1,2-bis(methylene)cyclohexane, and 2,3-dimethyl-1,3-butadiene.

Homologues of 1,2-bis(methylene)cyclohexane related to **11**, prepared by lengthier procedures, have been employed in syntheses of pentacene.[10] *cis*-1,4-Dichloro-2-butene has also been employed as a dienophile–diene synthon but requires "severe and carefully controlled reaction conditions [typically several days at 190–200 °C], was somewhat erratic", and gave only moderate yields.[11] Furthermore, *cis*-1,4-dichloro-2-butene does not react with either furan or 1,3-cyclohexadiene.[12] We shall report elsewhere on the application of reagents **1** in the synthesis of substituted polyacenes.

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Design, Preparation, and Electron Spin Resonance Detection of a Ground-State Undecet ($S = 5$) Hydrocarbon

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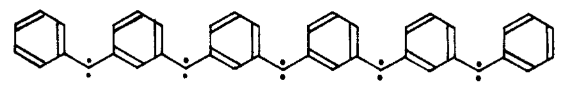
Synthetic organomagnetic materials such as organic ferromagnets[1] are a recent topic attracting both academic and industrial interest. As part of our program for obtaining purely organic ferromagnets,[2-4] we have synthesized and detected an aromatic hydrocarbon **1** which has an undecet electronic ground state with 10 parallel spins ($S = 5$). This is the highest spin multiplicity



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known to date for organic molecules. This novel aromatic hydrocarbon has been designed by utilizing topological symmetry of its π electron network.[2,3] The behavior of many spins in such hydrocarbons as well as in other organic high-spin molecules reported by several authors[5] is of key importance for the theory of organic magnetism.[2a,3,6]

Hydrocarbon **1** was generated at 77 K by photolysis of the pentakis(diazo) precursor **2** which was diluted in a single crystal of 1,3-dibenzoylbenzene (*Pbca* space group). The photolysis was carried out with an XBO 500-W high-pressure mercury lamp using a quartz rod which guided the light into an X-band TE_{102} cavity of a Bruker ESP300 spectrometer equipped with an Oxford ESR910 variable temperature controller. The mixed crystals were grown in the dark by slowly cooling a benzene-d_6 solution containing 1,3-dibenzoylbenzene and 0.0027 mol fraction of **2**.

The pentakis(diazo) compound **2** was prepared as in Scheme I. Bis(3-bromophenyl)methane[7] was lithiated and allowed to react with excess 3-benzylbenzaldehyde[8] to give **3**. Oxidation of **3** with $Na_2Cr_2O_7$ gave **4**, mp 249–253 °C in 58% yield based on the dibromide: IR 1660 cm^{-1}.[9] Pentahydrazone **5**, mp 100–103 °C,

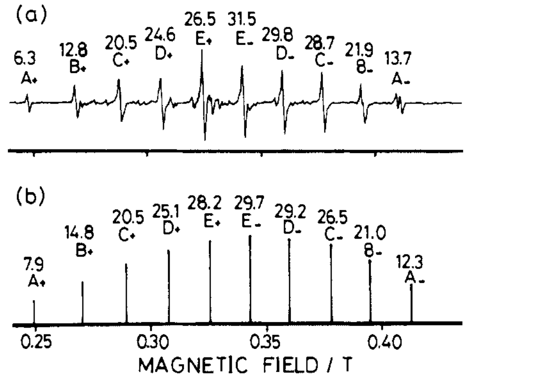
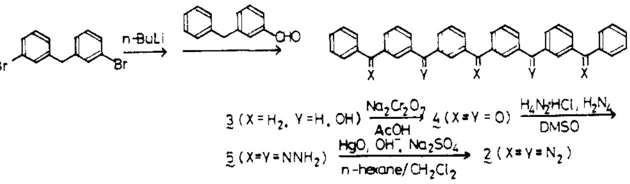


Figure 1. ESR spectra observed after photolysis at 77 K with the magnetic field along the *b* axis of the 1,3-dibenzoylbenzene crystal (*Pbca* space group). (a) Observed at 50 K. The microwave frequency is 9438.9 MHz. (b) Theoretical stick spectrum obtained by the exact diagonalization of the spin Hamiltonian at ν = 9438.9 MHz. The figures above each line represent the relative signal intensities.

Scheme I



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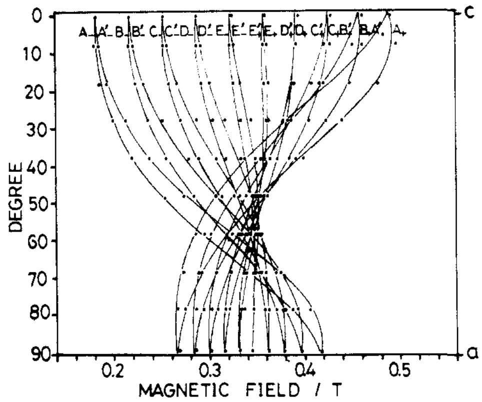

Figure 2. Angular dependence of the resonance fields of the $\Delta M_s = \pm 1$ allowed transitions observed at 77 K for the rotation of the magnetic field in the *ac* plane (ν = 9587.0 MHz). The primed and unprimed characters correspond to the two magnetically nonequivalent sites. The solid points represent the observed values and the solid curves the calculated ones.

