Organic biradical compounds with a mesogenic core and long alkoxy groups: preparation, structures and magnetic properties

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ABSTRACT: Series of organic biradical compounds **3a–3h** consisting of a mesogenic core (biphenyl, naphthalene, azobenzene and azoxybenzene) and long alkoxy groups with PROXYL or TEMPO radicals were prepared. The TEMPO derivatives (**3b**, **3d**, **3f**, and **3h**) were found to show fairly large antiferromagnetic interactions ($J = -34 \sim -45$ K) being well expressed by singlet-triplet model irrespective of the mesogenic cores and the behavior is understandable by taking a hand-in-hand like assembled structure into consideration. On the other hand, only weak antiferromagnetic interactions with Curie–Weiss behavior were observed in all of the PROXYL derivatives (**3a**, **3c**, **3e**, and **3d**) affording a sharp contrast with the TEMPO-based biradicals. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: radicals; aminoxyl radicals; magnetic property; supramolecular structure; crystal structure

INTRODUCTION

Considerable attention has been paid in the field of material science to the development of organic and molecular-based magnetic materials in recent years and stable aminoxyl radicals have well been recognized as the crucial building blocks for constructing a variety of spin systems.[1]

During the course of our studies to develop novel organomagnetic materials, we have been interested in developing multifunctional spin systems with inherent magnetic properties in synergy with other physical properties as conductivity, photo-functionality, or liquid crystalline property by using stable radicals, especially aminoxyl radicals, as the building blocks.[2] The spin systems with liquid crystalline property are of particular interest because of the possibility of generation of a large paramagnetic susceptibility anisotropy in the oriented molecular aggregates and/or that of the tunable magnetic properties through the phase transitions.[3] Therefore, we have been interested in preparing such spin systems that have various mesogenic cores on one hand and long alkyl substituents on the other hand to examine their structure/ magnetic property relations together with the possible liquid crystalline properties. The existence of a liquid crystalline phase has been found in a heptylbiphenyl

derivative with 4-(*N*-methyl)amino-TEMPO-substituent (**1**; R = CH$_3$(CH$_2$)$_6$, R' = CH$_3$)[4] and unusual thermo-magnetic properties have also been disclosed in this and in a cyanobiphenyl derivative (**2**; $n = 11$).[5] At the same time, it was clarified during the studies that the specific assemblies of molecules with supramolecular structures are relevant to the formation of mesogenic phases and thermomagnetic properties. We then designed several biradical compounds having mesogenic/aromatic cores as biphenyl, naphthalene, azobenzene or azoxybenzene as well as long alkyl groups with aminoxyls at their ends. In this paper, we wish to report the preparation, structures and magnetic properties of a series of biradical compounds in details to correlate their structure/magnetic property relations.[6]

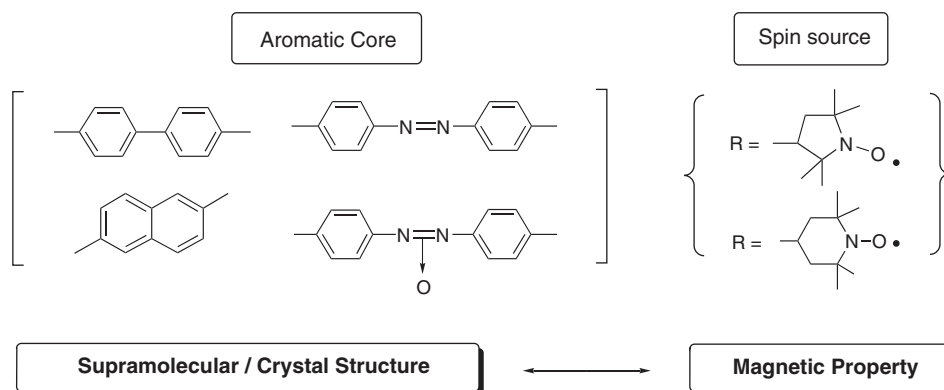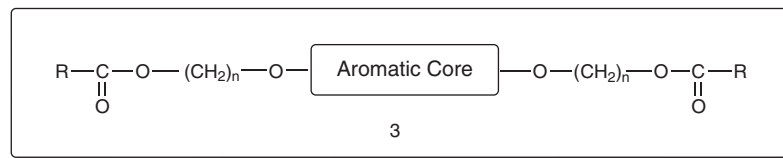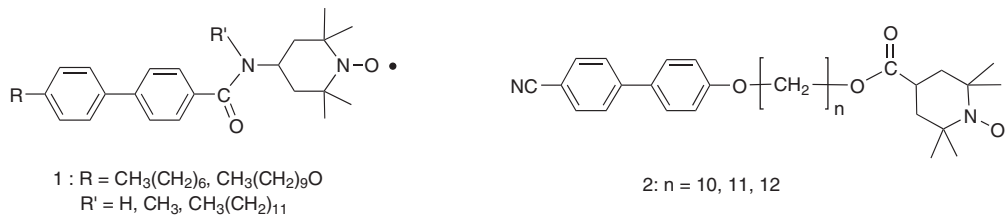## RESULTS AND DISCUSSION

