

New high-spin π systems

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Abstract – Organic molecules and materials with large numbers of unpaired spins promise to display novel combinations of magnetic, optical, and electrical properties. Two examples from our lab demonstrate the potential for strongly coupling magnetic and optical properties and the possibility of designing magnetic materials that are electrically insulating.

INTRODUCTION

The design and preparation of organic materials with novel magnetic properties is emerging as a major focal point of modern organic chemistry.¹ Magnetism, of course, results from the interactions of electron spins, and most useful magnetic phenomena require a large number of unpaired electrons with their magnetic moments aligned parallel. This high spin, or ferromagnetic, coupling of electron spins is at the heart of magnetism, but is not a common situation in organic systems. In recent years, however, many studies of high spin organic molecules (those with $S=1$ (triplet) or greater) have provided valuable insights into the spin-coupling mechanisms available to organic structures, and have suggested several general approaches to very high spin organic materials.

Before discussing specific examples, it may be useful to speculate as to potential applications for an organic ferromagnet or related new materials. One immediately considers magnetic storage devices (disks, tapes ...) of the sort commonly used in computer systems. However, as discussed elsewhere,¹ the magnetic properties most likely to be associated with an organic ferromagnet are not especially favorable for this type of application. A more promising approach would be to capitalize on the novel optical and electrical properties that could also result from the presence of a large number of unpaired electrons. The unpaired electrons are typically high-lying in energy (nonbonding) and not involved in strong, localized bonds. This could give rise to high polarizabilities, low energy electronic transitions, and other novel optical properties. In addition, these loosely held electrons may – or may not – be mobile, in the sense of producing conducting materials. The important point is that organic synthesis and systematic structural control provide

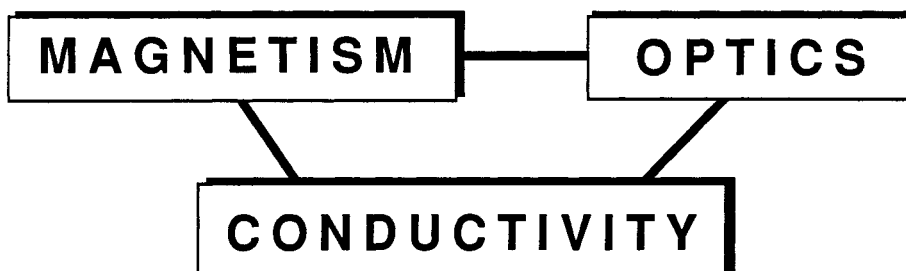


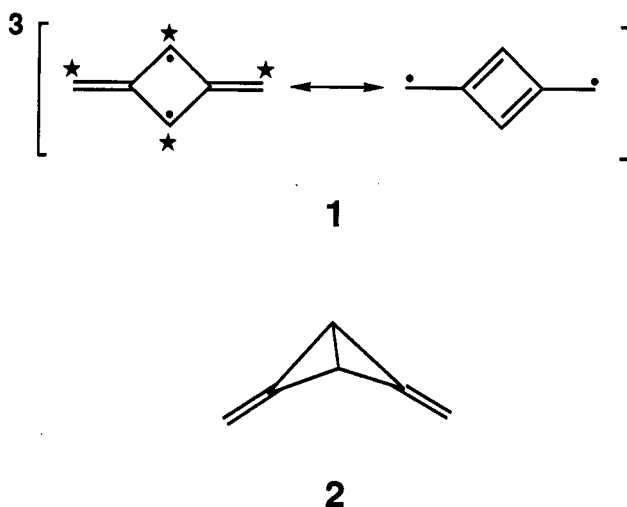
Fig. 1. Schematic emphasizing the interrelated physical properties that can result from unpaired electrons.

a means to rationally manipulate the interrelations among these properties (Figure 1). It is in this sense that we believe that materials with unprecedented properties will emerge. Their applications will depend on the particular mixture of electronic properties, and material properties (light weight, processability into thin films, etc.) that is attained.

Within this context, we will describe two recent studies from our labs that could serve as prototypes for higher order systems.

