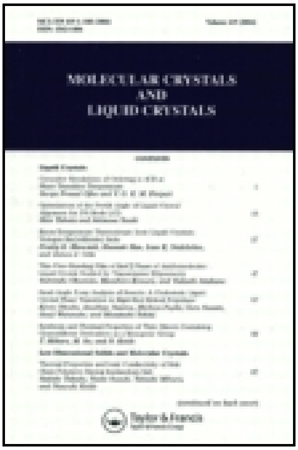

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phenoxyl Radicals Ferromagnetically Attached to a Cyclic π-Conjugation: 2,8,14-Trisoxyphenyltribenzotrisdehydro [12]Annulene

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To cite this article: Yong-Jin Pu, Masahiro Takahashi, Eishun Tsuchida & Hiroyuki Nishide (1999): Phenoxyl Radicals Ferromagnetically Attached to a Cyclic π-Conjugation: 2,8,14-Trisoxyphenyltribenzotrisdehydro [12]Annulene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 1-10

To link to this article: http://dx.doi.org/10.1080/10587259908023297

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 1-10
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Phenoxyl Radicals Ferromagnetically Attached to a Cyclic π-Conjugation: 2,8,14-Trisoxyphenyltribenzotrisdehydro [12]Annulene

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A dehydro[12]annulene C_3-symmetrically annelated with a phenoxyl-bearing benzene was synthesized. The dehydroannulene molecule was a quartet in the ground state, and the cyclic and planar π-conjugation of the dehydroannulene acted as an effective ferromagnetic coupler between the pendant spins.

Keywords: Quartet molecule; Phenoxyl radical; Annulene; Ferromagnetic interaction

INTRODUCTION

An extension of high-spin organic molecules to a larger molecule with a higher dimension is one of the approaches to realize a nanoscopic magnetic property for purely organic compounds.[1-3] Recently, polyradicals based on two-dimensional structures such as the star-shaped, dendric, macrocyclic and ladder structure, have been synthesized and succeeded in displaying a very high-spin alignment.[4-10] On the other hand, much attention has been paid to the chemistry of cyclic and planar π-conjugated compounds such as dehydroannulenes as a new family of carbon allotropes.[11, 12] A typical example, benzo-annelated- or tribenzo-trisdehydro[12]annulene **2** in CHART 1, is characterized by a triangular and coplanar π-conjugation and one of the smallest units of graphitic two-dimensional π-conjugation.

We designed a non-Kekulé-type π-conjugated linear polymer bearing

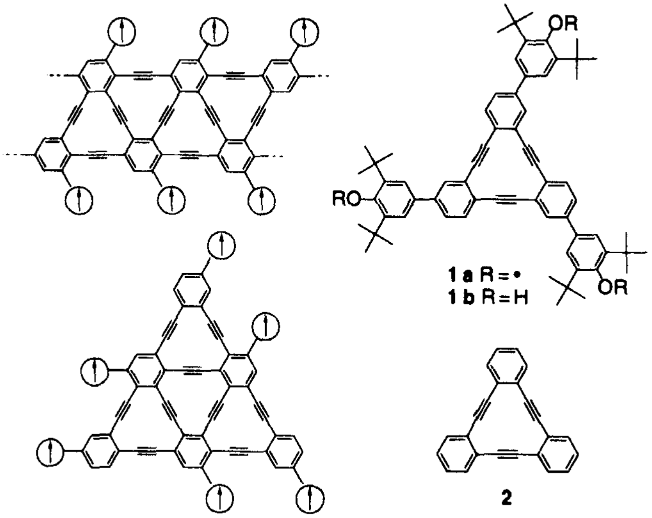
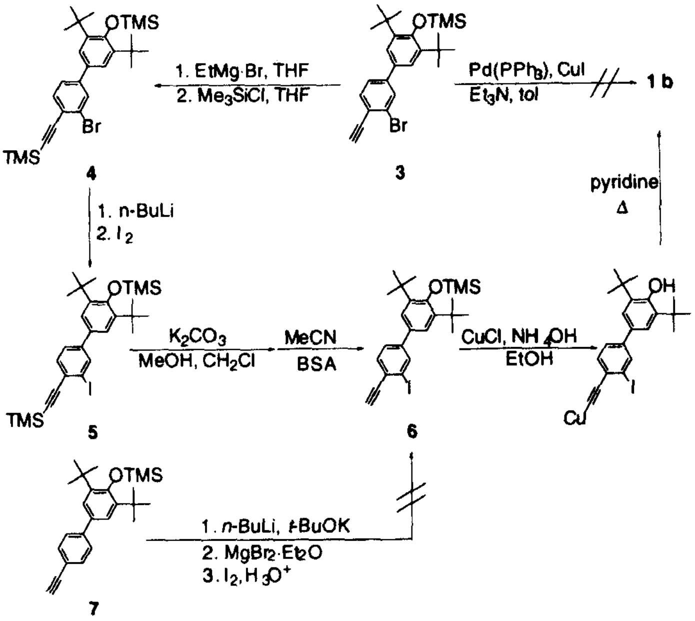


