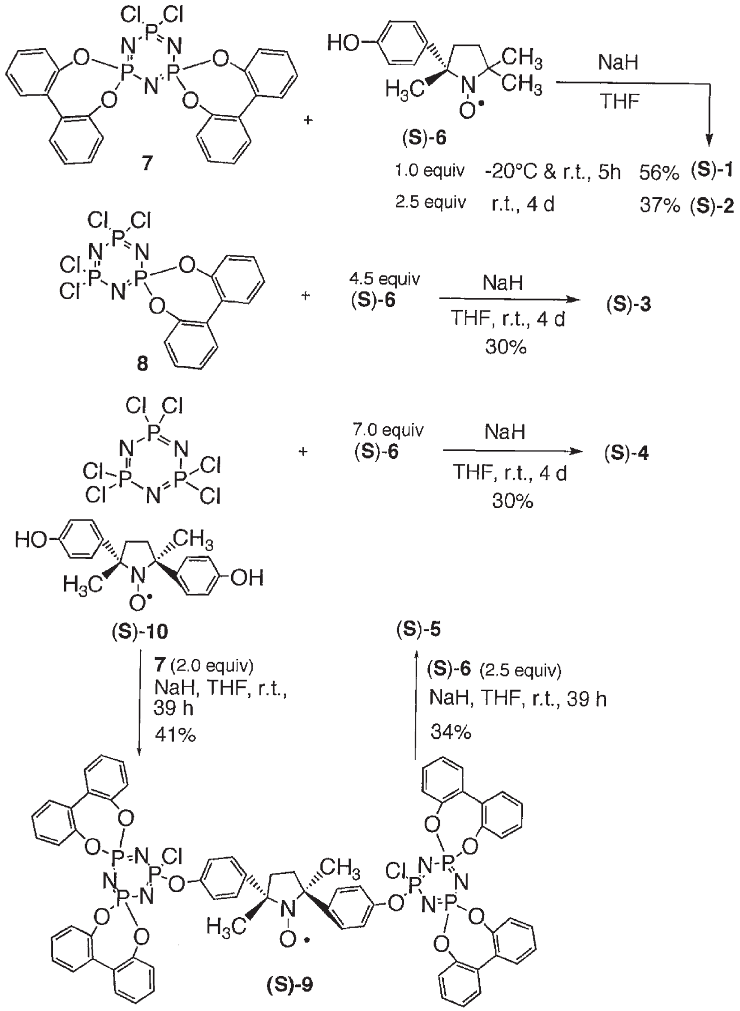
PREPARATION OF CHIRAL NITROXIDE-CYCLOTRIPHOSPHAZENE HYBRID COMPOUNDS

Enantiomerically enriched hybrid compounds (S)-**1**$\sim$(S)-**4** were synthesized in 30$\sim$56% isolated yields by the reaction of (2S)-2,5,5-trimethyl-2-(4-hydroxyphenyl)pyrrolidine-1-oxy1 (**6**) (88% ee) [6] with appropriate chlorocyclotriphosphazene derivatives such as $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (**7**) [7], $[N_3P_3Cl_4(O_2C_{12}H_8)]$ (**8**) [7] and $N_3P_3Cl_6$ in the presence of a base. These reactions were followed by purification by flash column chromatography on silica gel eluting with hexane/ethyl acetate and subsequent recrystallization from CH_2Cl_2/Et_2O (Scheme 1).The enantiomerically enriched 2,2′-bridged 2,2,2′,2′-trinitroxide-bis(cyclotriphosphazene) hybrid compound (S)-**5** was obtained in 34% isolated yield by the reaction of (S)-**6** with (S)-**9** which, in turn, was prepared in 41% yield by the reaction of (S)-**10** (97% ee)[6] with 2 equivalents of **7** (Scheme 1). The purity of the (S)-**1**$\sim$(S)-**5** obtained was found to be satisfactory by HPLC analysis, elemental analysis and FD- or ESI-MS analysis.

EPR SPECTROSCOPIC STUDIES

As expected, no coupling with a phosphorus atom was observed in all EPR spectra of the degassed and diluted solutions ($\sim 10^{-4}$ M) of (S)-**1** $\sim$(S)-**5** in 2-methyltetrahydrofuran (MeTHF) at 298 K or lower temperatures, indicating the absence of intramolecular through-bond spin polarization and through-bond electron-exchange interaction.

The EPR spectrum of (S)-**2** in MeTHF at 298 K is shown in Figure 1a. As confirmed by the computer simulation (Fig. 1b), the spectrum ($H_0 = 336.3\,\text{mT}, g = 2.0061$, $a_N = 1.36\,\text{mT}$) is most likely to consist of the following three components; an isolated NO radical species (triplet, $I = 1$, $a_N = 1.35\,\text{mT}$, $\Delta H_{pp} = 0.16\,\text{mT}$, relative intensity 100), a coupled NO radical species (quintet, $I = 1 \times 2$, $a_N = 0.675\,\text{mT}$, $\Delta H_{pp} = 0.32\,\text{mT}$, relative intensity 10) and a dipolar component due to the anisotropic molecular rotation. In glassy MeTHF solution at 77 K, (S)-**2** displays in the $\Delta m_s = \pm 1$ region only anisotropy of the g-value of the two independent spins giving no fine structure (Fig. 1c). However, the forbidden transition ($\Delta m_s = \pm 2$) at half the magnetic field is observed as a broad singlet ($H_0 = 168.1\,\text{mT}$, $\Delta H_{pp} = 3.3\,\text{mT}$) signal and the signal intensities of this transition are in proportion to the inverse of the absolute temperatures according to the Curie law in the range between 10 and 80 K (Fig. 2). Accordingly, depending on the molecular conformation, the molecule of (S)-**2** has proved to be able to have a triplet or nearly degenerate singlet-triplet ground state besides the dominant doublet state.



