

Figure 7. Liposidomycin B, a nucleoside antibiotic isolated from *Streptomyces* sp.

be encountered, and larger sample quantities can usually be isolated than in the case of nucleosides from nucleic acids. In such studies, CID has two main functions: to generate fragment ions which may bear structural information but which are not formed by spontaneous dissociation, and to establish the origins or decomposition pathways of fragment ions. For example, CID spectra of the complex nucleoside liposidomycin B (Figure 7) were used to establish the order in which structural subunits were lost by dissociation, thereby placing constraints on the interconnectivity of subunits.³² Such information is complementary to that obtained from 2D NMR experiments, but requires less material. If a detailed CID map is determined for one

member of a family of compounds, subsequent measurements made on related molecules can be used to rapidly assign sites of structural differences.

The recent discovery of methods for vaporization and ionization of very polar molecules has led to unforeseen results in which proteins in the range to 236 kilodaltons (kDa) and intact RNAs up to 25 kDa have been converted to solventless, gaseous ions in high yield and detected by mass spectrometry.^{75,76} The exceptional polarity of polynucleotides, which is conferred by the polyphosphate backbone, has long constituted a significant obstacle to the applications of mass spectrometry to nucleic acids and to many biological problems that require work at the polymer, rather than nucleoside or monomer, level. It appears certain that this obstacle as such is rapidly diminishing, and a new generation of applications of mass spectrometry to nucleic acids will follow.

Work described from this laboratory has been supported by the National Institutes of Health, presently Grants GM 29812 and GM 21584. I am grateful to Pamela F. Crain for a critical reading of this manuscript.

(75) Hillenkamp, F.; Karas, M.; Ingendoh, A.; Stahl, B. In *Biological Mass Spectrometry*; Burlingame, A. L., McCloskey, J. A., Eds.; Elsevier: Amsterdam, 1990; p 49.

(76) Smith, R. D.; Loo, J. A.; Edmonds, C. G.; Barinaga, C. J.; Udseth, H. R. *Anal. Chem.* 1990, 62, 882.

Spin Control in Organic Molecules

DENNIS A. DOUGHERTY

Contribution No. 8159, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received July 9, 1990 (Revised Manuscript Received October 22, 1990)

Magnetism has fascinated and served humanity for almost 3000 years.¹ Since the discovery of the lodestone (FeO-Fe₂O₃), many different magnetic materials have been developed, almost all based on transition metals and/or rare-earth elements. Technological application of magnetism also has a long history, from the compass to today's sophisticated magnetic memory systems. In contrast, the theory of magnetism has progressed more slowly, despite the efforts of great minds throughout history. The reason early theoretical models were not very valuable is now clear. Any viable theory of magnetism must be based on two inherently quantum mechanical concepts: electron spin and the Pauli exclusion principle. As such, only the 20th century has produced a competent model for magnetism, and that model continues to evolve. Studies over the last 20 years have revealed a bewildering array of new magnetic phenomena that continue to challenge our understanding of solid-state physics.²

In recent years, our group and others have embarked on a long-range program to prepare magnetic materials

based on organic molecules and/or polymers. One can imagine that such materials would have fundamentally new properties that would provide valuable insights into the nature of magnetism. There may also be practical value in such materials. From our perspective, though, the use of molecular structures³ in the design of new magnetic materials represents an intellectual challenge that defines a frontier of organic chemistry and needs no further justification.

Ultimately, the magnetic properties of any material are determined by the ways in which unpaired electrons in the material interact with each other. For example, a ferromagnet results if, over large regions of the material (domains), unpaired electrons are high-spin coupled (spins parallel) to each other. As with all forms of magnetism, ferromagnetism is strictly a solid-state phenomenon. There is no such thing as a ferromagnetic molecule. It is possible, however, for a condensed state of certain molecules to be ferromagnetic. The issue is spin control: the qualitative and quantitative aspects of spin-spin interactions among electrons. The present

Dennis Dougherty was born in Harrisburg, PA, in 1952. After receiving a B.S./M.S. from Bucknell University, he obtained a Ph.D. from Kurt Mislow at Princeton University. A year of postdoctoral study at Yale with Jerry Berson introduced him to biradicals and azo compounds, and in 1979 he joined the faculty of Caltech, where he is now Professor of Chemistry. In addition to the work described here, he also is interested in studies of molecular recognition and biomimetic catalysis in aqueous media. Outside of chemistry, his major interests are Ellen, Meghan, and Kayla.

(1) For valuable introductions to magnetism, see: Mattis, D. C. *The Theory of Magnetism I*; Springer-Verlag: Berlin, 1981 (see especially Chapter 1 for a fascinating account of the history of magnetism). Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.