CHART I

pendant radical groups and have successfully reported high-spin alignment between the pendant radicals through the π-conjugated and planarized polymer backbone for poly(4-oxyphenyl-1, 2-phenylenevynylene).[13, 14] The pendant-type polyradical is one of the potential candidates to realize a very high-spin organic molecule, because the spin coupling is not sensitive to spin defects, because the spins are expected to interact also among their remote spins, and because a chemically stable radical species can be introduced to the π-conjugation as the pendant group. However, to our knowledge, pendant-type radicals attached to a cyclic π-conjugation or an annulene have not been reported.

Recently, we preliminarily reported the title compound **1a** as the first cyclic π-conjugation bearing pendant radicals.[15] **1a** is the smallest unit of the pseudo-two dimensional π-conjugations ferromagnetically coupled with pendant spins (CHART 1). This paper describes the synthesis, redox behavior, π-conjugation, and high-spin state of **1a**.

RESULTS AND DISCUSSION



SCHEME I

Synthesis. Tribenzotrisdehydro[12]annulene **2** has been synthesized by the Castro reaction, or the cross-couplng of *o*-iodoethynylbenzene or the bromination of cyclic dieneyne obtained by the Wittig reaction followed by dehydrobromination.[16, 17] We first tried the cross-coupling of 2-bromo-4-(3', 5'-di-*tert*-butyl-4'-trimethylsiloxyphenyl)ethynylbenzene **3** which was derived from 2-bromo-4-(3', 5'-di-*tert*-butyl-4'-acetoxyphenyl)styrene, in the presence of palladium tristriphenylposphine and cuprous iodide in toluene with the **3** concentration of 0.049–0.0034 M at 100°C. However, the corresponding dehydro[12]annulene **1b** was not obtained. To improve the reactivity of the *o*-halogenoethynylbenzene, 4-(3', 5'-di-*tert*-butyl-4'-trimethylsiloxyphenyl)-2-iodo-ethynylbenzene **6** was synthesized. First, 4-(3', 5'-di-*tert*-butyl-4'-trimethylsiloxyphenyl)ethynylbenzene **7** was synthesized, and the *o*-position of **7** was reacted with electrophilic reagents, such as *n*-butyllithium and potassium *tert*-butoxide. Subsequently, this organometal was converted to a Grignard compound using magnesium bromide etherate, and then reacted with iodine. However, **6** could not be isolated in a reasonable yield.

Now, the bromo substituent in **3** could be replaced with iodine to give **6**. The ethynyl group of **3** was protected with the trimetylsilyl group. The bromo group of **4** was then substituted with the iodo group using *n*-butyllithium. Subsequently, the ethynyl groups of **5** were deprotected to afford the iodine derivative **6**. The cuprous acetylide of **6** was condensated in pyridine to yield the annulene **1b**.