SCHEME 1 Preparation of chiral nitroxide-cyclotriphosphazene hybrid compounds (S)-**1** $\sim$ (S)-**5**.

The EPR spectrum of the isotropic solution ($\sim 10^{-4}$ M) of (S)-**3** in MeTHF at 298 K displays a broad ($H_0 = 336.4\,\mathrm{mT}$, $\Delta H_{\mathrm{pp}} = 1.8\,\mathrm{mT}$) signal centered at $g = 2.0057$ (Fig. 3a), which is ascribed to the hyperfine coupling by intramolecular electron-exchange interactions among four NO radical groups. In glassy MeTHF solution at 77 K, (S)-**3** shows a complex spectrum which is considered to consist of an isolated NO

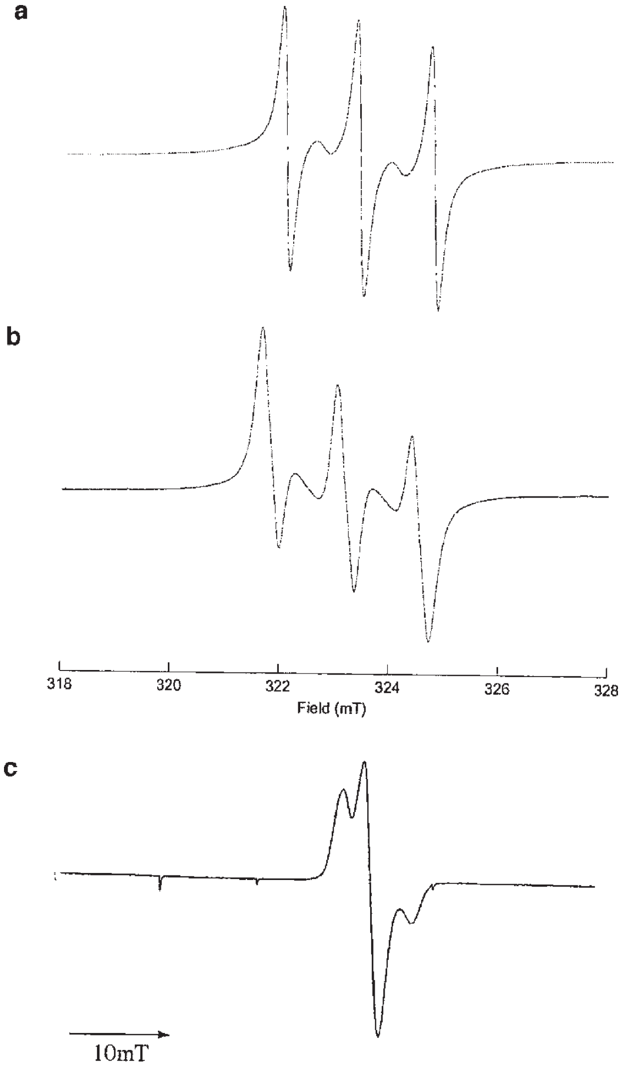


FIGURE 1 (a) EPR spectrum of a solution ($\sim 10^{-4}$ M) of (S)-**2** in MeTHF at 298 K. (b) Computer simulation of the above spectrum with the values given in the text. (c) EPR spectrum in a glassy solution ($\sim 10^{-4}$ M) of (S)-**2** in MeTHF at 77 K.

radical species ($S = 1/2$) and a doubly coupled NO radical species ($S = 1$) from which the zero-field splitting constants are determined to be $D = 10.5\,\mathrm{mT}$ ($|D/hc| = 9.8 \times 10^{-3}\,\mathrm{cm}^{-1}$) and $E = 0.32\,\mathrm{mT}$