NON-KEKULÉ BENZENE. COUPLING OPTICAL AND MAGNETIC BEHAVIORS

In a symposium on novel aromatic compounds, we cannot resist providing a brief summary of our recently reported studies on 2,4-dimethylene-1,3-cyclobutanediyl (1), the non-Kekulé isomer of benzene.² Our results demonstrate the remarkable changes in optical and magnetic properties on conversion of benzene to its non-Kekulé isomer. Structure 1 also provides an example of the ways optical and magnetic behaviors may be tightly coupled in high-spin organic molecules.



We initially viewed structure 1 as a test of topology-based methods³ for predicting the spin states of hydrocarbons. As shown, 1 is an alternant hydrocarbon for which the starred atoms outnumber the unstarred by two, and theory predicts a triplet ground state for such a structure. The EPR spectroscopy of 1 was just as predicted and fully supported the prediction of a triplet ground state.

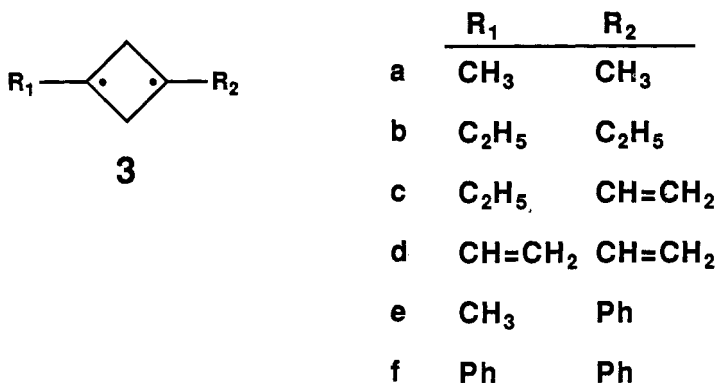
A surprising feature of 1, though, was its optical spectroscopy. This C_6H_6 structure is yellow-orange in color ($\lambda_{max} = 506 \text{ nm}$; ${}^3B_{2u} \rightarrow {}^3B_{1g}$; $f = 0.022$) and shows a bright green fluorescence. Thus, isomerization of benzene to 1 produces dramatic changes in both optical and magnetic properties. While such a chemical transformation would be difficult, similar physical changes can be induced photochemically.

Photolysis of 1 with visible light cleanly produces dimethylenebicyclobutane (2). This process can be reversed using light of a different wavelength and a low energy sensitizer. Thus, one can photochemically convert a colored, paramagnetic substance (1) to a colorless, diamagnetic structure (2), and then reverse the process. Note that since the visible transition in 1 is triplet-to-triplet, it could be manipulated by external magnetic fields. Of course, the $1/2$ system lacks many properties essential for the preparation of any type of "switch", most notably thermal stability. It does, however, nicely illustrate the tight coupling of optical and magnetic properties that can be achieved. We do not mean to imply that similar effects could not also be seen in transition metal-based systems. The potential advantage of organic systems, however, lies in the greater range of structural variation feasible, which would allow one to fine tune the spectroscopic properties of the system. An advantage of the transition metal-based systems is their much greater thermal and environmental stability, a challenge which must be faced if organic systems are ever to become practically useful.

PARTIALLY LOCALIZED, VERY HIGH-SPIN STRUCTURES.
DISCONNECTING MAGNETISM AND CONDUCTIVITY

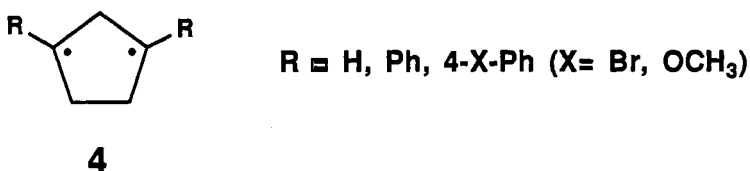
Magnetism, unlike conductivity, does not require delocalization of electrons. Most models for organic ferromagnets and most very high spin organic structures, however, are fully conjugated π systems, similar to the types of structures that are used as conducting polymers. Most natural, metallic magnets are also conductors or semiconductors. A major emphasis of our research has been the development of high-spin organic structures that are in some sense "localized". By localized, we mean that the spin is not completely contained in one contiguous π system, *i.e.*, the spin-containing substructures are to some extent insulated from one another. This could provide an approach to highly insulating magnetic materials. In addition, a fairly general problem in the conducting polymers field is the very poor solubility of the materials, a direct consequence of the planar, conjugated structure. Breaking up the conjugation generally increases solubility substantially, and so the strategy of using partially localized systems may produce materials that are more processable.