(2) Hurd, C. M. *Contemp. Phys.* 1982, 23, 469-493.

(3) Most magnetic materials are not molecular solids. Rather, they involve extended structures in the solid state, such as seen in metallic, ionic, or network solids.

Account will focus on studies of organic molecules that can provide fundamental insights into electron spin interactions, using work from our own labs to illustrate general findings. Such studies, we believe, must form the foundation for the rational development of novel magnetic materials.

Cyclobutanediyls: A General Class of High-Spin, Localized Biradicals

A typical organic molecule has each spin-up electron paired with a spin-down counterpart, and all such pairs are placed into low-energy, bonding molecular orbitals (MO). Such a molecule has no permanent magnetic moment, and a condensed state would be diamagnetic. Structures with an odd number of electrons (radicals) must have an excess of one spin type and so possess a permanent magnetic moment. A condensed state of such a structure could display any of a wide range of magnetic behaviors (paramagnetism, ferromagnetism, antiferromagnetism, spin glass, ...) ² depending on the natures and magnitudes of the interactions among the magnetic moments of the individual molecules.

There also exists an interesting class of even-electron organic molecules with two (or more) electrons that are not tightly paired into bonding MOs. These unpaired electrons are associated with two (or more) nonbonding MOs (NBMOs) that are degenerate, or nearly so. In the two-electron case—a biradical—the ground state can be either a low-spin singlet (S: antiferromagnetic coupling of the spins) or a high-spin triplet (T: ferromagnetic coupling of the spins). ⁴ Such structures provide the simplest proving ground for theories of the magnetic interactions of electron spins, and they have been the focus of much interest in recent years.

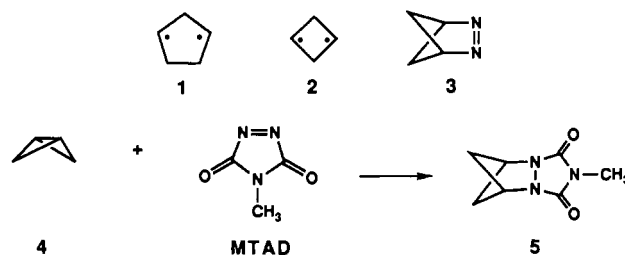
Apart from any insights into magnetism they may provide, the structures, reactivities, and spin preferences of biradicals and related structures are also intrinsically interesting. Biradicals and biradical-like structures are important intermediates in a wide variety of thermal and photochemical processes, and the reactivity and spectroscopy of the S and T states are expected to differ considerably. In addition, as will become apparent, spin preferences are manifestations of very subtle aspects of molecular electronic structure. Thus, studies of spin states of molecules provide demanding tests of modern electronic structure theories.

As we began our program to study biradicals, we emphasized triplets, rather than singlets. Our motivations were not so lofty as the pursuit of a ferromagnet; they were purely practical. Matrix isolation EPR spectroscopy provides a powerful, general technique for observing and characterizing triplets; singlets are EPR silent. The triplets we hoped to observe were structures we have termed localized biradicals. These are molecules that contain two well-defined radical substructures that are not in classical π conjugation with each other. The radical substructures themselves can be delocalized, as in allyl or benzyl.

In 1980, when we began this work, 1,3-cyclopentanediyli (1) had been characterized by Closs, ⁵ with some very intriguing results. For some time, however,

(4) Note the distinction between ferromagnetism, a solid-state concept, and ferromagnetic coupling, an indication of a high-spin interaction between two magnetic moments. A similar relationship exists between antiferromagnetism and antiferromagnetic coupling.

1 was the only example of a localized, hydrocarbon biradical to be directly observed. We chose cyclobutanediyl, 2, as a candidate for direct observation by EPR. It is, of course, not an especially dramatic con-



ceptual leap from 1 to 2, but we were seeking any system that might provide a second example of an observable, localized triplet biradical. An immediate problem, though, was that the logical diazene precursor 3, which could form 2 on loss of N_2 , represented an essentially unknown ring system. A critical discovery, then, was our finding that *N*-methyltriazolinedione (MTAD) could be coaxed into adding across the strained central bond of bicyclo[1.1.0]butane (4) to give urazole 5. ⁶ A standard sequence then produced 3. The TAD addition reaction is fairly general, and we have been able to use it to prepare a wide variety of new diazenes. As is often the case, a synthetic advance opened the door to a wide array of spectroscopic and mechanistic studies.