Preparation of radical compounds

The preparation of the biradical compounds **3a–3h** was carried out according to Scheme 1. The treatment of 11-bromo-1-undecanol **4** with either 3-carboxy-PROXYL or 4-carboxy-TEMPO gave either bromoundecanoxycarbonyl-PROXYL **5a** or the corresponding TEMPO derivative **5b** in moderate yields. When equimolar amount of bromoester **5a** or the corresponding TEMPO derivative **5b** was reacted with a mixture of 4,4'-dihydroxybiphenyl and potassium carbonate in THF/DMF (1:3) at 130 °C, mono-bromoundecanoxycarbonyl-PROXYL derivative

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1 : R = CH₃(CH₂)₆, CH₃(CH₂)₉O
R' = H, CH₃, CH₃(CH₂)₁₁

2: n = 10, 11, 12

3

Aromatic Core   Spin source

Supramolecular / Crystal Structure   ⟷   Magnetic Property

CHART

6a or the corresponding TEMPO derivative **6b** was obtained in 22% or 50% yield, respectively. On the other hand, bis-PROXYL-substituted biphenyl **3a** or the corresponding TEMPO derivative **3b** could be obtained, when two molar amount of either bromoester **5a** or **5b** was used in the condensation reaction. In the similar manner, biradical compounds with other mesogenic cores as naphthalene (**3c**, **3d**), azobenzene (**3e**, **3f**), and
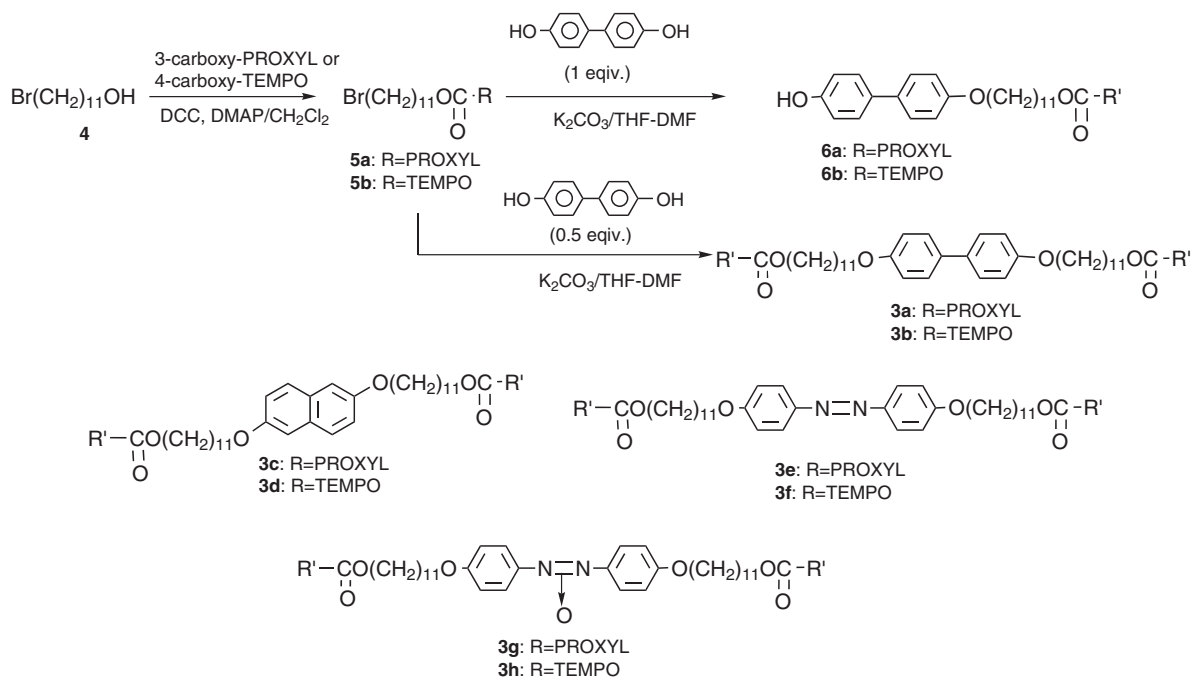
Scheme 1

azoxybenzene (**3g**, **3h**) could be prepared in moderate yields by using two molar amount of the bromoesters with one molar amount of 4,4′-dihydroxynaphthalene, 4,4′-dihdroxylazobenzene or 4,4′-dihdroxyazoxybenzene, respectively.