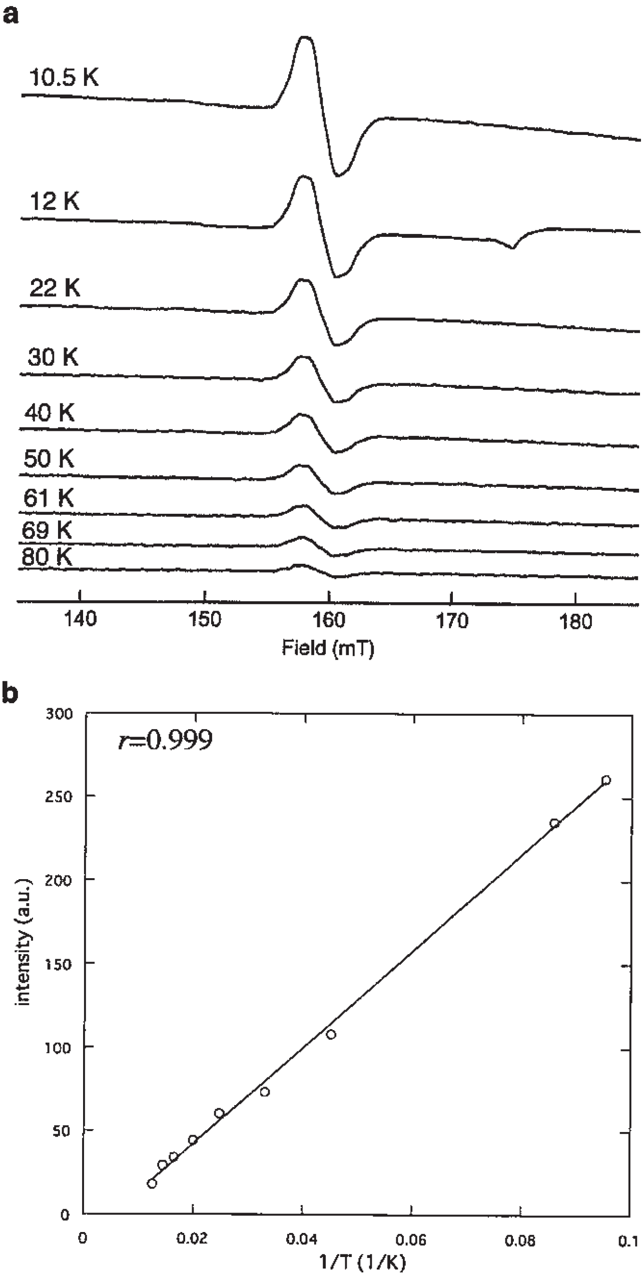


FIGURE 2 (a) Evolution of the half-field resonance signal of (S)-**2** in the $\Delta m_s = \pm 2$ region in MeTHF ($\sim 10^{-3}$ M) from 10 to 80 K. (b) Curie plot of the half-field resonance signal intensities with the inverse of the temperatures from 10 to 80 K.

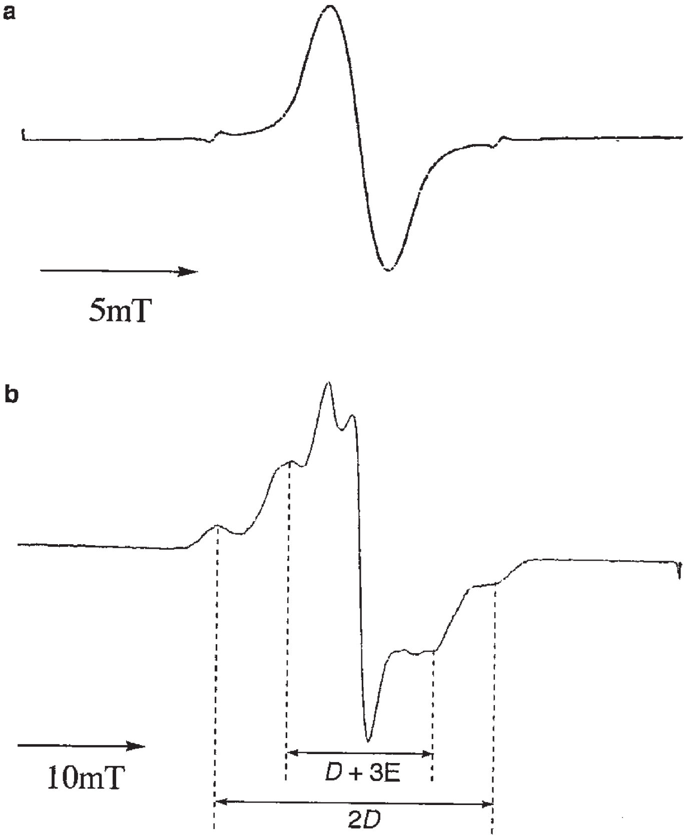


FIGURE 3 EPR spectra of (S)-**3** (a) in MeTHF solution ($\sim 10^{-4}$ M) at 298 K and (b) in MeTHF glassy solution ($\sim 10^{-4}$ M) at 77 K.

($|E/hc| = 3.0 \times 10^{-4}\,\mathrm{cm}^{-1}$) (Fig. 3b). The average spin-spin distance is estimated to be 6.4 Å within the point-dipole approximation [8]. Since the solubility of (S)-**3** in MeTHF is low, a CH_2Cl_2 solution ($\sim 10^{-2}$ M) of (S)-**3** was used to detect the half-field resonance in the $\Delta m_s = \pm 2$ region. The observation of a broad singlet ($H_0 = 159.3$ mT, $\Delta H_{pp} = 3.4$ mT) signal is consistent with a triplet or nearly degenerate singlet-triplet ground state for (S)-**3**, because the intensities of this signal are in proportion to the inverse of the absolute temperatures according to the Curie law in the range between 7 and 75 K (Fig. 4).