Structure. **1b** gave 12 absorption peaks in the ^{13}C-NMR reflecting its C_3 symmetrical structure. In the ^{1}H-NMR data, the signals for the nine protons on the annelated benzene ring were slightly shifted upfield ($\Delta\delta$ = 0.1-0.2) relative to the corresponding monomer due to the paramagnetic ring current. The MM2 calculation was conducted for **1b** (FIGURE 2). The tribenzotrisdehydro-[12]annulene core in the optimized structure was completely planar, and the dihedral angle between the phenoxyl and the annulene core was estimated to be 42°. This result was supported by the UV-vis absorption and fluorescence spectra of **1b** (TABLE 1). The UV-vis absorption maximum and fluorescence

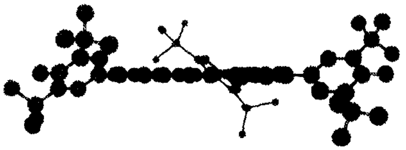


FIGURE 2 Optimized structure of **1b**.

TABLE 1 UV-vis Absorption and fluorescence maxima of the annulenes

annulene	UV-vis abs^a		fluorescence^b	
	λ_{max}/nm	$\varepsilon_{max}/10^4$	λ_{em}/nm	Φ
1b	333	1.2	500	0.12
2	276	0.85	485	0.07

a: chloroform solution, b: benzene solution; quantum yield (Φ) normalized with 9, 10-diphenylanthracen (Φ = 0.84) maximum of **1b** bathochromically shifted in comparison with those of **2**. These are ascribed to the development of π-conjugation in the benzo-annelated dehydroannulene caused by bearing three phenol groups.

Triradical Formation. The triphenoxyl radical **1a** was obtained by heterogeneously treating the toluene solution of **1b** with aqueous alkaline $K_3Fe(CN)_6$ solution. The toluene solution rapidly turned deep green: The appearance of a new absorption peak at λ_{max} = 641 nm suggests phenoxyl radical formation which is ascribed to a n-π* transition.

The triradical **1a** was also generated by electrochemical oxidation. The cyclic voltammogram of **1b** exhibited a completely reversible but simple redox wave in dichloromethane with tetrabutylammonium tetrafluoroborate and a small amount of tetramethylammonium hydroxide as an electrolyte and alkali, respectively, under a nitrogen atmosphere at room temperature (FIGURE 3). This result means that the triradical is chemically stable even in solution at room temperature and the radical generation is not accompanied by a subsequent chemical side reaction. The redox potential of the phenolate/phenoxyl *vs* Ag/AgCl was 0.01V and almost agreed with that of 2, 4, 6-tri-*tert*-butylphenol.

Differential pulse voltammetry was used to evaluate the oxidation of **1b** (FIGURE 3); however, it gave only a unimodal current peak. The annulene coupler is too long in the π-conjugation and/or steric distance to induce an effect in the redox reaction.

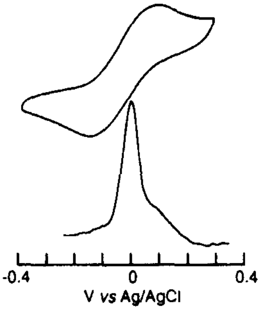


FIGURE 3 Cyclic voltammogram and differential pulse voltammogram of **1b** in the alkaline solution. *vs* Ag/AgCl, at 100mV/sec; $E_{1/2}(Fc/Fc^+)$ = 0.58V, 0.1M *n*-Bu_4NBF_4, 6eq. Me_4NOH.

For further oxidation up to +1.2V, an oxidation peak was observed at 1.0 V which can be ascribed to a cation radical formation on the annulene ring. However, the corresponding reduction current was not observed, probably due to the relative instability of the cation radical species.

ESR. The ESR spectrum of the **1a** toluene solution gave a strong simple signal at *g* = 2.0043 assigned to an oxy-centered radical. The Spin concentration (concn) was estimated by carefully integrating the ESR signal in comparison with that of the TEMPO solution as a standard. The spin concn of **1a** was *ca.* 0.8 spin/phenol unit. **1a** was appropriately stable at room temperature: The half-life of the radical estimated by the ESR intensity decrease was 0.6 day for **1a** in the toluene solution.

