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EPR Characterization of the Quintet State for a Hydrocarbon Tetraradical with Two Localized 1,3-Cyclopentanediyl Biradicals Linked by *meta*-Phenylene as a Ferromagnetic Coupler[†]

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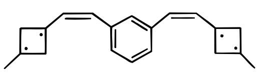
The study of the magnetic properties of high-spin organic molecules is a rapidly developing area with implications for basic research and material science.[1] While *meta*-phenylene has become a popular ferromagnetic coupling unit,[1,2] the tetraradical **1** constituted the first example in which it has been used to couple two localized biradicals, namely 1,3-cyclobutanediyl units linked by ethylene spacers.[3] The presence of the quintet spin state **1** was confirmed by EPR spectral data at 4 K.



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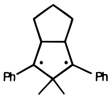

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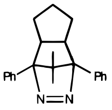
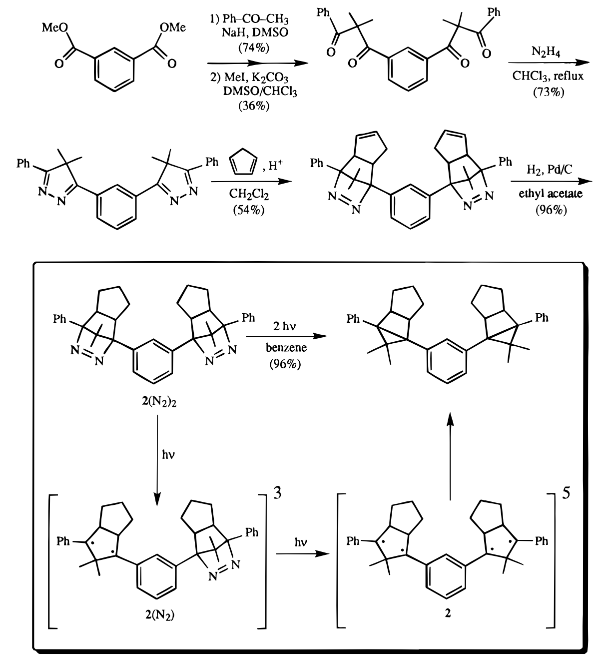


3(N$_2$)

Herein, we report the EPR characterization of the tetraradical **2** (Scheme 1) which is composed of two localized 1,3-cyclopentanediyl biradicals linked *directly* to *meta*-phenylene. The quintet system **2** offers as advantages not only that it is persistent at temperatures up to 100 K but also that its spectral characterization is considerably simplified by the fact that the ferromagnetic coupling between the biradicals is presumably significantly larger than that for tetraradical **1** (no allylic dilution of spin) and that the biradical precursor for the tetraradical **2** can be selectively generated. The study has also revealed a dramatic effect of the irradiation wavelength on the generation of the tetraradical **2** and the crucial importance of fourth-order zero-field splitting terms in the spin Hamiltonian to achieve satisfactory simulation of its quintet state EPR spectrum.

The synthetic sequence in Scheme 1 provides gram quantities of the bis-azoalkane **2**(N$_2$)$_2$ in 10% overall yield.[4] The photochemical properties of **2**(N$_2$)$_2$ resemble those of the corresponding mono-azoalkane **3**(N$_2$).[4] The UV absorption maximum of **2**(N$_2$)$_2$ lies at the same position (363 nm), and its extinction coefficient ($\epsilon = 240$ M^{-1} cm^{-1}) is expectedly about twice as large. On UV photolysis, **2**(N$_2$)$_2$ gives cleanly the bishousane (Scheme 1). The quantum yields for nitrogen extrusion were determined to be unity (±5%) for both **2**(N$_2$)$_2$ and **3**(N$_2$), which signifies that the desired extrusion of the two nitrogen molecules from the bis-azoalkane **2**(N$_2$)$_2$ takes place in a stepwise fashion.

Scheme 1



Irradiation of **2**(N$_2$)$_2$ in a low-temperature glass of 2-methyltetrahydrofuran (MTHF) at 77 K with (*i*) a conventional xenon lamp, (*ii*) all UV lines of an argon ion CW laser at 333, 351, and 364 nm, or (*iii*) monochromatic laser light at 351 or 364 nm afforded only the EPR signals of the triplet biradical **2**(N$_2$) shown in Figure 1a. The EPR spectrum of the triplet biradical **2**(N$_2$) was virtually superimposable with that of the triplet biradical **3**, and the zero-field splitting parameters, obtained by computer simulation (Figure 1b),[5] were $|D| = 0.0507$ cm^{-1} and $|E| = 0.0005$ cm^{-1}. The additional splitting of the forbidden resonance (Figure 1a) is due to hyperfine coupling to the two magnetically equivalent β protons of the ethano bridge and could be simulated with a coupling constant of 10.2×10^{-4} cm^{-1}.