The EPR spectrum of the isotropic solution ($\sim 10^{-5}$ M) of (S)-**4** in MeTHF at 298 K also displays a broad ($H_0 = 335.9$ mT, $\Delta H_{pp} = 1.5$ mT) signal centered at $g = 2.0069$ (Fig. 5a), which is attributed to

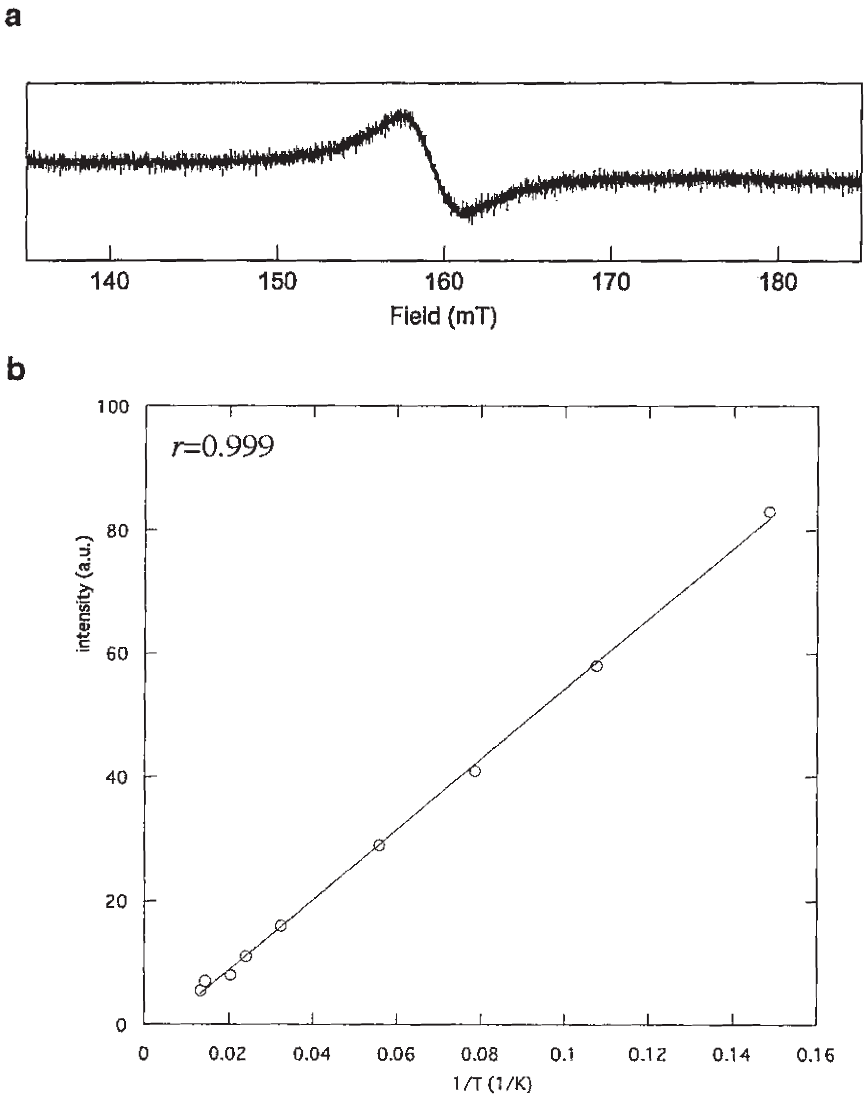


FIGURE 4 (a) The half-field resonance signal of (S)-**3** in the $\Delta m_s = \pm 2$ region in CH_2Cl_2 ($\sim 10^{-2}$ M) at 75 K. (b) Curie plot of the half-field resonance signal intensities with the inverse of the temperatures from 7 to 75 K.

hyperfine coupling by the six equivalent NO radical groups. In glassy MeTHF solution at 77 K, (S)-**4** displays in the $\Delta m_s = \pm 1$ region a broad singlet ($H_0 = 328.2\,\mathrm{mT}$, $\Delta H_{pp} = 3.4\,\mathrm{mT}$) signal (Fig. 5b). The observation of a broad singlet ($H_0 = 161.2\,\mathrm{mT}$, $\Delta H_{pp} = 2.8\,\mathrm{mT}$) signal in the

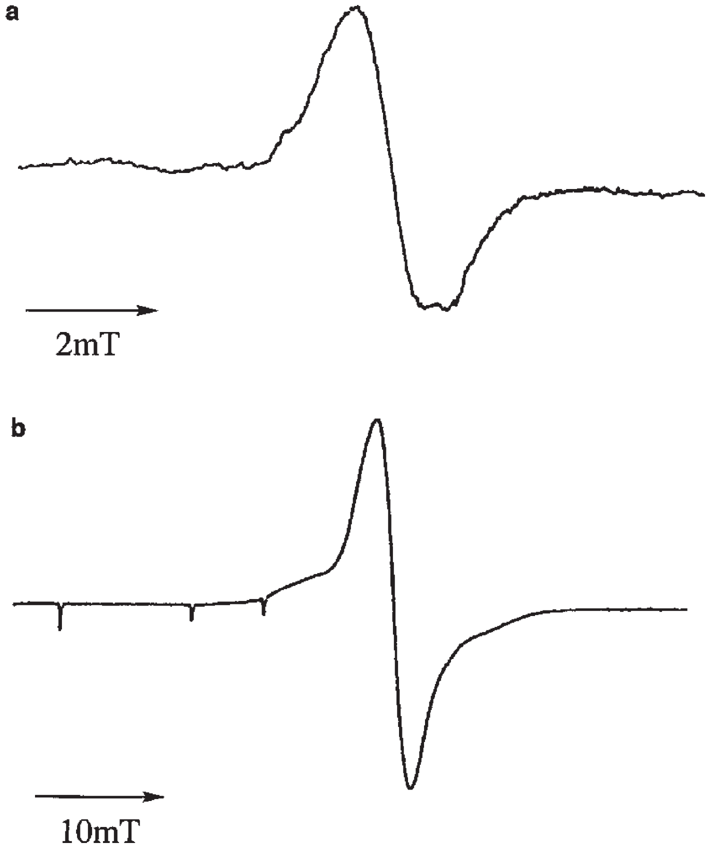


FIGURE 5 EPR spectra of (S)-**4** (a) in MeTHF solution ($\sim 10^{-5}$ M) at 298 K and (b) in MeTHF glassy solution ($\sim 10^{-5}$ M) at 77 K.