Since it was of interest to see the possibility of mesogenic properties of the biradicals, DSC as well as polarizing microscope measurements were then carried out, but unfortunately no distinct occurrence of any transition to a liquid crystalline phase could be discerned for the biradicals from their data of DSC as well as polarizing microscope measurements. It was also anticipated that the *trans*-azobenzene derivatives **3e** and **3f** would show photo-isomerization to the corresponding *cis*-azobenzenes by irradiation[10] and we then tried to isomerizes the TEMPO derivative **3f** by irradiation with the light of 365 nm under various conditions. Although the absorption spectral change could be observed in solution by the irradiation, the isolation of the *cis*-isomers was not possible so far as we examined probably because of unstable nature of the isomer in the solid state.

Magnetic properties of radical compounds

The temperature dependence data of their magnetic susceptibilities were obtained by the SQUID measurements from 2 to 300 K and the magnetic data for the PROXYL and the TEMPO derivative with biphenyl core (**3a** and **3b**) are shown in Fig. 1. Thus, weak antiferromagnetic interaction being based on Curie–Weiss law[11] was observed in the spins of the PROXYL derivative **3a** with a Curie constant of 0.64 emu K mol^{-1} and a Weiss temperature of -1.11 K. The value of the Curie constant is close to that expected for two non-interacting $S = 1/2$ spins (0.75) but somewhat smaller

probably because of concomitance of some diamagnetic impurities and the spin concentration is estimated to be 85%. On the other hand, antiferromagnetic interaction being well expressed by singlet-triplet model[12] was found for the corresponding TEMPO derivative **3b** with fairly large *J*-value of -43.7 K to show clear difference with that of the PROXYL derivative. As summarized in Table 1, antiferromagnetic interactions with the Curie–Weiss behavior was apparently observed in the spins of the PROXYL-based derivatives, that is **3a**, **3c**, **3e**, and **3g** irrespective of the mesogenic/aromatic cores. On the contrary, the predominance of the ST behavior was clarified in the spins of the TEMPO-based derivatives **3b**, **3d**, **3f**, and **3h** with fairly large *J*-values (*ca.* 34–45 K). Thus, a distinct difference in their intermolecular magnetic interactions was found to be present between two kinds of the biradical compounds. In turn, no significant difference was observed in the magnetic behavior of monoradicals **6a** and **6b**, being based on Curie–Weiss model irrespective of the kind of aminoxyls.

Molecular/crystal structures of biradical 3b and 3d

In order to see the structure-property relation, we tried to obtain their single crystals suitable for X-ray analysis and the corresponding single crystals could only be obtained for **3b** and **3d**, after several trials of recrystallization under various conditions. The difficulty to obtain the single crystals appears to be partially due to the existence of the long and flexible alkyl chains and also to the existence of possible diasteromeric mixtures for PROXYL-based derivatives, which we could not separate nor estimate the isomer ratios. The single-crystal diffraction data for **3b** and **3d** were recorded using a Quantum CCD area
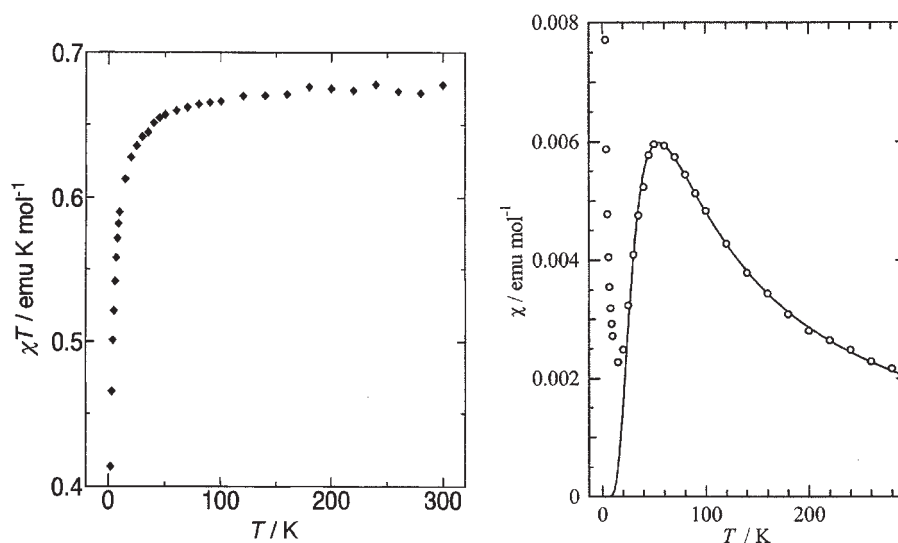