The ESR spectrum of **1a** with a low spin concn showed a hyperfine structure, which is attributed to the two protons of the phenoxyl ring and three

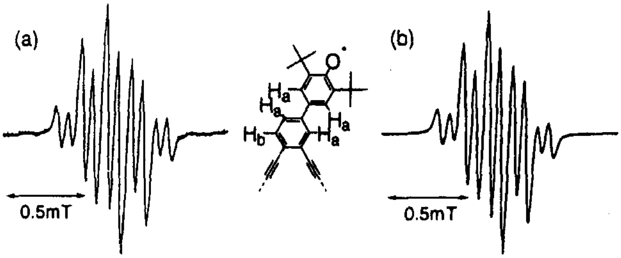


FIGURE 4 ESR spectra of **1a**. (a) with low spin concn and at room temp, (b) simulated spectrum(a_H(a) = 0.18 mT, a_H(b) = 0.08 mT).

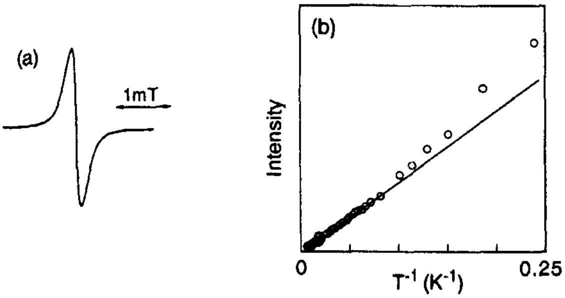


FIGURE 5 ESR spectrum of **1a** with high spin concn at 5 K and Curie plots for the peak in the ΔMs = ±2 region in toluene glass.

protons of the annulene skeleton (FIGURE 4). The hyperfine coupling constants (mT) were estimated to be 0.18 and 0.08. This result indicated an effectively delocalized spin distribution into the annulene skeleton most likely because of its planarized structure.

The ESR of **1a** with a high spin concn in the frozen toluene glass exhibited a ΔMs = ±2 forbidden transition ascribed to a triplet species at $g = 4$ (FIGURE 5a). The signal intensity was proportional to the reciprocal of the absolute temperature in the higher temperature region according to the Curie law however, the plots deviated significantly upward from linearity in the lower region (FIGURE 5b). This upward deviation supports a multiplet ground state for **1a** and a ferromagnetic interaction between the phenoxyl spins.

Magnetization and *S* at Low Temperature. The static magnetic susceptibility (χ) and magnetization (M) of **1a** were measured as a function of the magnetic field (H = 0–5 T) and temperature (T = 1.8–200K) using a SQUID magnetometer. The slope of the $1/\chi$ *vs* T plots gave a Curie constant and the spin concn of 0.81 spin/unit, which agreed with the spin concns estimated by ESR and calculated by saturated the magnetization at 1.8 K. The magnetization normalized by the saturated magnetization (M/Ms) is plotted *vs* the effective temperature (T-θ), compared with the theoretical Brillouin curves for S = 1/2, 2/2 and 3/2(FIGURE 6). θ is a coefficient of the weak antiferromagnetic interaction between the molecules, and is determined from curve fitting using the following $\chi_{\mathrm{mol}}T$ *vs* T data. The M/Ms plots of **1a** with a spin concn = 0.81 lie almost on the Brillouin curves for S = 3/2 at 1.8 - 20 K, indicating a quartet ground state and a ferromagnetic spin alignment between the pendant phenoxyl electrons through the cyclic π-conjugation tribenzotrisdehydro[12]annulene.

The exchange coupling constant, J, was estimated by curve fitting the $\chi_{\mathrm{mol}}T$ *vs* T data (Inset of FIGURE 6) to the equation derived from a triangular three spin model based on the Heisenberg Hamiltonian[18];

$$\chi_{\mathrm{mol}}T = \frac{N_{\mathrm{A}}g^2\mu_{\mathrm{B}}{}^2T}{k_{\mathrm{B}}(T-\theta)}\left[\frac{x_3}{12}\frac{2+10\exp(3J/k_{\mathrm{B}}T)}{2+2\exp(3J/k_{\mathrm{B}}T)}+\frac{x_2}{3+\exp(-2J/k_{\mathrm{B}}T)}+\frac{x_1}{4}\right] \tag{1}$$