Diazene 3 is also an intrinsically interesting structure. It displays unique thermal chemistry and photochemistry, which we studied extensively. ⁷ However, photolysis of 3 at 4 K in an EPR spectrometer, the experiment for which 3 was designed, was unsuccessful. No triplet EPR signal could be seen.

Spin Preferences in Localized Biradicals. Searching for a reason for our failure to directly observe triplet 2, we considered the possibility that the ground spin state of 2 was, in fact, a singlet. It was not obvious why 1 should have a triplet ground state, and perhaps 2 experiences different interactions. This prompted us to pursue a quantitative analysis of the factors that determine the ground spin states of such structures. We begin with some background on spin preferences.

For a biradical to have T lie below S, two conditions must be met. The overlap integral, *S*, between the two orbitals that contain the radicals must be 0, or nearly so. If it is not, the in-phase combination of orbitals will lie well below the out-of-phase, creating a large HOMO-LUMO gap and a strong preference for spin pairing into the lower orbital. Second, the exchange integral between the two orbitals, *K*, must be large. We can illustrate the interplay of these two by considering two prototype structures: atomic carbon and molecular hydrogen (H_2).

In atomic carbon a 3P ground state results from high-spin coupling of the two electrons in the singly occupied, orthogonal p orbitals. This is a manifestation of Hund's rule. It is clear that $S = 0$ in this case, and

(5) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857-3858. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688-4694.

(6) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092-4093. See also: Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090-4092.

(7) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 1131-1132. Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333-2334. Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211-4217.

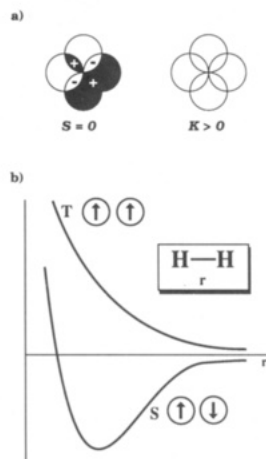


Figure 1. (a) Perpendicular p orbitals at an atomic center. The left figure illustrates the exact cancellation of regions of positive overlap by regions of negative overlap. The right figure shows that K is still substantial. (b) Dissociation curve for H_2 .

so the critical issue is the exchange interaction. Recall that the antisymmetrization of the wave function required by the Pauli principle gives rise to a novel type of two-electron interaction, embodied in the exchange integral (K). Basically, the Pauli principle forbids electrons of like spin from occupying the same region of space; their motions are correlated so as to keep them apart. A singlet pair of electrons is not similarly correlated and so experiences greater electron–electron repulsion and is destabilized. In atomic C the two p orbitals are very much coextensive in space: *they overlap extensively*. They are orthogonal (the overlap integral, S , equals 0) because regions of positive overlap cancel regions of negative overlap (see Figure 1). Such cancellation does not occur with K , and its magnitude is quite substantial. One can qualitatively evaluate K by considering the overlap of the orbitals *disregarding sign*. This identifies regions of space where the two electrons can interact quite strongly, leading to destabilizing Coulomb repulsions (Figure 1). Only in the triplet does the Pauli principle prevent this from happening, and so T lies below S.

It is tempting to extend Hund's rule, which was developed for atomic states, to molecules and conclude that all molecules with two electrons that are not strongly coupled to make a conventional bond should have a triplet ground state. However, the simplest molecule, H_2 , refutes this generalization. It has long been appreciated that the singlet state of H_2 lies below the triplet at *all* separations (Figure 1). Even at very large "bond lengths", where one has an essentially degenerate pair of NBMOs, T never drops below S. This illustrates an important point: in general, *Nature favors antiferromagnetic coupling of two weakly interacting electrons*. Hund's rule is a special case, which applies only when the two electrons are primarily on the same atomic center. This simple observation establishes that, in designing ferromagnets, one cannot simply create a large number of spins, crystallize or otherwise condense them, and then hope for the best. Most solid samples of radicals and other high-spin molecules will, at low temperatures, behave as anti-ferromagnets.

In H_2 (at long bond lengths) S is greatly diminished, but so is K . The orbitals share no region of overlap in

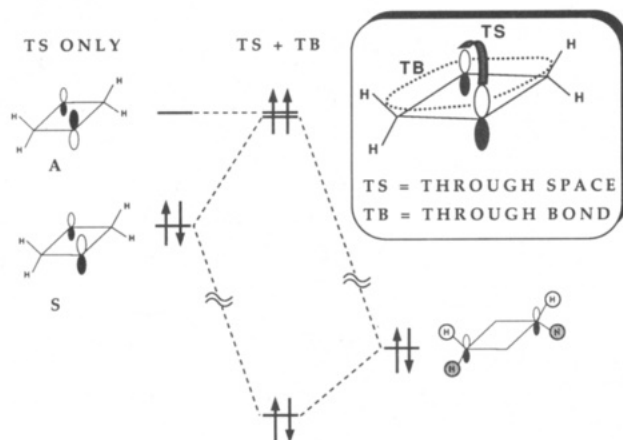


Figure 2. Orbital mixing diagram for **2**. The energy scale (vertical axis) is only qualitative; the π_{CH_2} orbitals are actually much lower.

which the Pauli principle can operate. Generally, K drops off faster with distance than S , and so S lies below T at all distances.