Considering first systems with only two spins, we have prepared a wide variety of cyclobutanediyls (3), and shown that all have triplet ground states.⁴ These triplet biradicals are intrinsically interesting models for reactive intermediates and photochemical excited states, and we have studied their chemistry extensively.⁵

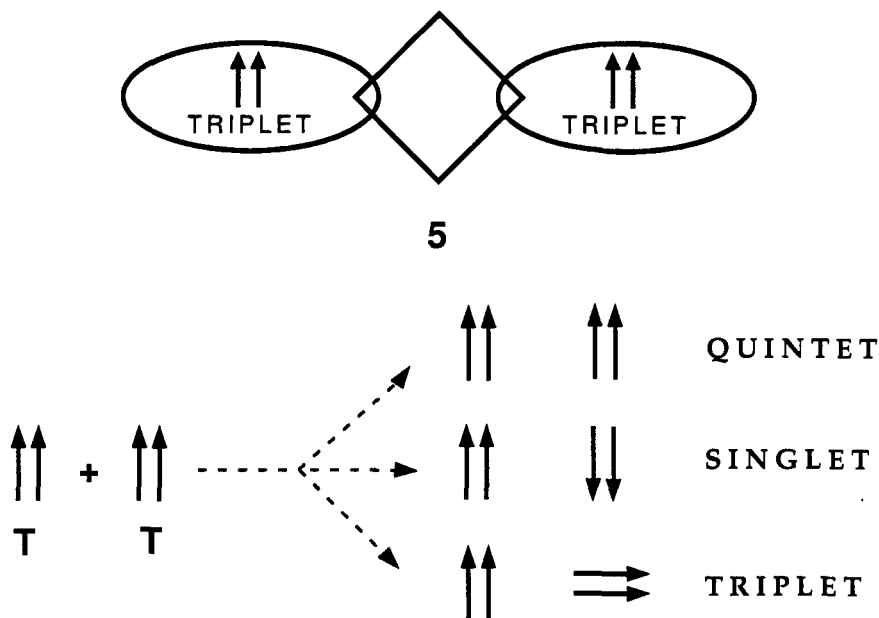


At the same time, structures 3 provide a valuable insight concerning spin coupling mechanisms. Consider the diphenyl system, 3f. It can be thought of as two weakly interacting benzyl (or cumyl) radicals. In general, weakly interacting radical pairs will produce a *singlet* ground state, barring some special geometrical orientation that is not possible for 3. Yet, 3 itself has a *triplet* ground state. We have analyzed this effect in some detail⁶ and shown that it is a consequence of through-bond coupling mediated by the CH₂ groups of the ring. The effect is general, as all cyclobutanediyls prepared to date have triplet ground states. Thus, if one wants to high spin (ferromagnetically) couple two organic radicals, a reliable way to do so would be to link them through a four-membered ring. Stated differently, a cyclobutane appears to be a general ferromagnetic coupling unit. More recent work from our lab⁷ suggests that the cyclopentanediyl system (4), the parent of which was first observed by Closs,⁸ may also be a general ferromagnetic coupler, although more examples are needed.

