Cyclobutane as a General Ferromagnetic Coupling Unit. Design and Synthesis of a New, Hydrocarbon Quintet[1]

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High spin states are commonly encountered among transition row metals and their complexes, arising from singly occupied d orbitals on the metal. High spin organic molecules, on the other hand, are a comparatively unnatural phenomenon, and their generation almost always results from a great deal of design and contrivance. In recent years, a series of organic molecules (1) with spin as high as $S = 6$ (multiplicity = $2S + 1 = 13$; tridecet) has been documented, in which meta coupled phenyl carbenes provide the building blocks toward ever higher spin states.[2] These delocalized systems are based on a design which predicts high spin (ferromagnetic) coupling between adjacent units when the contiguous π topology of the molecule precludes the pairing of all electrons into bonds (non-Kekulé), provided the nonbonding MO's span common atoms (nondisjoint).[3] Similar π topology arguments have produced quintet tetraradical 2.[4]

1

2

5

A   B

3
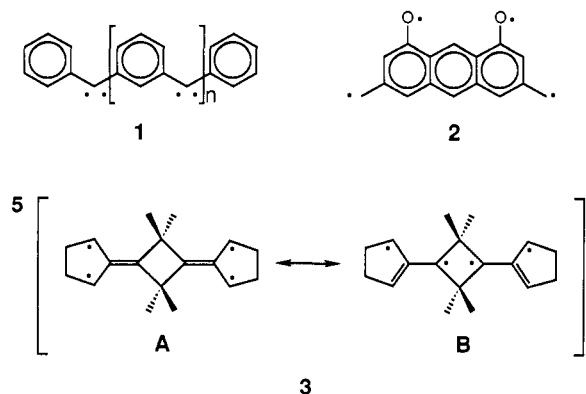
We present herein an example of an alternative ferromagnetic coupling mechanism between two triplets to give the higher spin state quintet ($S = 2$, four parallel spins). Tetraradical 3 combines two triplet 2-alkylidenecyclopentanediyls 4,[5] derivatives of the classic non-Kekulé molecule, trimethylenemethane (TMM).[6]

Coupling *between* the two TMMs occurs through the ground-state triplet, *localized*[7] biradical 1,3-cyclobutanediyl 5,[8] as evidenced by resonance structure B.

4   5

The synthesis (Scheme I) of the precursor bisdiazene 6[9] required the bisfulvene, 7.[9] This was prepared by capitalizing upon a creative application of Barton[10a] and Kellogg[10b] cycloaddition chemistry, first employed in related systems by Freund and Hünig.[11]

Photolysis[12] of 6 in either 2-methyltetrahydrofuran or poly-(methylmethacrylate) matrices at temperatures between 4 and 77 K in the cavity of an EPR spectrometer results, after as little as 15 s irradiation, in the triplet spectrum shown in Figure 1a. This is a typical "powder" or randomly oriented triplet spectrum. The zero-field splitting (zfs) values, thermal stability, and hyperfine splitting in the $\Delta m_s = 2$ region (ca. 14 G) allow us to assign monoazobiradical 8 as the carrier of the signal. In particular, the spectral parameters closely match those of biradical 9 ($|D/hc| = 0.0255$ cm^{-1}; $|E/hc| = 0.0030$ cm^{-1}; hyperfine splitting = 13.5 G)[13] and a variety of other 2-alkylidene-1,3-cyclopentanediyls 4.[5]

8   9
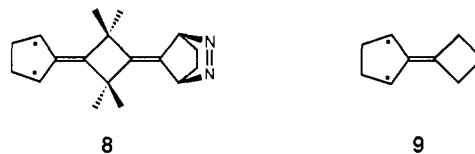
Further irradiation of the sample results in spectra typified by that shown in Figure 1b. In the $\Delta m_s = 1$ region, the six lines due to 8 are still evident. There are also many new lines which we assign to the quintet state of 3, based on the following observations. The new lines, most clearly the two outer pairs (2600, 2710, 3830, and 3935 G), increase upon prolonged photolysis, while those due to 8 *decrease* in intensity. This suggests that the carrier of the new signal is photochemically derived from 8, as expected for 3. A quintet gives rise to a maximum of 12 transitions in the $\Delta m_s = 1$ region.[2,14,15] The two outer pairs completely determine the zfs values of a quintet (Figure 1) and allow prediction of the other transitions using a simulation program.[14a] As shown in Figure 1b, the quintet zfs values ($|D/hc| = 0.0207$ cm^{-1}; $|E/hc| = 0.0047$ cm^{-1}) produce good agreement between simulated and experimental spectra.[16] Interestingly, a new line is also evident in the $\Delta m_s = 2$ region of the spectrum (ca. 1700 G), a relatively unusual observation for $S = 2$ spectra.[14a]

We believe that the quintet is the ground state of 3 based on two observations. First, the spectra are quite intense at tem-

(1) Portions of this work were reported at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, September 25–30, 1988.

