Singlet–triplet energy gap in a cyclophane-based organic diradical with parallel exchange coupling pathways†

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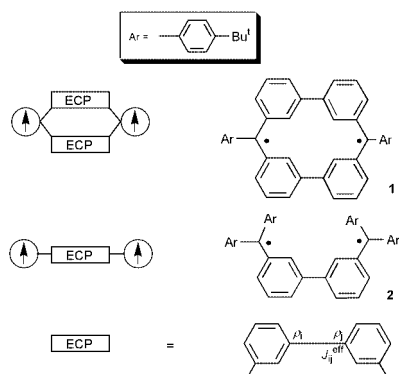
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The novel cyclophane diradical 1 possesses a singlet ground state with a singlet–triplet energy gap (ΔE_{ST}) of −0.20 and −0.24 kcal mol^{-1}, as measured with SQUID magnetometry and EPR spectroscopy, respectively. This large ΔE_{ST} may in part be associated with the two parallel 3,3′-biphenyl exchange coupling pathways (ECPs).

Elucidation of the structural factors affecting the singlet–triplet energy gap (ΔE_{ST}) in organic diradicals is of primary importance in the design of building blocks for molecular magnets and extended polyradicals.[1–5] The value of ΔE_{ST} may also be viewed as a measure of covalent bond strength in typical, singlet ground state, molecules.[6] Both the sign and magnitude of the ΔE_{ST} are predominantly determined by the through-bond exchange coupling.[1,2] As we wish to probe the dependence of $|\Delta E_{ST}|$ on the number of connecting exchange coupling pathways (ECPs) between the radicals,[7,8] we have designed a cyclophane-based diradical **1**, in which two 3,3′-biphenyl units correspond to two parallel ECPs.[2,8] A molecule with one ECP, an analogue of **1**, is diradical **2**.[9] (Diradical **1** may be related to the extended polycarbene proposed by Mataga in 1968 and **2** is a derivative of the well known Schlenk hydrocarbon.[10,11])

In the Heisenberg Hamiltonian model for a diradical ($H = -2JS_1 \cdot S_2$, $S_1 = S_2 = \frac{1}{2}$), $\Delta E_{ST} = 2J$. Here, J is the effective exchange interaction, which may be expressed in terms of the spin densities, ρ_i and ρ_j, and the effective exchange integral, J_{ij}^{eff}, between the connecting sites i and j,[12,13] giving

$$J = J_{ij}^{\text{eff}}\rho_i\rho_j, \quad \text{for the one-ECP system} \quad (1)$$

$$J = 2J_{ij}^{\text{eff}}\rho_i\rho_j, \quad \text{for the two-ECP system} \quad (2)$$

Therefore, $|\Delta E_{ST}|$ should be exactly doubled when the introduction of the second identical ECP does not affect the $J_{ij}^{\text{eff}}\rho_i\rho_j$ terms. The disjoint character of **1** and **2** is an important factor in minimizing the perturbation of ρ_i and ρ_j.[14] However, conformations of **1** and **2** will affect both $\rho_i\rho_j$ and J_{ij}^{eff}. Consequently, **1** should be viewed as an initial attempt to address the problem of multiple ECPs in diradicals. This novel approach to control
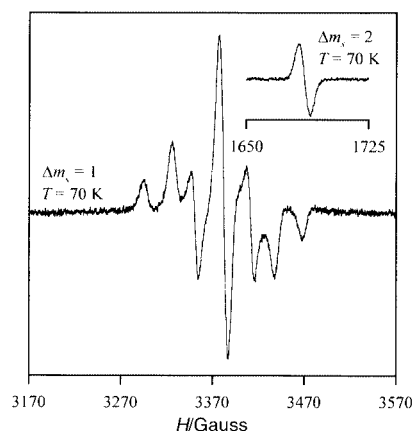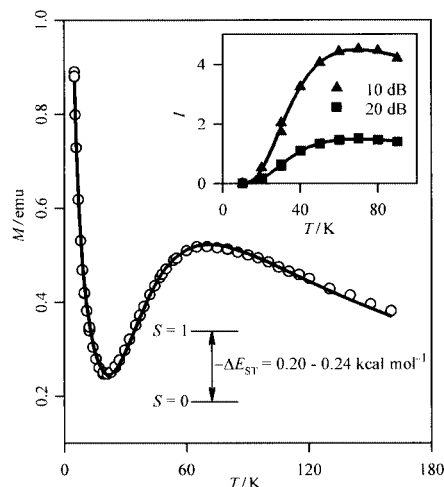
† Electronic supplementary information (ESI) available: synthesis and characterisation data for **4**; minimum conformation for diradical **1**. See http://www.rsc.org/suppdata/cc/b0/b001273o/

exchange coupling should have implications for organic magnetism and weak covalent bonding.

Negishi coupling of compound **3** gave the macrocyclic diether **4**. Two stereoisomers of **4** were isolated in an overall yield of *ca.* 30% (Scheme 1).[15,16]† Both isomers possess qualitatively similar spectral data. FAB MS of **4** are dominated by the isotopic cluster ions corresponding to $(M - OCH_3)^+$, as expected for triarylmethyl ethers. ^{1}H and ^{13}C NMR spectra for **4** show the expected symmetry: all four benzene rings of the macrocycle are equivalent and the two 4-*tert*-butylbenzyl ether moieties are also equivalent.