$\Delta m_s = \pm 2$ region and the proportion of its signal intensities to the inverse of the absolute temperatures according to the Curie law in the range between 10 and 50 K is consistent with the existence of a multiplet or nearly degenerate singlet-multiplet ground state for (S)-**4** (Fig. 6).

Similarly to (S)-**2**, the EPR spectrum of the isotropic solution ($\sim 10^{-4}$ M) of (S)-**5** in MeTHF at 298 K displays a broad triplet ($H_0 = 336.4$ mT, $\Delta H_{pp} = 0.4$ mT, $g = 2.0065$, $a_N = 1.29$ mT) (Fig. 7a). In a glassy solution ($\sim 10^{-3}$ M) of (S)-**5** at 77 K, a spectrum showing only anisotropy of the g-value of the three independent spins is observed in the $\Delta m_s = \pm 1$ region (Fig. 7b). Due to the low solubility of (S)-**5**, a CH_2Cl_2 solution ($\sim 10^{-3}$ M) of (S)-**5** is used to detect the

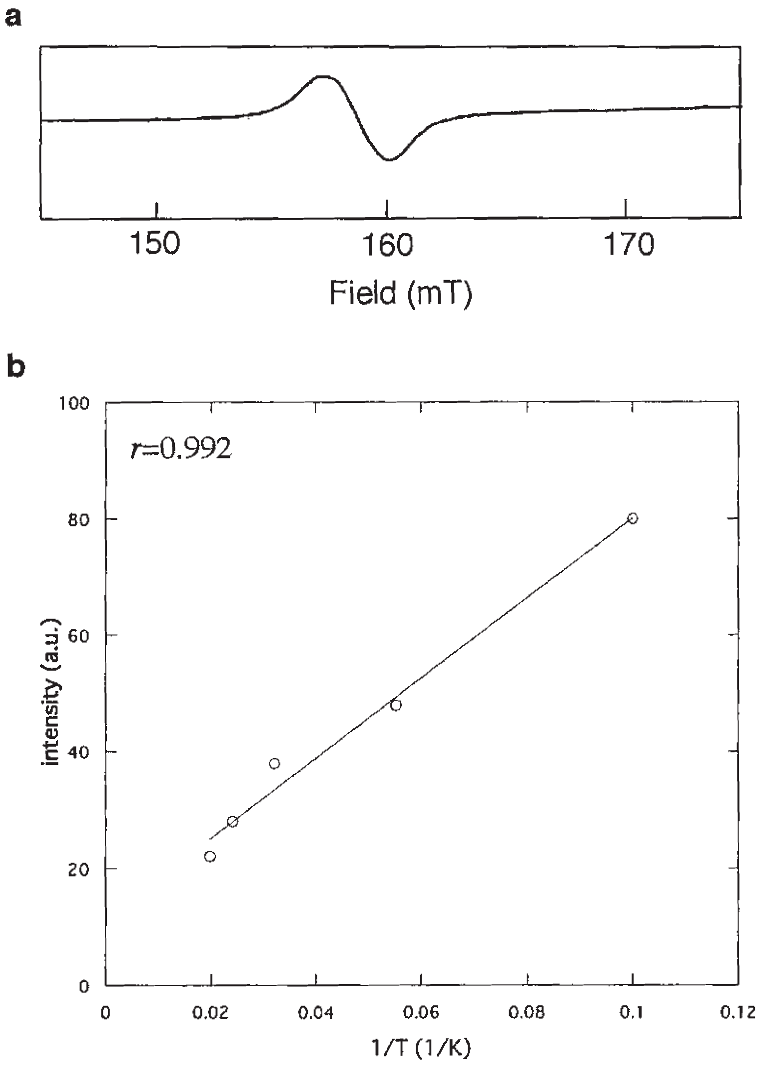


FIGURE 6 (a) The half-field resonance signal of (S)-**4** in the $\Delta m_s = \pm 2$ region in MeTHF ($\sim 10^{-3}$ M) at 77 K. (b) Curie plot of the half-field resonance signal intensities with the inverse of the temperatures from 10 to 50 K.

signal in the $\Delta m_s = \pm 2$ region. The observation of a broad singlet ($H_0 = 159.6$ mT, $\Delta H_{pp} = 3.7$ mT) signal and the proportion of its signal intensities to the inverse of the absolute temperatures according to the Curie law between 7 and 75 K indicates the presence of a quartet