(2) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235–238. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076–5078. (c) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *Ibid.* **1986**, *108*, 368–371. Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *Ibid.* **1986**, *108*, 2147–2156. (d) Iwamura, H. 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14, 1989.

(3) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 1, pp 23–39. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594.

(4) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251–1265.

(5) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446–453. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4, pp 151–194.

(6) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242–248.

(7) The term "localized" is applied herein to biradicals in which the two radical centers are not in classical π conjugation; they may, however, be separately delocalized.[8]

(8) Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356–1366.

(9) 7: ^{1}H NMR (CDCl$_3$) δ 1.69 (s, 12 H), 6.40 (m, 4 H), 6.50 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 30.1, 50.9, 120.2, 131.0, 137.4, 171.8. 10: ^{1}H NMR (CDCl$_3$) δ 1.21 (s, 12 H), 1.80 (m, 4 H), 2.00 (m, 4 H), 2.95 (s, 6 H), 4.67 (br s, 4 H). 6: ^{1}H NMR (CD$_2$Cl$_2$) δ 1.03 (m, 4 H), 1.22 (s, 12 H), 1.60 (m, 4 H), 5.28 (br s, 4 H).

(10) (a) Barton, D. H. R.; Guziec, F. S.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1794–1799. (b) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045–4060.

(11) Freund, W.; Hünig, S. *J. Org. Chem.* **1987**, *52*, 2154–2161.

(12) EPR/photolysis conditions were as in ref 8.

(13) Jain, R.; McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 552–560.

(14) (a) For a useful discussion of quintet EPR as it pertains to systems such as 3, see: Seeger, D. E. Ph.D. Dissertation, Yale University, 1983. (b) Note that for larger D values, more than 12 lines can appear. See: Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134–6145.

(15) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251–1259.

(16) A calculation of the D value for 3 along the lines of ref 2a and 2b produces $|D/hc| = 0.0212$ cm^{-1}. Details will be provided in the full account of this work.

Scheme I[a]
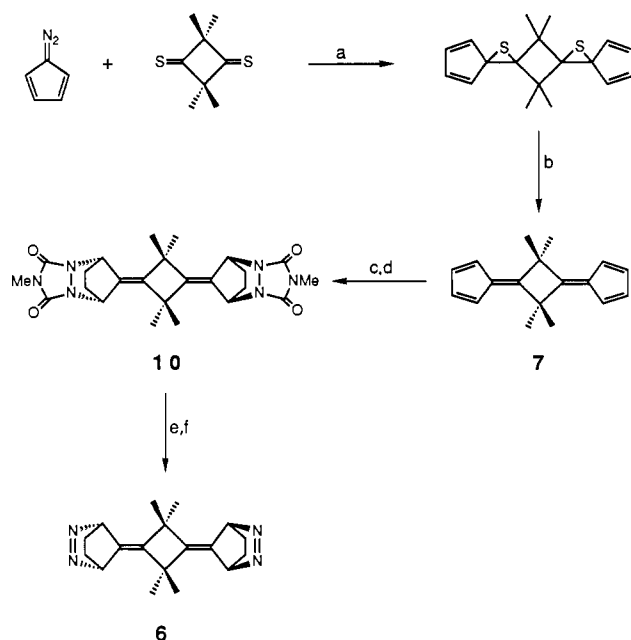
[a] (a) Mixture of products (syn/anti dithiiranes, monothiirane and **7**), 4 weeks, room temperature, dark; (b) PPh$_3$; (c) *N*-methyltriazolinedione; (d) NH$_2$NH$_2\cdot$H$_2$O, O$_2$; syn isomer unstable to hydrogenation conditions; (e) KOH, 2-PrOH, reflux, 2 h; (f) NiO$_x$.
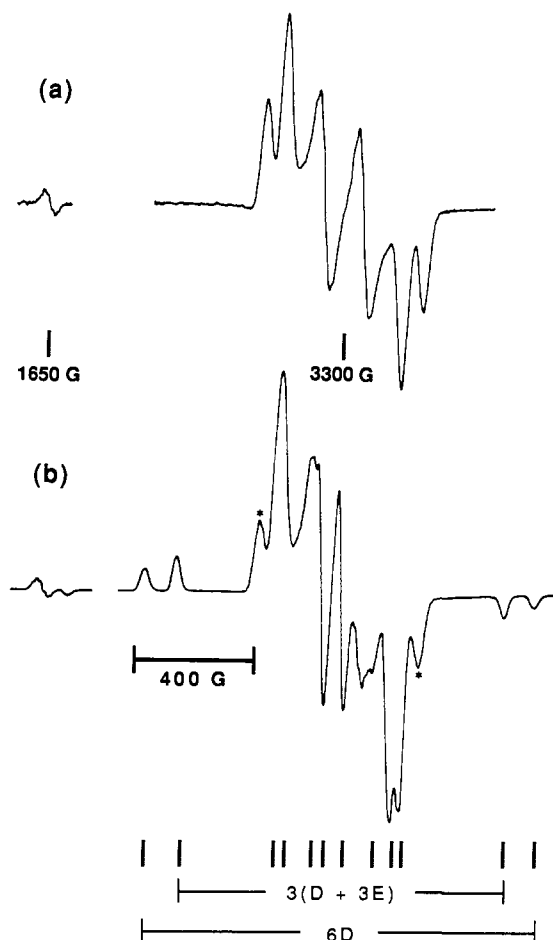