Additional EPR resonances in the $g \approx 2$ and $g \approx 4$ region were observed when monochromatic laser light at 333 nm was employed (Figure 1c) and were assigned to the quintet tetraradical **2**. Such a wavelength dependence of the tetraradical generation from the azo precursor **2**(N$_2$)$_2$ is unprecedented. The fact that the quintet tetraradical **2** cannot be detected on irradiation above 340 nm (Figure 1a) suggests that it is photolabile. Indeed, irradiation of the quintet tetraradical at 351 nm (0.4 W) in the glass matrix resulted in bleaching of the quintet EPR spectrum to the extent of ca. 70% within 45 s. In contrast, prolonged 333-nm irradiation caused no significant spectral changes. During the initial 333-nm irradiation period, the EPR spectrum showed noticeable changes with irradiation time, as expected for the evolution of a mixture of two paramagnetic species, namely a precursor biradical and a product tetraradical. The time profiles obtained from the EPR signal intensities of the biradical **2**(N$_2$) and the tetraradical **2** followed satisfactorily a monoexponential and double-exponential growth function, which provides evidence for the stepwise nitrogen extrusion in the low-temperature glass. Upon prolonged irradiation, the ratio between the signal intensities of the tetraradical and biradical remained constant.

As it was not possible to obtain the EPR spectrum solely of the tetraradical **2**, the spectrum of the pure quintet spin state

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[†] Dedicated to Prof. Dr. Siegfried Hünig, Professor Emeritus at the University of Würzburg, on the occasion of his 75th birthday; his pioneering synthetic work in this area has made this contribution possible.

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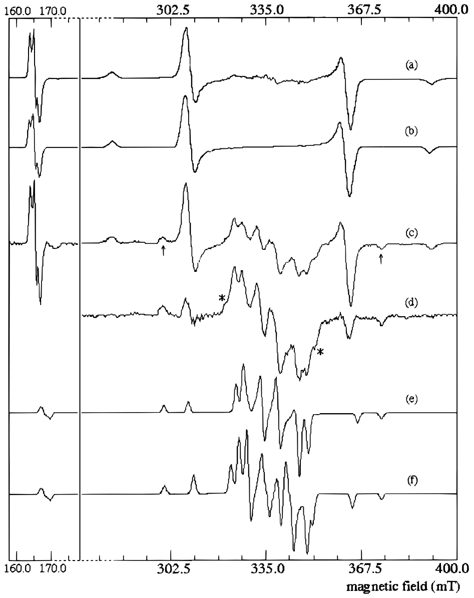

Figure 1. Experimental ($\nu = 9.434$ GHz) and computer-simulated EPR spectra obtained from the bis-azoalkane **2**$(N_2)_2$ in MTHF glass at 77 K. (a) Spectrum obtained on multiline UV irradiation (333, 351, and 364 nm) assigned to the triplet biradical **2**(N_2). (b) Simulation for a triplet state using the spin Hamiltonian in eq 1 with $g = 2.002$. (c) Spectrum obtained on monochromatic 333-nm irradiation assigned to a mixture of the triplet biradical **2**(N_2) and the quintet tetraradical **2**. (d) Difference spectrum [Figure 1c − 1.337 × Figure 1a] for removal of contributions from triplet **2**(N_2). (e) Simulation for a quintet state using the spin Hamiltonian in eq 1 with $g = 2.003$. (f) Simulation for a quintet state using the spin Hamiltonian in eq 2 with $g = 2.003$.

was obtained by spectral subtraction (Figure 1d). Computer simulation with the spin Hamiltonian[3,5,6] in eq 1, where all zero-

$$\mathcal{H}^{\text{2nd}} = D\{S_z^2 - S(S+1)/3\} + E(S_x^2 - S_y^2) + g\beta\mathbf{B}\cdot\mathbf{S} \qquad (1)$$