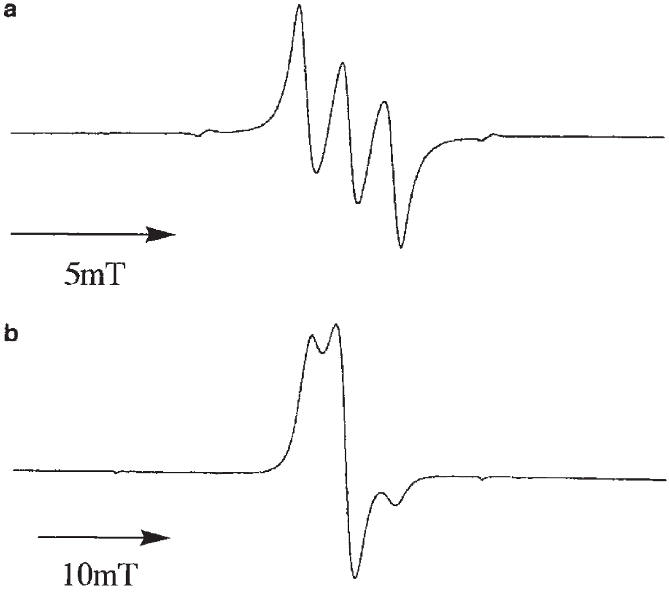


FIGURE 7 EPR spectra of (S)-**5** (a) in MeTHF solution ($\sim 10^{-4}$ M) at 298 K and (b) in MeTHF glassy solution ($\sim 10^{-3}$ M) at 77 K.

or nearly degenerate doublet-quartet ground state together with the dominant doublet state for (S)-**5** (Fig. 8).

Thus, (S)-**2** and (S)-**5** having two radical groups on the same phosphorus atom show very weak intramolecular through-space electron-exchange interactions at 298 K and almost no magnetic interaction at 77 K, while (S)-**3** and (S)-**4** which have two and three radical groups disposed on the same side of a cyclotriphosphazene ring, respectively, have turned out to show strong intramolecular through-space electron-exchange interactions at both 298 and 77 K.

MAGNETIC SUSCEPTIBILITY MEASUREMENT

The magnetic susceptibility has been measured at temperatures ranging between 2 and 300 K using a SQUID susceptometer at an applied field of 0.5 T. As far as the bulk magnetic properties are concerned, all solid samples of (S)-**1** $\sim$ (S)-**5** show weak antiferromagnetic interactions below 20 K (Fig. 9). The constant χT value between 20 and 300 K for each compound corresponds to the total amount of free $S = 1/2$ spins with the g-factor of 2.0, indicating that the radical purity of the obtained nitroxides (S)-**1** $\sim$ (S)-**5** is satisfactory and that

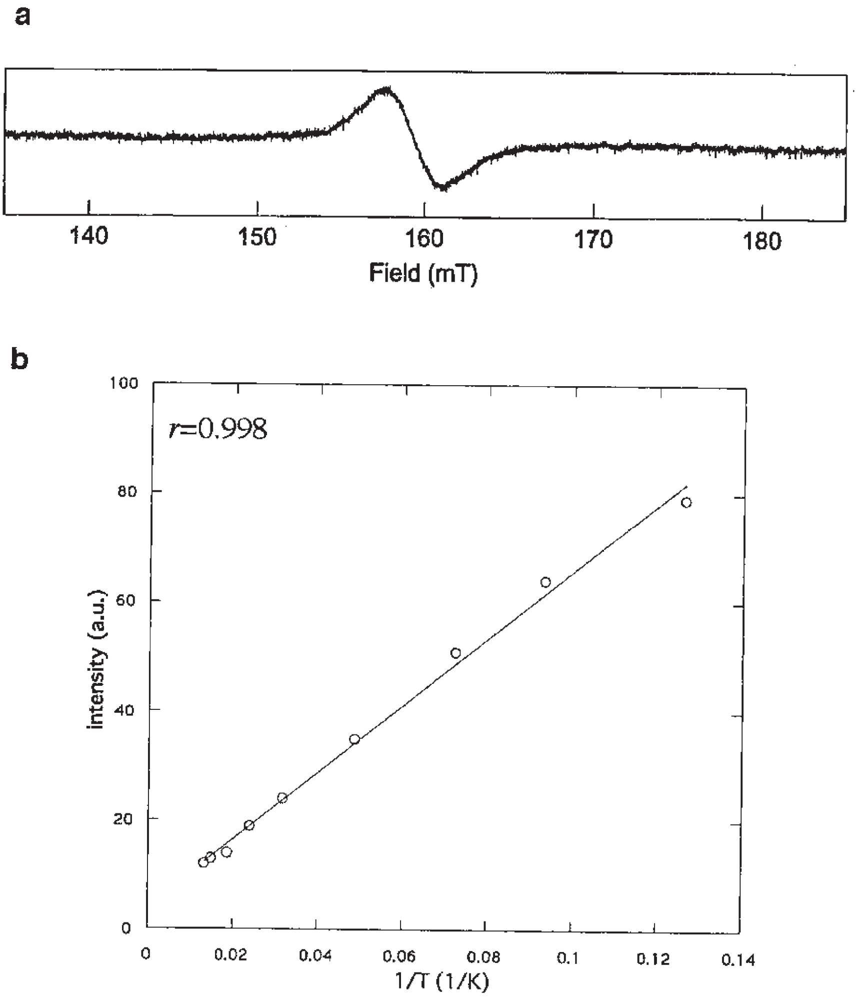


FIGURE 8 (a) The half-field resonance signal of (S)-**5** in the $\Delta m_s = \pm 2$ region in CH_2Cl_2 ($\sim 10^{-3}$ M) at 75 K. (b) Curie plot of the half-field resonance signal intensities with the inverse of the temperatures from 7 to 75 K.

the intra- and inter-molecular exchange interactions are much smaller than the thermal energy k_BT of 20 K.