Figure 1. (a) Triplet EPR spectrum of **8** obtained upon brief photolysis of **6**. $|D/hc| = 0.0253$ cm^{-1} and $|E/hc| = 0.0042$ cm^{-1}. (b) Quintet EPR spectrum of **3** obtained upon extended photolysis of **6**. The vertical bars indicate the expected positions of the 12 transitions, from which the quintet zfs parameters can be obtained, as shown. Some **8** is also present, and the starred peaks are pure triplet **8** signals.

peratures as low as 3.8 K. Second, a Curie plot is linear in the range 17–80 K.[17] The usual interpretation of such observations is that the quintet is the ground state, although exact degeneracies among differing spin states cannot be ruled out.

An especially intriguing feature of **3** is its thermal stability. All cyclobutanediyls (**5**) prepared to date, including those with radical-stabilizing substituents, decay in the 20–55 K range and are not easily observed at temperatures above 60 K.[18] However, **3** is indefinitely stable at liquid nitrogen temperatures (77 K) and can be readily generated at this temperature. The cause of this enhanced stability is under further investigation.

Clearly, the localized biradical, 1,3-cyclobutanediyl, does ferromagnetically couple the two TMM triplets. This is the first rationally designed organic quintet that does not owe its high spin preference to the topology of a delocalized π system.[19] It has long been appreciated that magnetism, unlike conductivity, does not require delocalization, but **3** is the first organic realization of this concept. Our results suggest that cyclobutane is a general, ferromagnetic coupling unit, and further studies of this effect and extensions to still higher spin states are underway.

(17) The limitations on the usefulness of Curie plots have been discussed in detail. See: (a) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 195. (b) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972. (c) In the present system, as in most related studies, signal saturation occurs at $T < 15$ K, making this temperature range unusable for the Curie plot. (d) For a thorough discussion of the complexities involved in Curie plots for $S = 2$ molecules, see ref 14a, p 205.

(18) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240–2252.

(19) A variety of structures containing four stable radicals, such as galvinoxyls, appended to a central atom have been prepared and quintet states observed. The nature of the spin coupling mechanism and the relative energies of the various spin states are not known. See, for example: Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108–114, and references therein.

Ab Initio Molecular Orbital Studies of Chemical Shielding in Transition-Metal Compounds: ^{95}Mo Shielding in Molybdate and Thiomolybdate [MoO$_n$S$_{(4-n)}$]$^{2-}$ Anions

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Ab initio molecular orbital methods for chemical shielding have been extensively applied to first- and second-row elements[1–5] but

(1) Kutzelnigg, W. *Israel J. Chem.* **1980**, *19*, 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1985**, *105*, 1360. Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 6623 and references cited therein.

(2) Hansen, Aa. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035. Bouman, T. D.; Hansen, Aa. E.; Voight, B.; Rettrup, S. *Int. J. Quantum Chem.* **1983**, *23*, 595. Bouman, T. D.; Hansen, Aa. E. *Chem. Phys. Lett.* **1988**, *149*, 510.

(3) Facelli, J. C.; Grant, D. M.; Bouman, T. D.; Hansen, Aa. E. *J. Comput. Chem.*, in press.