Figure 1. Magnetic data of biradicals **3a** (left) and **3b** (right)

Table 1. Magnetic data of biradicals **3a**–**3h** and monoradicals **6a**, **6b**

Compound	Magnetic interaction	C^a (emu K mol^{-1})	θ^b (K)	J^c (K)
3a	antiferromagnetic[d]	0.64 (85)	−1.11	—
3b	antiferromagnetic[e]	—	—	−43.7 (87)
3c	antiferromagnetic[d]	0.52 (69)	−1.34	—
3d	antiferromagnetic[e]	—	—	−44.7 (98)
3e	antiferromagnetic[d]	0.75 (100)	−2.72	—
3f	antiferromagnetic[e]	—	—	−38.5 (93)
3g	antiferromagnetic[d]	0.75 (100)	−1.07	—
3h	antiferromagnetic[e]	—	—	−33.9 (89)
6a	antiferromagnetic[d]	0.31 (83)	−2.58	—
6b	antiferromagnetic[d]	0.30 (80)	−1.31	—

[a] Curie constant. The numbers in parentheses denote the estimated spin concentration in percentage.
[b] Weiss temperature.
[c] Exchange interaction.
[d] Curie–Weiss model.
[e] Singlet–Triplet model.

detector on a Rigaku AFC-7R diffractometer at room temperature and the data are summarized in Table 2.

The molecular structures of biradicals (**3b** and **3d**) with biphenyl as well as naphthalene cores obtained by the X-ray analyses are shown in Fig. 2 (upper: biphenyl derivative **3b**, lower: naphthalene derivative **3d**). Thus, both molecules have similar structural features with alkyl groups extending from the central aromatic rings like long arms and with the TEMPO groups at both ends tilting largely from the central rings like hands (a TEMPO group appears to be corresponding to a hand) with fingers of aminoxyl groups irrespective of the aromatic rings.

Table 2. Summary of crystal data for **3b** and **3d**

	3b	**3d**
Formula	$C_{54}H_{88}N_2O_8$	$C_{52}H_{84}N_2O_8$
Formula weight	893.30	865.2
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$/a	P2$_1$/a
A/Å	11.104(8)	10.7581(4)
B/Å	8.54(3)	8.4192(9)
C/Å	28.61(3)	28.2880(13)
β/degrees	91.19(3)	98.4747(11)
V/Å^3	2712.3(72)	2534.2(3)
Z	2	2
D (calc)/g cm^{-3}	1.094	1.13
Number of measured reflections	9193	5588
Number of independent reflections	3500	5249
Number of used reflections	732[a]	3086[b]
Number of parameters refined	289	289
R	0.089	0.116
R_W	0.090	0.056

[a] Refinement F > 3σ.
[b] Refinement F > 2σ.

In the crystal structure of biradical **3b**, the molecules are stacking aslant along the *a*-axis to form columnar structures, in which the aromatic rings are not stacking in parallel but actually in stepwise manner (Fig. 3, upper). In the columnar structure, TEMPO groups and alkoxybiphenyl moieties are stacking separately. Such an assembled feature is rather similar to the previous monoradical crystals of a heptylbiphenyl derivative with 4-(*N*-methyl)amino-TEMPO-substituent[4] or a cyanobiphenyl derivative with undecanoxylcarbonyl-TEMPO substituent[5] and, moreover, a hand-in-hand like assembling is additionally possible in this case (*vide infra*). A similar assembled feature was observed in the crystal structure of biradical **3d** with a naphthalene core (Fig. 3, lower).