was obtained in 91% yield by heating **4**, hydrazine hydrochloride, and anhydrous hydrazine in dimethyl sulfoxide at 100 °C for 2 h and then treated with HgO, Na_2SO_4, and a small amount of a saturated ethanol solution of KOH at 20 °C for 3 h. Recrystallization twice from *n*-hexane gave **2** as deep-red crystals, 104–110 °C dec: 400-MHz ^{1}H NMR (CD_2Cl_2) δ 7.0–7.4; λ_{max} 291 (ϵ 1.20×10^5) and 518 nm (5.20×10^2); IR (KBr) 3050, 2040, 1590, 1480, 680 cm^{-1}.

Figure 1a shows a typical ESR spectrum of **1** observed at 50 K, exhibiting a pattern characteristic of the $\Delta M_s = \pm 1$ allowed transitions from the undecet spin sublevels. This fine structure has been related to M_s as $A_\pm(\pm 5 \leftrightarrow \pm 4)$, $B_\pm(\pm 4 \leftrightarrow \pm 3)$, $C_\pm(\pm 3 \leftrightarrow \pm 2)$, $D_\pm(\pm 2 \leftrightarrow \pm 1)$, and $E_\pm(\pm 1 \leftrightarrow 0)$. The relative separations of each of the pairs in Figure 1a are $(A_- - A_+):(B_- - B_+):(C_- - C_+):(D_- - D_+):(E_- - E_+)$ = 9.4:7.2:5.1:3.0:1.0, which are close to the ratios of 9:7:5:3:1 expected for the fine structure from $S = 5$ in the high-field limit.

The resonance fields, the signal intensities, and their angular dependence of the observed spectra were described well by the effective spin Hamiltonian,

$$\mathcal{H} = g\beta \vec{H}\cdot\vec{S} + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2) \quad (1)$$

with $S = 5$, $g = 2.003$, $D = -0.0168$ cm^{-1}, and $E = +0.0036$ cm^{-1}. The observed resonance fields and intensities in Figure 1a agree with those in Figure 1b, which were calculated from eq 1, assuming the negligible Boltzmann factor at 50 K. The angular dependence in Figure 2 confirms the agreement between theory and experiment, proving **1** to be an undecet molecule. To ascertain the undecet ground state, we examined the ESR spectra in the range 5–77 K. Only the spectrum arising from the $S = 5$ state of **1** was observed as shown in Figure 1, signals due to the S = 1, 2, 3, and 4 states of **1** being undetected. Furthermore, the total intensity of the undecet lines decreased with increasing temperature, as quantitatively expected for an isolated undecet ground state. Thus, we concluded that the observed undecet state is the electronic ground state of **1**. The negative sign of D was determined by considering the Boltzmann factor at 5 K.

Hydrocarbon **1** has not only five delocalized unpaired π electrons due to topological symmetry,[2,3] as predicted by the simple MO[9] as well as VB[2,6c,d] theories, but also five localized unpaired electrons in the σ nonbonding orbitals at the five divalent carbon atoms. The spin-density distribution obtained from the UHF calculation using a generalized Hubbard model[4g,6f] gives the following picture. There are five net π spins which are parallel and distributed over the carbon skeleton with changing the sign of spin densities alternately from carbon to carbon, while the other five localized spins are exchange coupled ferromagnetically to the π spins at each divalent carbon atom. Since the π spin densities have the same sign at each of the divalent carbon atoms as determined from topological symmetry, all 10 unpaired spins in **1** are ferromagnetically coupled with each other, leading to the S = 5 ground state. The realization of such an organic high-spin molecule as **1** strongly suggests the possible occurrence of organic superparamagnetism originating from properly designed macromolecules with extremely large spins.

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Observation of a New Low-Energy Fluorescent $^1(\pi,\pi^*)$ Excited State in Strongly Coupled Porphyrin Dimers

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Elucidating the electronic interaction between porphyrinic macrocycles held in close proximity is crucial to understanding the mechanisms of important biological and chemical processes such as electron transfer in photosynthesis[1] and bimetallic catalysis.[2] This is evident in the photosynthetic reaction center where the interaction between the bacteriochlorophylls of the dimeric primary electron donor (P) gives rise to unusual features such as the long-wavelength band of P in its neutral form or the near-infrared band in its oxidized form.[1] Interestingly, a number of recently synthesized lanthanide and actinide porphyrin sandwich complexes exhibit analogous spectral characteristics, namely, a broad absorption feature immediately to the red of the monomer-like Q bands in the neutral species and a near-infrared band in the oxidized species.[3-7] We report here the first observation of luminescence from bis-porphyrinate complexes, specifically, the neutral complexes of Th^{IV}. The location of the fluorescence identifies the absorption immediately to the red of the Q bands as vibronic transitions to a previously unknown $^1(\pi,\pi^*)$ state of the dimer. This new (π,π^*) state is the lowest energy excited state in the singlet manifold and apparently arises from substantial porphyrin–porphyrin π-orbital overlap.

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