High-Spin Oxyphenylbenzo-Annelated Dehydro[12]annulene

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A ground state quartet molecule, 2, 8, 14-trisoxyphenyltribenzotrisdehydro[12]annulene, was synthesized; the dehydroannulene acted as an effective ferromagnetic coupler for the pendant spins.

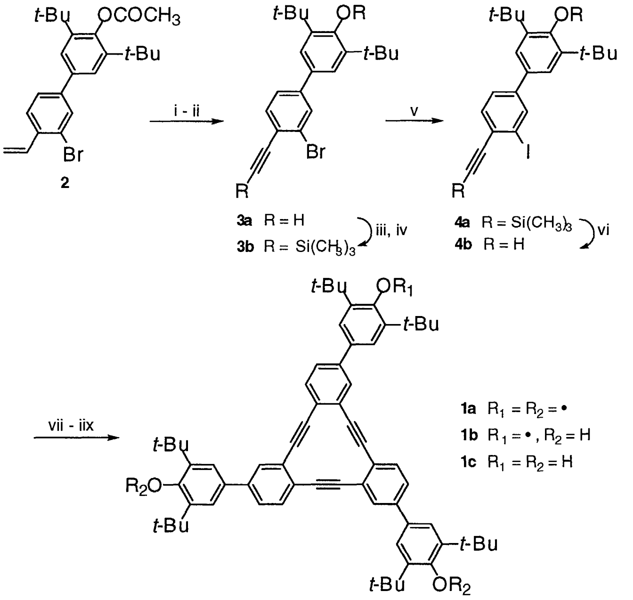
The research on very high-spin organic molecules using intramolecular through-bond magnetic ordering has been exhaustively continued in connection with realizing purely-organic derived and unknown magnetism.[1-3] One of the potential candidates to provide very high-spin molecules is a π-conjugated linear polymer bearing pendant radical groups on every monomer unit, which are substituted on the polymer backbone to satisfy the π-conjugated and ferromagnetic connectivity of the radicals. For example, we synthesized poly[4-(3', 5'-di-*tert*-butyl-4'-oxyphenyl)-1, 2-phenylenevinylene] and reported a ferromagnetic interaction between the pendant radical's spins through its π-conjugated and planarized backbone.[4] To increase such a high-spin alignment, research on the very high-spin molecules recently focuses on the (pseudo-)two-dimensional extensions, *i.e.*, star-shaped, dendric, macrocyclic, and ladder homologs.[3, 5]

Tribenzotrisdehydro[12]annulene is an allotropic unit of graphitic two-dimensional π-conjugation: this annulene is characterized by a triangular and coplanar π-conjugation.[6] However, no annulene bearing (a) spin(s) have been reported. In this paper, we have first synthesized the dehydro[12]annulene C_3-symmetrically annelated with a radical(spin)-bearing benzene ring, 2, 8, 14-(3', 5'-di-*tert*-butyl-4'-oxyphenyl)tribenzotrisdehydro-[12]annulene **1a**, and examined its high-spin state.

Tribenzotrisdehydro[12]annulene has been reported to be synthesized *via* the Castro reaction of *o*-iodoethynylbenzene.[6, 7] **4b** was synthesized as shown in Scheme 1. The vinyl group of 4-(3', 5'-di-*tert*-butyl-4'-acetoxyphenyl)styrene **2**[4] was converted to the ethynyl group. However, the bromo substituent in **3a** was unsuitable for the annulene formation; it was replaced with iodine in reasonable yield (**4a**).[8] Subsequently, the hydroxyl and ethynyl groups of **4a** were deprotected and the cyclization of **4b** yielded **1c**.[9]

The ^{13}C-NMR of **1c** was characterized by 12 carbon absorption peaks ascribed to the C_3 symmetrical structure. The diatropic character of the [12]annulene core was discerned from the small but distinct upfield shifts ($\Delta\delta$ = 0.1-0.2) of the nine protons on the annelated benzene relative to the corresponding **4b**, which correlates with the paramagnetic ring current of 12π electrons of the annulene ring. The UV-vis absorption maximum (λ_{max}) and fluorescence maximum (λ_{em}) were 333 ($\varepsilon = 1.2\times10^4$) and 500 nm for **1c**, which bathochromically shifted in comparison with those of tribenzotrisdehydro[12]annulene (λ_{max} = 276 nm, $\varepsilon = 8.5\times10^3$, λ_{em} = 485 nm). These can be ascribed to the development of π-conjugation.