A fairly close contact is observed between the spin-bearing oxygen atoms of the neighboring molecules up to 3.52 Å (Fig. 4, upper and middle), in which the orientation of both spins is suggested to be somewhat distorted, for example, the angle around the central oxygen atom of O⋯O—N moiety is estimated to be *ca.* 110° presumably to avoid the steric repulsion of the bulky methyl groups around the spin centers. Although several short contacts (3.43–3.54 Å) are observed between the oxygen atom of a spin center and the hydrogen atoms of methyl groups of the neighboring molecules, the former short contact between the oxygen atoms is thought to be predominantly responsible for the singlet-triplet behavior in this biradical crystal.[13] It is noteworthy that there exists fairly strong antiferromagnetic interaction with singlet-triplet behavior in this biradical **3b**, even if the molecule itself appears to be too large to give such an interaction,[14] and that is presumed to be due to the supramolecular structure based probably on a hand-in-hand motif found in this biradical crystal (Fig. 3, lower). Similarly, a fairly close contact is also observed in the crystal structure of biradical **3d** between the oxygen atoms of the neighboring molecules up to 3.50 Å in this case.
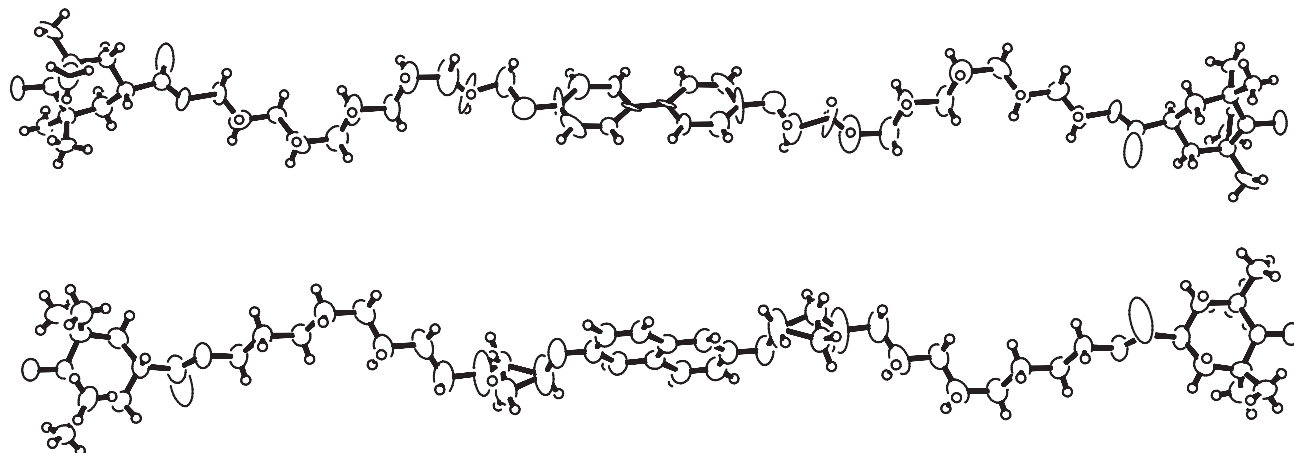
Figure 2. Molecular structures of biradical **3b** (upper) and **3d** (lower)

The similar magnetic property of this compound with that of the biradical **3b** could be understandable by taking similar structural feature into consideration. Thus, the TEMPO group appears to play a significant role like a hand together with the hydrophobic alkyl and aromatic groups for assembling the large molecules in the crystals of **3b** and **3d** and, at the same time, to give the relatively strong intermolecular spin–spin interactions. Also, similar structural features can be presumed for other biradicals **3f** and **3h** because of the similarity of the magnetic behavior and the *J*-values in spite of the difference of the mesogenic/aromatic cores.

Although it is hardly possible to see the structure-property relations for the PROXYL-based biradical compounds (**3a**, **3c**, **3e**, and **3g**) with no information of their crystal structures, it might be possible to presume that the decrease of intermolecular interactions in their assembled structures of the PROXYL-based biradicals would result in the weak intermolecular spin–spin interactions probably because of the decrease of the symmetry from TEMPO to PROXYL as well as the existence of the racemic mixtures derived from the existence of an asymmetric carbon atom in each PROXYL derivative.

CONCLUSIONS

Organic biradical compounds having such mesogenic/aromatic cores as biphenyl, naphthalene, azobenzene or azoxybenzene cores together with long alkyl groups and TEMPO or PROXYL radicals (**3a–3h**) were prepared and their structure-property relationships were investigated. Fairly large antiferromagnetic interactions being well expressed by ST model observed in the spins of TEMPO-based biradical compounds could rationally be understood by taking hand-in-hand like assembled structures into consideration with relatively short contact between the TEMPO groups of the neighboring molecules. It is

well anticipated that the occurrence of fairly large intermolecular magnetic interactions even in such large molecules is due mainly to the specifically assembling nature of the TEMPO derivatives and thus such a supramolecular approach as described in this paper is expected to open a way to new organic spin systems with intriguing molecular/crystal structures and novel magnetic properties.