The essential recipe, then, for creating a high-spin ground state sounds a bit paradoxical: the two electrons must occupy the same region of space, yet their quantum-mechanical overlap must be near 0. It should be clear that nodal properties of orbitals will play a critical role, since it is the cancellation of opposite phases of the p orbitals that zeros the overlap in atomic C. We can now address structures such as **1** and **2**. High-quality ab initio calculations we performed indicate that **2**,⁸ like **1**,^{5,9} does have a triplet ground state, and the magnitude of the preference in **2** (1.7 kcal/mol) is roughly twice that for **1** (0.9 kcal/mol). Superficially, **1** and **2** resemble elongated H_2 more than atomic C, and so it was not obvious why T lies below S.^{8,10}

The cause of the triplet ground state in **1** and **2** is through-bond coupling,¹¹ mediated by the ring CH_2 groups. One way to visualize the interaction is via the orbital mixing diagram for **2** shown in Figure 2. Consider first the direct, through-space interaction of the two radical p orbitals. The interaction is substantial: they overlap considerably. This produces a large HOMO–LUMO gap and a singlet ground state. However, the CH_2 groups of **2** have filled orbitals of π symmetry that can mix with the p orbitals, but only with the symmetric combination (the HOMO). This "through-bond" interaction of the radical p orbitals raises the energy of the HOMO to a level that, by coincidence, is very nearly degenerate with the LUMO. Obtaining a degenerate HOMO–LUMO pair is equivalent to erasing the overlap between the radical p orbitals. This happens because through-bond coupling introduces new nodes: the HOMO is the *out-of-phase* combination of the CH_2 π orbitals and the radical p orbitals. Although overlap is erased, exchange repulsions remain large because the two p orbitals that hold the unpaired electrons interact substantially. Clearly, the situation resembles atomic C, so **2** displays a ferromagnetic coupling of the two spins, and a triplet

(8) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284–290. Pranata, J.; Dougherty, D. A. *J. Phys. Org. Chem.* **1989**, *2*, 161–176.

(9) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245–2246.

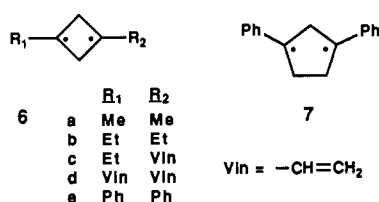
(10) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533–6542.

(11) (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (b) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

ground state. In **1**, the through-space effect is smaller because the radical centers are farther apart in the five-membered ring than the four-membered ring, but the through-bond effect is also smaller because only one CH₂ group is coupling. Again the two effects almost precisely balance one another, and a triplet ground state results.

A few more observations about the through-bond coupling mechanism may be useful. Inorganic chemists will recognize that it is precisely analogous to superexchange, a relationship that has been noted previously.¹² Like superexchange, through-bond coupling need not always produce a triplet ground state. When the through-space effect is very weak, through-bond coupling (superexchange) can open up a HOMO-LUMO gap, thereby favoring a singlet ground state (antiferromagnetic coupling). Also, by taking linear combinations of the HOMO and LUMO, one can obtain the localized GVB-pair orbitals for the biradical systems.⁸ This analysis allows a direct evaluation of the roles of overlap and exchange, and it can be clearly shown that, in **2**, through-bond coupling reduces GVB-pair overlap to nearly 0, while maintaining a significant degree of GVB-pair exchange.

Direct Observation of Cyclobutanediyls. Convinced by our theoretical studies that the four-membered-ring system was a good target, we continued our pursuit of directly observable localized biradicals. The experimental breakthrough required only a minor conceptual advance. Dimethylcyclobutanediyl **6a** is observable in its triplet ground state by EPR at 4–25 K.¹³ This observation, and a considerable amount of synthetic work, led to a whole series of observable cyclobutanediyls **6**, the first series of its kind.¹⁴ The study of the EPR spectroscopy and reactivity of these species produced many valuable insights into the fundamental nature of such structures.