field splitting terms higher than second order are neglected, produced the spectrum in Figure 1e with $|D| = 0.0116$ cm^{-1} and $|E| = 0.00215$ cm^{-1}. When the zero-field splitting is small relative to the Zeeman interaction the seperation between the outer g ≈ 2 resonances (arrows in Figure 1c) of the quintet tetraradical corresponds to the 6-fold *D* parameter as is found in the present case (74.7 mT equivalent to 6 × 0.0116 cm^{-1}). The same level of theory, namely the neglect of zero-field splitting terms higher than second order (eq 1), allows one to calculate an *a priori* expectation value for the *D* parameter of a quintet system (D_Q) by employing the formula $D_Q = (D_B + D_C)/3$, where D_B and D_C are the *D* parameters of the biradical components and the coupling unit.[6] D_B is known accurately from the EPR spectrum of the biradical **2**(N_2) in Figure 1a,b (0.0507 cm^{-1}), and D_C can be approximated by taking the value for *meta*-xylylene (0.011 cm^{-1}).[3d] Hence, since it is expected that the *D* values of 1,3-cyclopentanediyl biradicals and *meta*-phenylene have opposite signs,[3c] D_Q for the tetraradical **2** can be estimated as 0.0132 cm^{-1}. This value is only 15% higher than the *D* parameter obtained by computer simulation according to eq 1, which provides strong support for the assignment to the quintet state **2**.

A comparison of the EPR spectra from the quintet tetraradical **2** and the triplet biradical **2**(N_2) reveals a significant shift of the outer $g \approx 2$ resonances of the quintet spectrum (arrows in Figure 1c) relative to the the outer $g \approx 2$ resonances (Figure 1a) of the triplet spectrum, a salient spectral feature, which was not observed[2] in the spectrum for the quintet state **1**. This difference is directly related to the allylic spin delocalization in tetraradical **1**, which reduces the effective value of D_C for *meta*-phenylene (see above) by a factor of ca. 1/4 and, thus, causes the outer resonances of the triplet biradical and the quintet tetraradical **1** to coincide.[2] It should also be noted that the allylic spin delocalization in tetraradical **1** is expected to lower the effective magnetic exchange parameter between the triplet biradical subunits by the same factor,[3c] which allows us to assume that *meta*-phenylene acts as a significantly stronger ferromagnetic coupler in **2**. Be this as it may, the observation of its quintet state at 77 K and the absence of any detectable contributions of its triplet state speaks unambiguously for ferromagnetic coupling, which is astounding since the steric congestion appears to be quite similar to other *meta*-phenylene systems for which no magnetic or even antiferromagnetic coupling was observed.[7] Since the ferromagnetic properties of *meta*-phenylene are strongly dependent on π conjugation,[3a,7] one may conclude that the radical centers of *meta*-phenylene in **2** are not strongly twisted out of conjugation.

Although the computer simulation according to eq 1 reproduces the overall features of the experimental quintet state spectrum (Figure 1c,d) the detailed agreement is poor due to the discrepancies in the $g \approx 2$ resonance region. In particular, the two partially resolved resonances at approximately 322.0 and 351.5 mT (asterisks in Figure 1d) on each side of the center group of resonances are absent in the simulated spectrum. To achieve better agreement between simulated and experimental quintet EPR spectra, we have introduced fourth-order zero-field splitting terms into the spin Hamiltonian (eq 2), where $B_4^iO_4^i$ are Stevens operators.[8]

$$\mathcal{H}^{\text{4th}} = \mathcal{H}^{\text{2nd}} + B_4^0O_4^0 + B_4^2O_4^2 + B_4^4O_4^4 \qquad (2)$$

Such higher-order contributions are generally omitted[3,5] during the EPR analysis of organic high-spin states due to the smaller spin−orbit interactions in hydrocarbons.[6] Nevertheless, in the case of tetraradical **2**, the fit between the experimental and simulated spectra improves significantly upon inclusion of fourth-order terms according to eq 2 (Figure 1d,f). The zero-field splitting parameters are now $|D| = 0.00955$ cm^{-1} and $|E| = 0.0029$ cm^{-1}, and although the fourth-order coefficients are small (in 10^{-5} cm^{-1}: $B_4^0 = 10.0$, $B_4^2 = -8.84$, and $B_4^4 = 5.34$), they are crucial to reproduce the resonances at 322.0 and 351.5 mT. It should be noted that the simulation of the quintet spin state (Figure 1f) remained virtually unchanged when allowance was made for a slight *g* anisotropy or when forbidden transitions were included.[5]

The triplet biradical **2**(N_2) and the quintet tetraradical **2** are the most persistent localized polyradical species known to date with half-lives of ca. 30 and 55 h, as determined by monitoring the clean monoexponential decay of their EPR signals at 77 K. The higher persistence of the tetraradical **2** (up to 100 K) relative to **1** (at 4 K) can be entirely rationalized with the trends observed for the related triplet biradicals:[9] 1,3-cyclopentanediyl triplet biradicals are more persistent than their 1,3-cyclobutanediyl counterparts, and phenyl substitution at the radical centers provides for longer lifetimes.

In conclusion, the quintet spin state of **2** represents the first example of a tetraradical based on two localized 1,3-cyclopentanediyl units, with not only interesting electron paramagnetic behavior but also unexpected optical properties.

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