EXPERIMENTAL

Materials

3-Carboxy-PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy), 4-carboxy-TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), 4,4-Dihydroxybiphenyl and 2,6-dihydroxy naththalene used in this study are commercially available and were used without further purification. 4,4′-Dihydroxyazobenzene was prepared by the treatment of the diazonium salt generated from 4-aminophenol with alkaline copper (II) sulfate.[7] 4,4′-Dihydroxyazoxybenzene was prepared by the method of Leonald and Curry.[8]

Instrumentation

Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. UV-visible spectra were obtained on JASCO Ubest-35 spectrometer. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. ESR spectra were recorded on a JEOL JES-FE3XG spectrometer and each *g*-value was determined using Mn^{2+}/MgO marker as an internal standard. Susceptibility measurements were carried out on a QUANTUM DESIGN MPMS-5 SQUID susceptometer, using *ca.* 10 mg for each powdered sample in the usual way.[9]
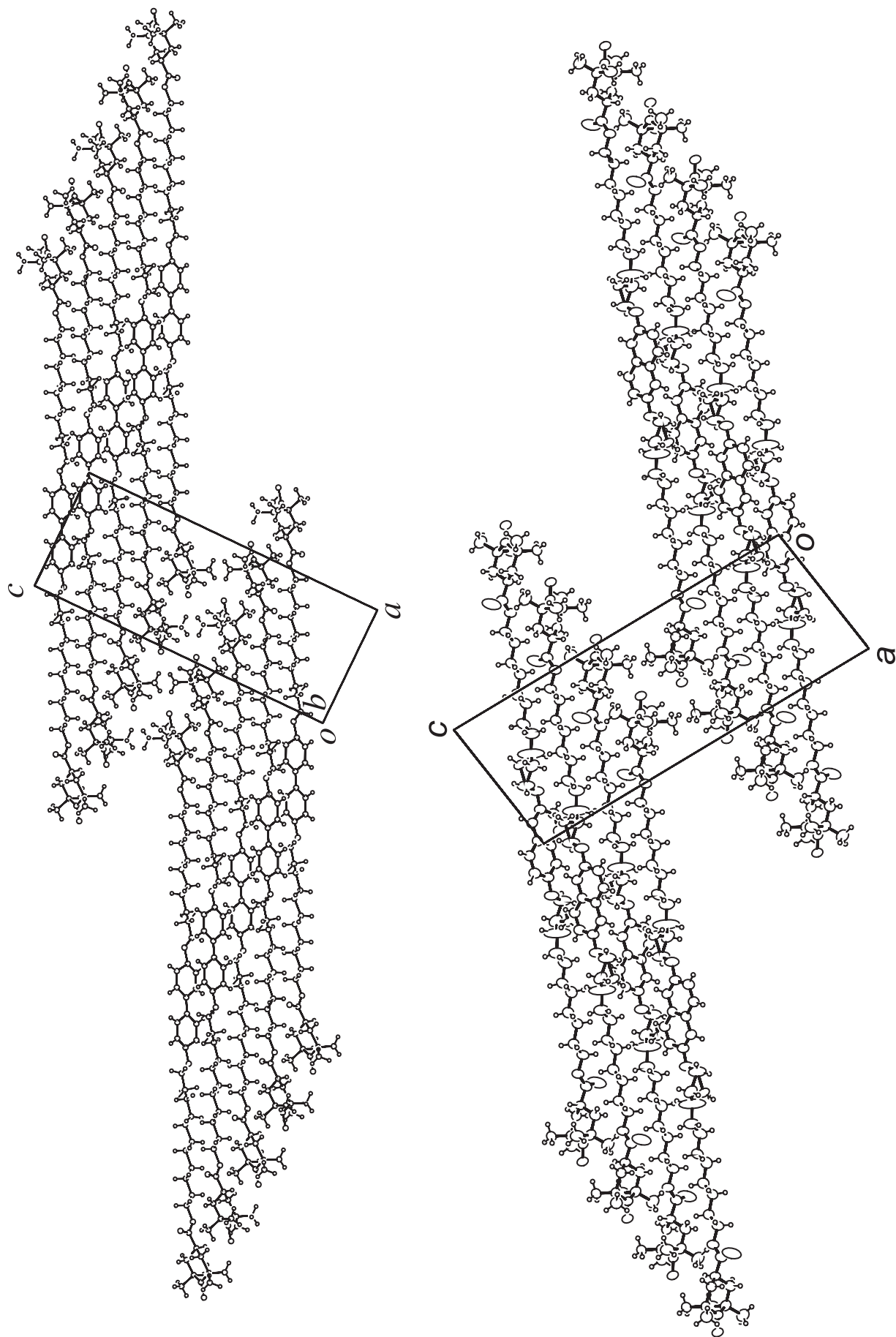
Figure 3. Crystal structures of biradical **3b** (upper) and **3d** (lower)
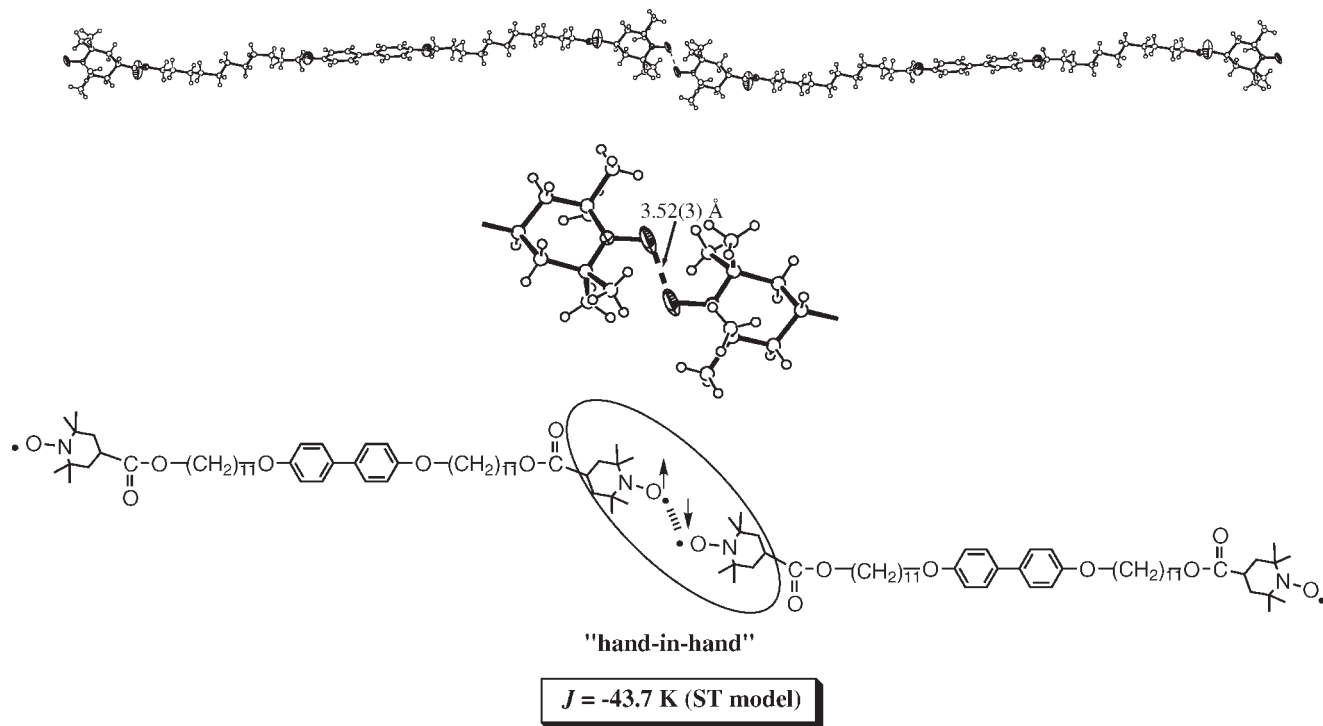
Figure 4. Intermolecular interaction between biradical **3b** (upper) and therir O–O contact (middle) together with schematic drawing of ''hand-in-hand'' structure (lower)