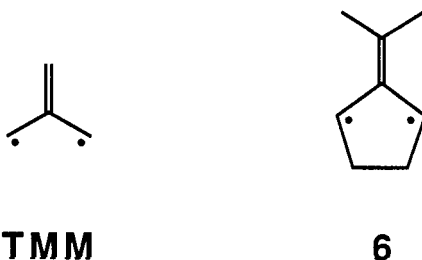
These nonconjugated ferromagnetic coupling units suggest an approach to the insulating magnetic polymers discussed above. One can envision a polymer composed of spin-containing units (organic radicals, triplet biradicals, radical anions or cations, nitroxyls ...) linked by cyclobutanes or cyclopentanes. The aliphatic coupling units would disrupt the absolute planarity of the structure, thereby enhancing solubility, and further alkyl groups could be appended if necessary.



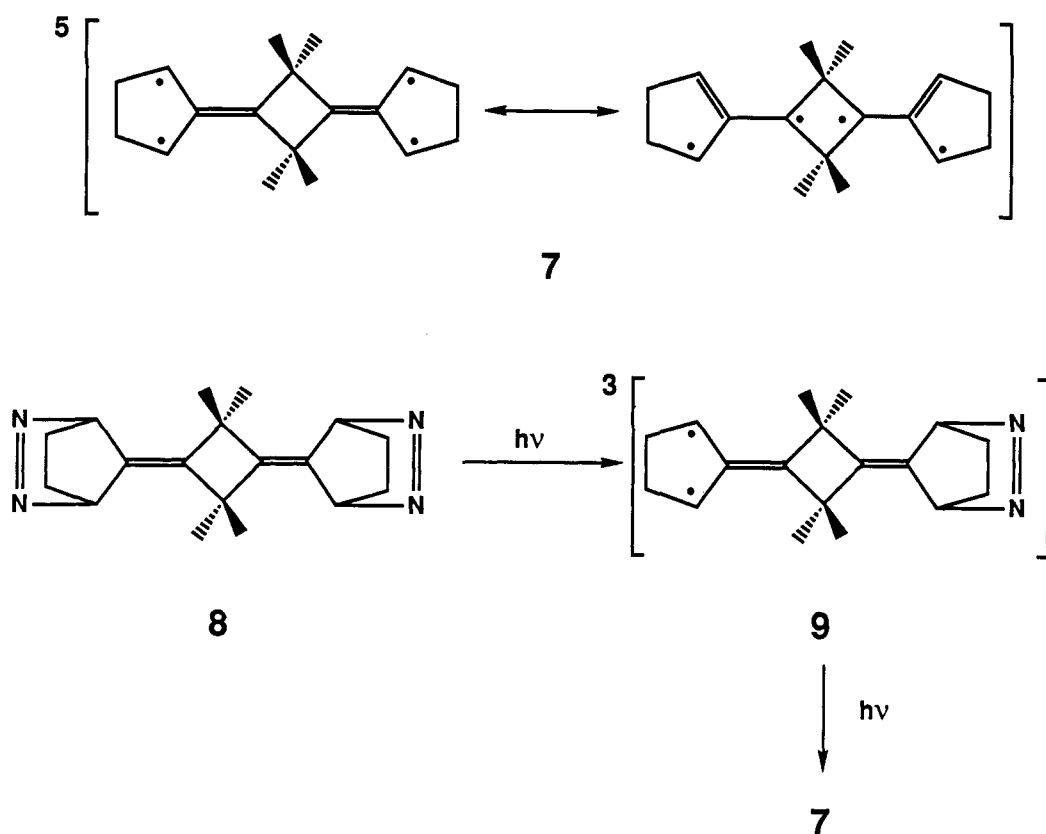
In order to evaluate the viability of this scheme, we wished to further test the generality of cyclobutane as a ferromagnetic coupling unit. We sought a structure such as 5, in which two triplets are coupled via a cyclobutane, to produce a tetraradical. The general case of four electrons in four essentially degenerate, non-bonding molecular orbitals (NBMO) is quite complex. There are 70 ways to place the electrons in the NBMO, and these configurations give rise to 36 states: 15 singlets (S), 20 triplets (T), and 1 quintet (Q). The situation is substantially simplified, however, if each of the two building blocks in 5 possesses a strong intrinsic triplet preference. Then, as shown, only three states are possible: Q, S, and T.