The toluene solution of **1c** was heterogeneously treated with a trace or a large excess of the aqueous alkaline $K_3Fe(CN)_6$ solution, to give the monoradical **1b** or the triradical **1a**, respectively. The ESR spectrum of the monoradical **1b** gave a ten-line hyperfine structure at g = 2.0043 which is attributed to the nearest neighbor 4 protons and the more remote 1 proton (a_H = 0.18 and 0.08 mT, respectively). This suggested an effectively delocalized spin distribution into the annulene skeleton most likely because of its planarized structure.



Scheme 1. Reagents and conditions. i, Br_2, $CHCl_3$, 0 °C, 10-20 min; ii, KOH, H_2O, DMSO, 60 °C, 5 h; iii, *N*, *O*-Bistrimethylsilylacetamide, CH_3CN, 60 °C, 3 h; iv, a) C_2H_5MgBr, THF, 70 °C, 10-12 h, b) $(CH_3)_3SiCl$, THF, 70 °C, 5 h; v, a) *n*-BuLi, THF, -80 °C, 15 min, b) I_2, THF, rt., 1 h; vi, K_2CO_3, CH_3OH, CH_2Cl_2, rt., 3-5 h; vii, CuCl, NH_4OH, EtOH, rt., 3 h; iix, pyridine, Δ, 90 °C, 7-10 h.

The ESR of the frozen toluene glass of the triradical **1a** exhibited ΔMs = ±2 forbidden transition ascribed to a triplet or a quartet species at g = 4 (Figure 1). The signal intensity was proportional to the reciprocal of the absolute temperature in the higher temperature region, but the plots substantially deviated upward from linearity in the lower region. This upward deviation supports a multiplet ground state for **1a**.

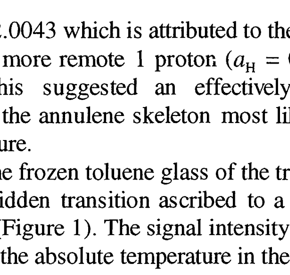


Figure 1. ESR spectrum of **1a** with spin concn = 0.81 spin/phenol unit at 5 K and Curie plots for the peak in the ΔMs = ±2 region in toluene glass.

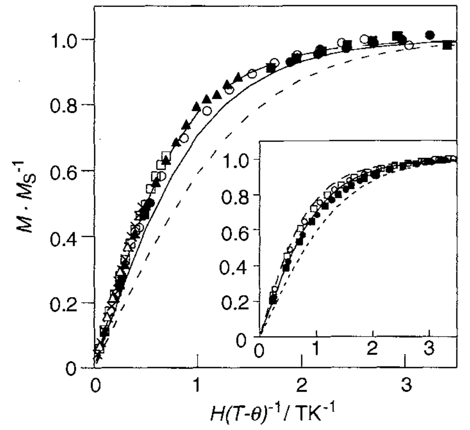


Figure 2. Normalized plots of magnetization (M/M_s) *vs* the ratio of magnetic field and temperature ($H/(T-\theta)$) for the **1a** with spin concn = 0.80 spin/phenol unit in toluene at T = 1.8(●), 2.0(■), 2.25(○), 5(▲), 10(□), 15(×), 20(△), and the theoretical curves corresponding to the S = 1/2, 2/2 and 3/2 Brillouin functions. Inset: the plots for the **1a** (T = 1.8(○), 2.0(□)) and the linear triradical (T = 1.8(●), 2.0(■)) with spin concn = 0.71 spin/phenol unit.

Static magnetic susceptibility and magnetization of **1a** in the frozen toluene were measured using a SQUID magnetometer. The magnetization plots of the triradical **1a** with a spin concn = 0.81 spin/phenol unit lie almost on the theoretical Brillouin curve for S = 3/2 at 1.8 - 20 K (Figure 2) and indicate a quartet ground state. Even **1a** with a spin concn = 0.71 gave magnetization plots close to the S = 3/2 curve (Inset of Figure 2). This was in contrast to those of the corresponding linear triradical, 1-(3', 5' -di-*tert*-butyl-4'-oxyphenyl)-3-[4'-(3'', 5''-di-*tert*-butyl-4''-oxyphenyl)phenylethynyl]-4-[5'-(3'', 5''-di-*tert*-butyl-4''-oxyphenyl)-2'-methylphenylethynyl]benzene **4**, with a spin concn = 0.70, which lie almost on the S = 2/2 curve (Inset of Figure 2). These results demonstrate that a spin defect is not fatal for the ferromagnetic spin alignment between the pendant phenoxyl electrons through the tribenzotrisdehydro[12]annulene and that the cyclic π-conjugation or the plural interaction pathways are effective to avoid the influence of spin defects.