X-ray structure determination

X-ray diffraction data were collected on a Rigaku AFC-7R diffractometer with Mo-Kα radiation at room temperature. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation and detailed crystallographic data (atomic coordinates, hydrogen atom coordinates, anisotropic displacement parameters, bond length, and angles) have been deposited with the Cambridge Crystallographic Data Centre. Details are available from the Editorial Office.

Preparation of esters 5a and 5b

To a stirred mixture of 11-bromo-1-undecanol **4** (0.27 g, 1.07 mmol), 3-carboxy-PROXYL (0.20 g, 1.07 mmol) in dichloromethane (30 cm^3) was added DCC (1,3-dicyclo-hexylcarbodiimide, 0.27 g, 1.31 mmol) and DMAP (4-dimethylaminopyridine, 0.16 g, 1.31 mmol) at ambient temperature and stirring was continued for 1 day. After filtration of the resulted precipitates of urea, the solution was concentrated *in vacuo* and the crude product was purified by column chromatography on silica gel by using benzene/diethylether as eluant to give ester **5a** as a pale yellow oily substance (0.37 g, 82%). ESR (benzene):

triplet, $g = 2.006$, $a_N = 1.54$ mT; m/z (FAB-MS) 419 (M+1). In the similar manner, the corresponding TEMPO derivative **5b** was obtained also as pale yellow oil in 84% yield. ESR (benzene): triplet, $g = 2.006$, $a_N = 1.54$ mT; m/z (FAB-MS) 433 (M+1).