CRYSTAL STRUCTURE OF (S)-2

A single crystal of (S)-**2** of adequate quality for X-ray crystallographic analysis was obtained by recrystallization from CH_2Cl_2/Et_2O. The

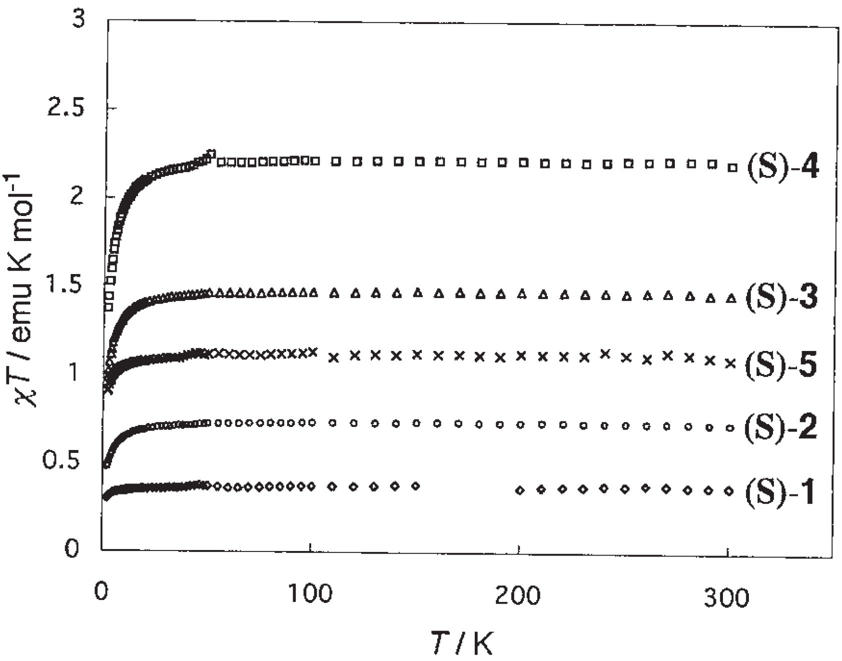


FIGURE 9 Temperature dependence of the magnetic susceptibility of (S)-**1** ~ (S)-**5** measured between 2 and 300 K at an applied field of 0.5 T. (S)-**1**: Curie constant $C = 0.372$ emu K mol^{-1} (radical purity 99%), Weiss temperature $\theta = -1.22$ K; (S)-**2**: $C = 0.731$ emu K mol^{-1} (97%), $\theta = -0.83$ K; (S)-**3**: $C = 1.47$ emu K mol^{-1} (98%), $\theta = -0.59$ K; (S)-**4**: $C = 2.22$ emu K mol^{-1} (99%), $\theta = -0.56$ K; (S)-**5**: $C = 1.11$ emu K mol^{-1} (99%), $\theta = -0.34$ K.

crystal structure is characterized by the herringbone-like homochiral molecular arrangement in the 2_1 column along the b axis, in which one of the two NO groups of a molecule interacts with the two nearest NO groups (both O···O distances: 5.734 Å) in two adjacent molecules to give a one-dimensional chain of NO groups while the other NO group is isolated (Fig. 10) [9]. Since no other intermolecular magnetic interaction is observed, these through-space NO···ON interactions are most likely to be responsible for the observed weak antiferromagnetic behavior below 50 K. In contrast, the intramolecular O···O distance (13.349 Å) is too long to effect an appreciable magnetic interaction, as confirmed by the EPR studies described above.

In accordance with this crystal structure, the magnetic behavior of (S)-**2** can be best fitted to a one-dimensional regular Heisenberg-linear chain model of S = 1/2 with an antiferromagnetic coupling constant

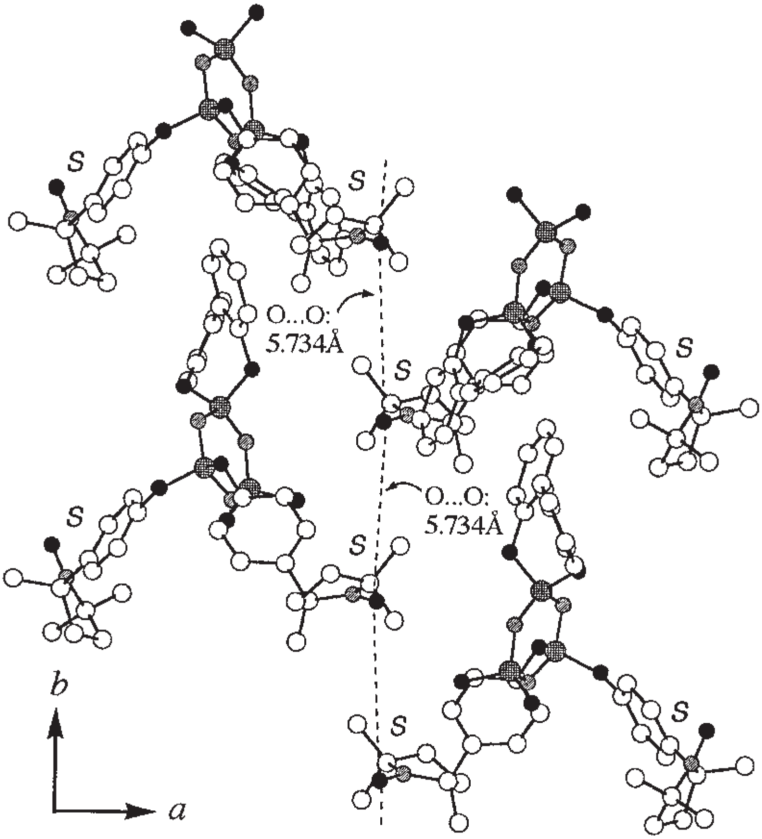


FIGURE 10 Crystal structure of (S)-**2** viewed down the *c* axis. The carbon, nitrogen, oxygen, and phosphorus atoms are represented by open, cross-hatched, closed, and grid circles, respectively. All hydrogen atoms and one of two biphenyl groups are omitted for the sake of clarity.