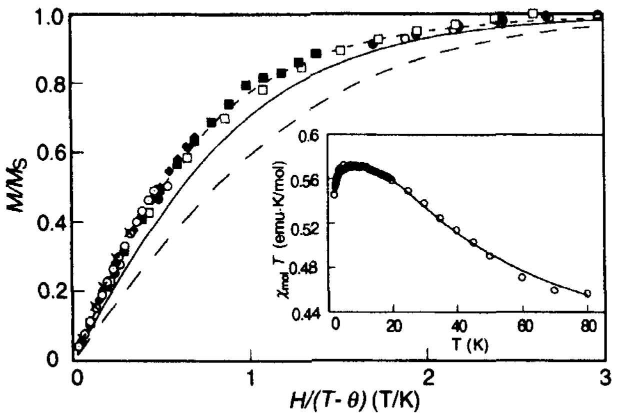


FIGURE 6 Normalized plots of magnetization (*M/Ms*) *vs* the ratio of magnetic field and temperature (*H/*(*T-θ*)) for the **1a** with spin concn = 0.81 spin/unit in frozen toluene at 1.8(O), 2.0(●), 2.25(□), 5(■), 10(◆), 15(O), 20(X) K, and the theoretical Brillouin curves for S = 1/2, 2/2 and 3/2. Inset: $\chi_{mol}T$ *vs* T plots(O) of **1a** with spin concn = 0.81 spin/unit in frozen toluene glass. Solid line is a theoretical curve calculated using eq. (1) for **1a** (J = 24 cm^{-1}, x_3 = 0.53, x_2 = 0.40 and θ = -0.052 K)

where x_3, x_2 and x_1 are the fractions of the quartet, triplet and doublet species, respectively. $2J$ = 48 cm^{-1} was estimated from the curve fitting. This $2J$ value of **1a** is adequate in comparison with those reported for the ferromagnetic coupler-conjugated phenoxyls. As the tribenzotrisdehydro[12]annulene can be further modified into a two-dimensional extension, the pendant-type and cyclic triradical **1a** is an effective quartet unit for the purpose of synthesizing a very-high-spin polyradical.

EXPERIMENTAL SECTION

2-Bromo-4-(3', 5'-di-*tert*-butyl-4'-trimethylsiloxyphenyl)trimethylsilylethynylbenzene 4. Ethyl magnesium bromide (12.7 ml, 12.7 mmol) in THF was added to a solution of 2-bromo-4-(3', 5'-di-*tert*-butyl-4'-trimethylsiloxyphenyl)ethynylbenzene **3** (4.3 g, 9.4 mmol) in THF (10 ml) at 0°C under nitrogen. The solution was stirred overnight at 70°C, then, trimethylsilylchloride (1.9 ml, 15 mmol) was added to this solution. The reaction was monitored by TLC. After the reaction was complete, the mixture was cooled, and an aqueous ammonium chloride was added. The organic layer was extracted with diethylether, washed with water, dried over sodium sulfate, filtered, and evaporated. Recrystallization from ethanol following flash chromatography in hexane afforded 4.3 g (86%) of the product as a colorless solid: Mass(m/z) 531(M^++1), 529(M^+-1), 529.7(calcd); IR(KBr, cm^{-1}) 3038, 2959, 2162; ^{1}H NMR(δ:ppm, $CDCl_3$) 0.29(s, 9H), 0.43(s, 9H), 1.45(s, 18H), 7.43–7.51(m, 4H), 7.75(d, 1H); ^{13}C NMR(δ:ppm, $CDCl_3$) -0.1, 3.9, 31.2, 35.3, 99.6, 103.4, 122.9, 124.5, 125.2, 126.1, 130.4, 130.6, 133.6, 141.4, 143.4, 153.7.