Scheme 1

Diradical **1** is generated from **4** using the previously developed carbanion methodology for polyarylmethyl radicals such as **2** (Scheme 1).[9,17] NMR spectra for carbodianion **1**$^{2-}$ as its lithium salt in tetrahydrofuran-d$_8$ (THF-d$_8$) at an ambient temperature show analogous molecular symmetry to that of **4**.[17] The EPR spectrum of **1** in frozen 2-methyltetrahydrofuran–tetrahydrofuran (2-MeTHF–THF) at 70 K shows a six-peak pattern in the $\Delta m_s = 1$ region, characteristic of a triplet ($S = 1$) state with the center peak assigned to $S = \frac{1}{2}$ impurities (Fig. 1).[18] The presence of the $S = 1$ state is confirmed by a weak transition in the $\Delta m_s = 2$ region. For **1**, the zero field splitting parameters (zfs), $|D/hc| = 0.0081$ cm^{-1} and $|E/hc| \approx 8 \times 10^{-4}$ cm^{-1}, are somewhat larger than those for **2** ($|D/hc| \approx 0.005$ cm^{-1} and $|E/hc| \approx 0$ cm^{-1}). Because **1** is constrained to the 'syn' conformation and **2** was previously established to possess the 'syn' conformation,[9] this difference in $|D/hc|$ values

Fig. 1 EPR spectroscopy for diradical **1**, *ca.* 0.003 M in 2-MeTHF–THF (*ca.* 5/1).

Fig. 2 Experimental determination of the singlet–triplet energy gap (ΔE_{ST}). Main plot: magnetization (M) by SQUID magnetometry. The solid line corresponds to a numerical fit with the following parameters (parameter dependence): $J/k = -61.4$ K (0.70), mol of diradical $= 1.88 \times 10^{-6}$ (0.69), mol of monoradical $= 1.16 \times 10^{-7}$ (0.05). Insert plot: EPR intensity (I) for the $\Delta m_s = 2$ signal *vs* temperature (T). The solid lines are two-parameter, $J/k = -55.5$ K and normalization constant, numerical fits with parameter dependence of 0.76. The EPR and SQUID data are obtained for **1** in 2-MeTHF/THF (*ca.* 5/1) and THF, respectively.

may arise from a significant delocalization of spin density into the proximate biphenyl moieties in **1**.[18,19] Furthermore, macrocyclic **1** is relatively persistent; more than half of the EPR signal intensity of **1** in 2-MeTHF–THF is left intact after 2 days at room temperature. However, attempts to isolate **1** as a solid were not successful.

At 4 K, the EPR spectrum for the $S = 1$ state becomes almost undetectable, suggesting that the observed $S = 1$ state is thermally populated. Measurement of the intensity (I) of the $\Delta m_s = 2$ signal *vs.* temperature (T) gives a curve with a maximum near $T = 70$ K. A numerical fit, based upon a simple two-center Heisenberg Hamiltonian ($H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$), gives $J/k = -53 \pm 3$ K (Fig. 2).[2]

For 0.04 M **1** in THF, a plot of magnetization (M) *vs.* T in the range 5–100 K shows a broad maximum at $T_{max} \approx 60$ K and an upward turn at low temperatures, consistent with a singlet ground state of **1** and the presence of $S = \frac{1}{2}$ impurities.[20] A three-parameter fit to M *vs.* T gives $J/k = -60 \pm 2$ K (Fig. 2). At very low temperature, such as 3 K, M of a diradical with $J/k \approx -60$ K should be negligible. Numerical fits of M *vs.* magnetic field (H) data at 3 K to the Brillouin function with variable S and M at saturation (M_s) give $S = 0.5$, as expected for an $S = \frac{1}{2}$ impurity. M_s is within a few percent of the calculated value from the M *vs.* T fit.

Diradical **2** was reported to have J/k in the range -21 to -23 K.[9] Therefore, both **1** and **2** have singlet ($S = 0$) ground states and thermally populated $S = 1$ states; $\Delta E_{ST} = 2J$ for **1** (-0.20 to -0.24 kcal mol^{-1}) is about 2–3 times the value of $\Delta E_{ST} = 2J$ for **2** (-0.08 to -0.09 kcal mol^{-1}).

Previous work on derivatives of **2** indicated that the steric hindrance, causing out-of-plane twisting of the π-conjugated system, diminishes $|\Delta E_{ST}|$.[2,21] Possible conformations of **1** and **2** were obtained from MacroModel calculations.[22] The preference for the '*syn*' over the '*anti*' conformation in **2** (3 kcal mol^{-1}) is in agreement with the EPR data. The torsional angles indicate that the 3,3'-biphenyl moieties are significantly more twisted and bent in **1** (59–68°) *vs.* **2** (30°) (see ESI†); this implies that the J_{ij}^{eff} in **1** is smaller than in **2**. However, the torsional angles between the 3,3'-biphenyl and arylmethyl moieties in **1** and **2** are ~ 30 and 44°, respectively. This suggests that both ρ_i and ρ_j in **1** may be larger than in **2**. Therefore, it is reasonable to assume that the $J_{ij}^{eff}\rho_i\rho_j$ terms in eqns. (1) and (2) are comparable.[23]

In conclusion, the singlet–triplet energy gap in diradical **1**, with two parallel exchange coupling pathways, is more than doubled when compared to diradical **2**, with one exchange coupling pathway.

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