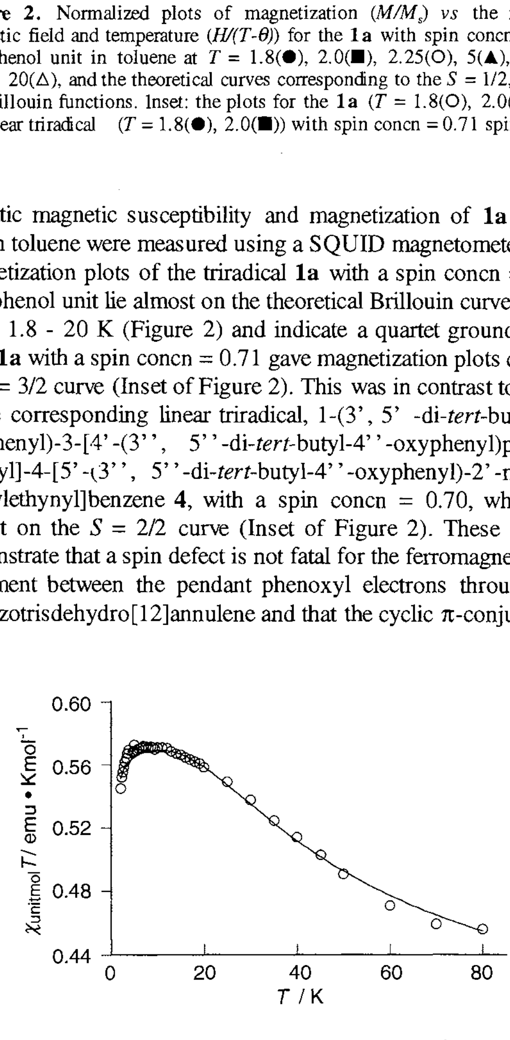


Figure 3. $\chi_{\mathrm{unitmol}}T$ *vs* T plots(○) of **1a** with spin concn = 0.81 spin/phenol unit in frozen toluene glass. Solid line is a theoretical curve calculated using eq.[11] for **1a** (J/k_B = 34.9 K, x_1 = 0.53, x_2 = 0.40, and θ = -0.052).

The exchange coupling constant of the intramolecular spin alignment (positive for ferromagnetic coupling) was estimated by curve fitting the $\chi_{\mathrm{unitmol}}T$ *vs* T data (Figure 3) to the equation derived from a triangular three spin model based on the Heisenberg Hamiltonian.[10,11] The experimental plots agree with the solid line of the triangular three spin model, and the best fit parameters[12] were J/k_B = 35 K. The J value of **1a** is larger than that of the linear triradical **4** (J/k_B = 23 K). The stronger interaction in **1a** suggests a more effective spin distribution of the pendant phenoxyl through the backbone conjugation or the restricted planar annulene.

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8 Selected data for **4a**: Mass(m/e) 576.7(calcd), 576(M$^+$); δ_H(500 MHz, $CDCl_3$) 0.29, 0.43(s, 9H, TMS), 1.45(s, 18H, *t*-Bu), 7.41(s, 2H, Ph), 7.47(d, J = 1 Hz, 2H, Ph), 8.01(q, 1H, Ph); δ_C(125 MHz, $CDCl_3$) -0.13, 3.93(TMS), 31.2, 35.3(*t*-Bu), 98.8, 101.7(ethynyl), 106.7, 124.5, 126.1, 127.4, 130.5, 132.7, 136.8, 141.4, 143.3, 153.7(CH).

9 Selected data for **1c**: FAB Mass(m/e) 913.6(M$^+$), 913.3(calcd); IR(KBr, cm^{-1}) ν 2957(CH), ν 3640(OH); δ_H(500 MHz, $CDCl_3$) 1.49(s, 54H, *t*-Bu), 5.32(s, 3H, OH), 7.34 - 7.36(dd, J = 1.8, 8.3 Hz, 3H, Ph), 7.38(s, 6H, Ph), 7.42 - 7.43(d, J = 8.3 Hz, 3H, Ph), 7.52(d, J = 1.8 Hz, 3H, Ph); δ_C(125 MHz, $CDCl_3$) 30.46, 34.63(*t*-Bu), 93.1, 93.5(ethynyl), 123.8, 124.4, 126.9, 127.3, 130.2 130.8, 132.5, 136.5, 142.5, 154.2(CH).

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11 Equation; $\chi_{\mathrm{unitmol}}T = Ng^2\mu_B{}^2T[x_1\{2+10\exp(3J/k_BT)\}/12\{2+2\exp(3J/k_BT)\} + x_2/\{3+\exp(-2J/k_BT)\}+(1-x_1-x_2)/4] / k_B(T-\theta)$.

12 J, θ, x_1 and x_2 are the average value of the exchange coupling constant, a coefficient of the weak antiferromagnetic interaction between the molecules, and the fractions of the quartet and triplet species, respectively.