between spins, J/k_B of -2.4 K (Fig. 11), according to the following Eq. (1), where x is $|J|/k_BT$ and 0.975 denotes the radical purity [10].

$$\chi_m T = \left[(Ng^2\mu_B^2/k_B) \times (A + Bx + Cx^2)/(1 + Dx + Ex^2 + Fx^3) + 0.375\right] \times 0.975 \tag{1}$$

CONCLUSIONS

From the EPR spectroscopic studies, it has been indicated that distinct intramolecular through-space electron-exchange interactions exist at 298 and 77 K between two or three neighboring radical moieties which

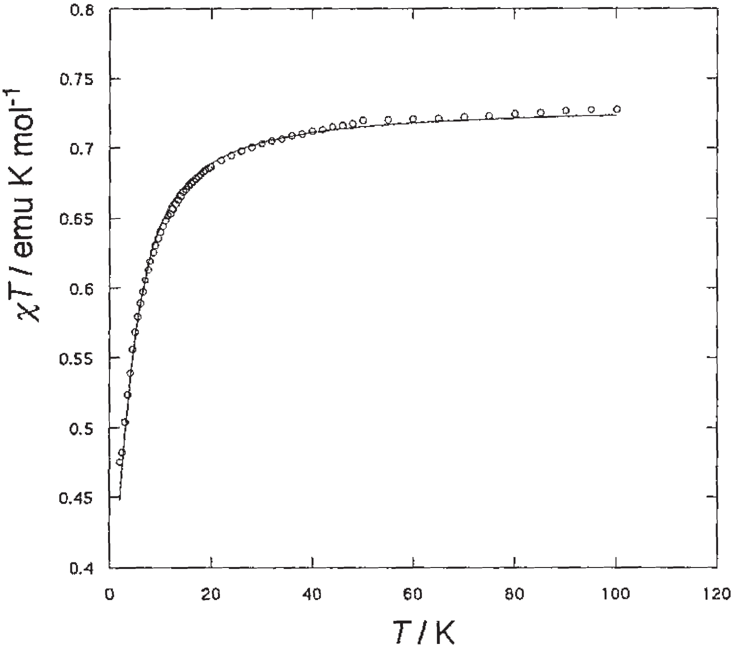


FIGURE 11 Magnetic susceptibility of (S)-**2** in the χT vs. T plot measured between 2 and 300 K at an applied field of 0.5 T. The circles represent the χT values of the polycrystalline sample, while the solid line ($r = 0.997$) is calculated from Eq. (1) with the parameter $|J|/k_B = 2.4\,\mathrm{K}, g = 2.006, \alpha = 1$, and a radical purity of 0.975.

are disposed on the same side of the cyclotriphosphazene ring with respect to (S)-**3** and (S)-**4**. However, the through-space magnetic interactions between two radical groups on the same phosphorus atom are very weak with regard to (S)-**2** and (S)-**5**. The half-field resonance corresponding to a triplet state configuration is observed in glassy solution for all compounds, and the intensities of this signal are in proportion to the inverse of the absolute temperatures according to the Curie law in the range between ca. 10 and 75 K, implying the intramolecular paramagnetic nature in this temperature range.

The magnetic susceptibility measurements indicate that all powder samples of (S)-**1** ~ (S)-**5** are paramagnetic between 20 and 300 K and show weak antiferromagnetic interactions between 2 and 20 K. From the above EPR study results and the X-ray crystallographic analysis of (S)-**2**, it has been suggested that the observed antiferromagnetic behaviors for all of them in the solid state may be ascribed to an intermolecular origin.

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[9] The X-ray data were collected at 294 K on an Enraf-Nonius Kapp CCD diffractometer. The crystal structure was solved by the direct methods (SIR) and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. All of the crystallographic calculations were performed by using CrystalStructure software package of the Molecular Structure Corp. Crystal data for (S)-**2**: $C_{50}H_{50}N_5O_8P_3$, $Mr = 941.90$, $0.50 \times 0.40 \times 0.40$ mm, monoclinic, space group $P2_1$ (#4), $a = 13.9687(3)$, $b = 11.3822(2)$, $c = 16.1455(5)$ Å, $\beta = 110.8350(9)^\circ$, $V = 2399.18(10)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.304\,\text{gcm}^{-3}$, $2\theta_{\max} = 55.0^\circ$, MoK$\alpha$ ($\lambda = 0.71069$ Å), $\mu = 1.83\,\text{cm}^{-1}$, ω scans, $T = 298$ K, 7740 independent reflections, 5739 observed reflections ($I > 3.0\sigma(I)$), 645 refined parameters, $R = 0.057$, $R_w = 0.068$, $\Delta\rho_{\max} = 0.44$ eÅ^{-3}, $\Delta\rho_{\min} = -0.57$ eÅ^{-3}. CCDC-217205 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).

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