4-(3', 5'-Di-*tert*-butyl-4'-trimethylsiloxyphenyl)-2-iodo-trimethylsilylethynylbenzene 5. A solution of **4** (3.2 g, 6.0 mmol) in THF (52 ml) was cooled to −80°C. *n*-Butyllithium (1.6 M, 4.0 ml) in hexane was slowly added. After the addition, the reaction mixture was stirred for 15 min. Subsequently, iodine (3.1 g, 12 mmol) in THF (5.5 ml) was added to this solution, and the solution was stirred for 1 hr. After adding saturated aqueous sodium sufite, the organic layer was extracted with diethylether, washed with water, dried over sodium sulfate, filtered, and evaporated. Recrystallization from ethanol following flash chromatography in hexane afforded 2.24 g (64.4%) of the product as a colorless solid: Mass(m/e), 576(M^+), 576.7(calcd); IR(KBr, cm^{-1}) 3035, 2958, 2160; ^{1}H NMR(δ:ppm, $CDCl_3$) 0.29(s, 9H), 0.43(s, 9H), 1.45(s, 18H), 7.41(s, 2H), 7.47(d, 2H), 8.01(d, 1H); ^{13}C NMR(δ:ppm, $CDCl_3$) -0.1, 3.9, 31.2, 35.3, 98.8, 101.7, 106.7, 124.5, 126.1, 127.4, 130.5, 132.7, 136.8, 141.4, 143.3, 153.7.

4-(3', 5'-Di-*tert*-butyl-4'-trimethylsiloxyphenyl)-2-iodo-ethynylbenzene 6. Compound **5** (1.30 g, 2.26 mmol) and a catalytic amount of anhydrous potassium carbonate were stirred in a solution of methanol (2.3 ml) and dichloromethane (2.3 ml) at room temperature under nitrogen. The reaction was monitored by TLC, and the solution was stirred for 3–5 hr. The mixture was extracted with dichloromethane. The organic layer was dried over sodium sulfate, filtered, and evaporated to afford 0.87 g (89%) of the product as a yellow solid. Without further purification, this compound (0.87 g, 2.0 mmol) was dissolved in acetonitrile (11 ml). *N, O*-Bistrimethylsilylacetoamide (1.0 ml, 4.1 mmol) was added to the solution. The solution was stirred for 3–5 hr at 60°C under nitrogen. The reaction was monitored by TLC. The solvent was removed in vacuo. The residue was recrystallized from ethanol following chromatography in hexane to afford 0.96 g (95%) of the product as a colorless solid: Mass(m/z) 504(M^+), 504.5(calcd); IR(KBr, cm^{-1}) 3294, 3036, 2957, 2108; ^{1}H NMR(δ:ppm, $CDCl_3$) 0.44(s, 1H), 1.45(s, 18H), 3.41(s, 1H), 7.40(s, 1H), 7.48–7.52(m, 2H), 8.01(d, 1H); ^{13}C NMR(δ:ppm, $CDCl_3$) 3.9, 31.2, 35.3, 81.0, 85.4, 100.9, 124.6, 126.3, 126.4, 130.5, 133.4, 136.9, 141.5, 143.8, 153.8.

2, 8, 14-Trisoxyphenyltribenzotrisdehydro[12]annulene 1b. Compound **6** (0.90 g, 2.1 mmol) dissolved in ethanol (20 ml) was added to a solution of cuprous chloride (0.47 g, 4.7 mmol) dissolved in aqueous ammonium hydroxide (55 ml). After stirring for 2 hr, the precipitation was separately washed with water and ethanol. Pyridine (6.0 ml) was added to the dry precipitate (0.16 g, 0.31 mmol), and the solution was refluxed for 7–10 hr under nitrogen. After the solvent was removed in vacuo, the residue was purified by flash chromatography (5:3; hexane:chloroform) to afford 0.030 g (32%) of the product as a yellow solid: FAB Mass(m/z) 913.6(M^+), 913.3(calcd); IR(KBr, cm^{-1}) 3640, 2957; ^{1}H NMR(δ:ppm, $CDCl_3$) 1.49(s, 54H), 5.32(s, 3H), 7.34–7.36(dd, 3H), 7.38(s, 6H), 7.42–7.43(d, 3H), 7.52(s, 3H); ^{13}C NMR(δ:ppm, $CDCl_3$) 30.5, 34.6, 93.1, 93.5, 123.8, 124.4, 126.9, 127.3, 130.2, 130.8, 132.5, 136.5, 142.5, 154.2.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 09305060 and 277/08246101) from the Ministry of Education, Science and Culture, Japan, and by the NEDO Project on Technology for Novel High-Functional Materials.

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