Preparation of monoradicals 6a and 6b

A stirred mixture of ester 5a (0.45 g, 1.07 mmol), 4,4′-dihydroxybiphenyl (0.20 g, 1.07 mmol) and potassium carbonate (0.45 g, 3.3 mmol) in a mixed solvent of DMF/THF (3:1) was heated to reflux and stirring was continued for 20 h. After the reaction mixture was cooled to room temperature, it was filtrated, washed by THF and the filtrate was washed thoroughly by water and extracted by ethylacetate. The combined organic layer was dried over anhydrous magnesium sulfate and then the solvent was concentrated *in vacuo* to give a solid substance. Further purification by column chromatography on silica gel and recrystallization from diethylether yielded the radical **6a** as a pale yellow powdery solid (0.13 g, 23%). M.p. 106–108 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.54$ mT; m/z (FAB-HRMS) Found: 524.3353. Calcd. for $C_{32}H_{47}NO_5$ (M+1) 524.3376. In the similar manner, the corresponding TEMPO derivative **6b** was obtained also as pale orange powdery solid in 50% yield. M.p. 135–137 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.55$ mT; m/z (FAB-HRMS) Found: 539.3642. Calcd. for $C_{33}H_{49}NO_5$ (M+1) 539.3611.

Preparation of biradicals 3a–3h

Except for using twice as much amount of the bromoesters (**5a**, **5b**) and potassium carbonate as above, a similar procedure was applied for the preparation of the biradicals **3a**–**3h** and their data are as follows;

3a: yellow powdery solid (60%). M.p. 77–83 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.55$ mT; m/z (FAB-HRMS) Found: 864.6143. Calcd. for $C_{52}H_{84}N_2O_8$ (M+2) 864.6227.

3b: orange plates (41%). M.p. 122–126 ^{a}C; ESR (benzene): triplet, $g = 2.007$, $a_N = 1.54$ mT; m/z (FAB-HRMS) Found: 892.6531. Calcd. for $C_{54}H_{88}N_2O_8$ (M+2) 892.6541; Found: C, 72.23; H, 9.99; N, 3.03. $C_{54}H_{88}N_2O_8$ requires: C, 72.77; H, 9.72; N. 3.14%.

3c: yellow powdery solid (37%). M.p. 87–92 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.53$ mT; m/z (FAB-HRMS) Found: 838.6002. Calcd. for $C_{50}H_{82}N_2O_8$ (M+2) 838.6072.

3d: orange plates (40%). M.p. 113–119 ^{a}C; ESR (benzene): triplet, $g = 2.007$, $a_N = 1.53$ mT; m/z (FAB-HRMS) Found: 866.6524. Calcd. for $C_{52}H_{86}N_2O_8$ (M+2) 866.6384; Found: C, 71.86; H, 10.01; N, 3.16. $C_{52}H_{84}N_2O_8$ requires: C, 72.07; H, 10.00; N. 3.23%.

3e: yellow powdery solid (29%). M.p. 72–77 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.52$ mT; m/z (FAB-HRMS) Found: 892.6193. Calcd. for $C_{52}H_{84}N_4O_8$ (M+2) 892.6289.

3f: orange yellow powdery solid (31%). M.p. 129–133 ^{a}C; ESR (benzene): triplet, $g = 2.007$, $a_N = 1.53$ mT; m/z (FAB-MS) 921 (M+2); Found: C, 70.79; H, 9.82; N, 5.45. $C_{54}H_{86}N_4O_8$ requires: C, 70.55; H, 9.43; N. 6.10%.

3g: yellow powdery solid (42%). M.p. 86–91 ^{a}C; ESR (benzene): triplet, $g = 2.006$, $a_N = 1.53$ mT; m/z (FAB-HRMS) Found: 908.6260. Calcd. for $C_{52}H_{84}N_4O_9$ (M+2) 908.6238.

3h: orange needles (34%). M.p. 126–131 ^{a}C; ESR (benzene): triplet, $g = 2.007$, $a_N = 1.56$ mT; m/z (FAB-MS) 937 (M+2); Found: C, 69.32; H, 9.55; N, 5.90. $C_{54}H_{86}N_2O_9$ requires: C, 69.34; H, 9.27; N. 5.99%.

Acknowledgements

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$$\chi_P = \frac{2N\beta^2 g^2}{kT\left[3 + \exp\left(\frac{-2J}{kT}\right)\right]}$$

where β the electronic Bohr magneton, N is Avogadro's number, g is the Zeeman factor, k is Boltzmann's constant and J is the interaction parameter (exchange interaction) appearing in the spin Hamiltonian $H = -J\,\mathbf{S}_1 \cdot \mathbf{S}_2$. Cf. Bleaney B, Bowers KD. *Proc. R. Soc. London, Ser. A.* 1952; **214**: 451–465. The deviation from the fitting curve below 10 K for **3b** (Fig. 1, right) is probably due to a small amount of paramagnetic impurities and/or lattice defects.

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