The prototypical triplet biradical is trimethylenemethane (TMM), which is relatively stable.⁹ The thermal stability is greatly enhanced by incorporating the TMM into a five-membered ring to produce a 2-alkylidene-1,3-cyclopentenediyl (6, Berson TMM).¹⁰ In fact, structures such as 6 can be stable up to room temperature, in rigid media. We thus chose tetraradical 7 as one target structure. It contains the essential features of 5: two robust triplets linked through a cyclobutane such that, in some resonance forms, a cyclobutanediyl is present.



As described in detail elsewhere,¹¹ photolysis of bisdiazene 8 in rigid media at 4 or 77 K first produces triplet biradical 9, as identified by EPR. Further photolysis produces a new spectrum which is attributable to the quintet state of 7. The observation of strong quintet signals at temperatures as low as 3.8 K; a linear Curie plot from 17-80 K; and the absence of any new signals at higher temperatures all indicate that the quintet is the ground state of 7. A remarkable feature of 7 is its thermal stability. Unlike all previously observed cyclobutanediyls (3), which decompose readily at temperatures below 60 K,⁵ quintet 7 is indefinitely stable at 77 K and higher. The origin of this increased stability is unknown at present.



The results for 7 strongly indicate that cyclobutane is a general, ferromagnetic coupling unit. Further efforts are underway in our labs to explore the use of cyclobutane and other coupling units in the design and preparation of even higher spin molecules and materials.

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REFERENCES

1. Symposium on Ferromagnetic and High Spin Molecular Based Materials; 197th American Chemical Society National Meeting; April 9-14, 1989; Dallas, TX, USA. Proceedings: *Mol. Cryst. Liq. Cryst.*, in press.
2. G.J. Snyder; D.A. Dougherty, *J. Am. Chem. Soc.*, **111**, 3927-3942 (1989). G.J. Snyder; D.A. Dougherty, *J. Am. Chem. Soc.*, **111**, 3942-3954 (1989). G.J. Snyder; D.A. Dougherty, *J. Am. Chem. Soc.*, **108**, 299-300 (1986). G.J. Snyder; D.A. Dougherty, *J. Am. Chem. Soc.*, **107**, 1774-1775 (1985). See also: P. Dowd; Y.H. Paik, *J. Am. Chem. Soc.*, **108**, 2788-2790 (1986).
3. See, for example, A.A. Ovchinnikov, *Theor. Chim. Acta*, **4**, 297-304 (1978). D.J. Kelin, C.J. Nelin; S. Alexander; F.A. Matsen, *J. Chem. Phys.*, **77**, 3101-3108 (1982); W.T. Borden; E.R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587-4594 (1977).

4. R. Jain; M.B. Sponsler; F.D. Coms; D.A. Dougherty, *J. Am. Chem. Soc.* **110**, 3430-3435 (1988). R. Jain; G.J. Snyder; D.A. Dougherty, *J. Am. Chem. Soc.* **106**, 7294-7295 (1984).
5. M.B. Sponsler; R. Jain; F.D. Coms; D.A. Dougherty, *J. Am. Chem. Soc.* **111**, 2240-2252 (1989).
6. J. Pranata; D.A. Dougherty, *J. Phys. Org. Chem.* **2**, 161-176 (1989). A.H. Goldberg; D.A. Dougherty, *J. Am. Chem. Soc.*, **105**, 284-290 (1983). See also, C. Doubleday, Jr.; J.W. McIver, Jr.; M. Page, *J. Am. Chem. Soc.* **104**, 6533-6542 (1982).
7. F.D. Coms; D.A. Dougherty, *Tetrahedron Lett.*, **29**, 3753-3756 (1988). E. Stewart, unpublished results.
8. S.L. Buchwalter; G.L. Closs, *J. Am. Chem. Soc.*, **97**, 3857-3858 (1975); **101**, 4688-4694 (1979).
9. P. Dowd, *Accts. Chem. Res.* **5**, 242-248 (1972).
10. J.A. Berson, *Accts. Chem. Res.* **11**, 446-453 (1978).
11. J.A. Novak; R. Jain, D.A. Dougherty, *J. Am. Chem. Soc.*, in press.