The EPR spectroscopy of organic triplets can be very informative. For example, triplet EPR provides a sensitive, direct probe of the average distance (r) separating the two spins. In particular, the zero-field splitting (zfs) parameter D arises from a dipolar coupling of the spins, and so it is proportional to r^{-3} . Thus, it was satisfying to see that D progressively decreases as more delocalization is introduced along the series **6**. In fact D scales very well with the spin densities one would expect at the cyclobutane radical centers based on analogous monoradicals. A similar proportionality to monoradical spin densities could be seen in the hyperfine coupling constants to the ring (CH₂) protons. These results established that the spin densities in the two halves of **6** are similar to those in isolated monoradicals: there are no special delocalization effects

(12) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884–4899.

(13) Jain, R.; Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7294–7295.

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

across the cyclobutane. We have recently prepared the substituted cyclopentanediyl **7**, and its spectroscopy follows the same pattern.¹⁵

The EPR signals of the cyclobutanediyls decayed at elevated temperatures, and product studies showed that the decay process was C–C bond formation (ring closure).¹⁶ Thus, we could directly observe perhaps the most fundamental of organic reactions: direct coupling of two radicals to make a C–C bond. Of course, this was the spin-forbidden, triplet-to-singlet version of the reaction, and spin dynamics were expected to play a major role. Kinetic studies, which were substantially complicated by matrix site effects, revealed ring-closure activation energies of 1–2 kcal/mol. The Arrhenius log A values were in the range 6–8, very low for a simple, unimolecular reaction. We interpreted this rate retardation by roughly a factor of 10⁶ to be a manifestation of the spin-forbiddenness of the reaction.¹⁷ For several of the structures, quantum mechanical tunneling was important in the decay, an unusual situation for a reaction involving primarily motions of heavy (non-H) atoms.¹⁸

An important generalization from these results is that all the cyclobutanediyls and cyclopentanediyls prepared to date appear to have T ground states. This indicates that the through-bond mechanism described above is fairly robust, a feature we will exploit further below.

Topologically Interesting π Systems. Non-Kekulé Benzene

Magnetism arises when the overlap integral between orbitals is small, but the exchange integral remains large; and we have already described two ways in which this can occur. The first is the Hund's rule type interaction of orthogonal orbitals, as in simple atoms and carbenes. The second is the introduction of a through-bond coupling (superexchange) unit that negates direct overlap while maintaining exchange. There is a third class of molecules in which a high-spin ground state can occur. These are fully conjugated, planar π systems with topologies (connectivities) that produce two NBMOs that are degenerate at the Hückel level and nearly so at higher levels. Since the NBMO degeneracy is set by the topology, the issue of spin preference can be analyzed solely in terms of exchange repulsions.

Table I shows five prototypes. Both T and S ground states are known, and theory and experiment are not always in agreement. It is beyond the scope of this Account to fully cover this broad field. Many outstanding workers have contributed over the past 20 years to the development of what we believe is a useful working model for the prediction of spin preferences in certain types of π systems.¹⁹ We shall try to give some feeling for the status of the field, using systems we have studied to illustrate the important principles.

An especially interesting example of such a structure is **11**, which is called 2,4-dimethylene-1,3-cyclobutanediyl or 1,3-dimethylenecyclobutadiene (either way it is DMCBD). It is a C₆H₆, six- π -electron struc-

(15) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753–3756.

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

(17) See ref 16 for a list of other reactions of triplet biradicals with similarly small log A values.

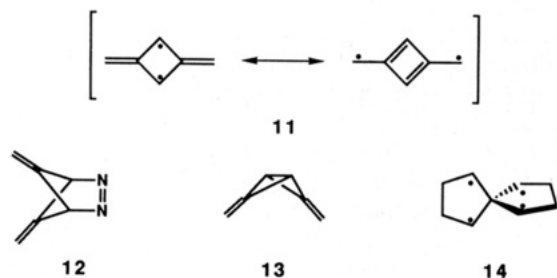
(18) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700–1701.

Table I

	GROUND STATE ^a		NBMO	
	Theory	Expt.		
 TMM	T	T		
 8	S ^b	(S) ^{c,d}		
 9	T	T		
 10	S	T		
 11	T	T		

^aAppropriate references can be found in the text. ^bSquare structure. ^cRectangular structure. ^dBally, T.; Masamune, S. *Tetrahedron* 1980, 36, 343-370.

ture, and we think of it as the non-Kekulé²⁰ isomer of benzene. The left resonance structure looks like a trimethylenemethane (TMM), but the right looks like a cyclobutadiene. Since the former is a triplet, but the latter a singlet, we considered 11 to be an interesting test of topology-based rules for predicting spin preferences.



An ideal precursor to 11 is diazene 12, which contains the diazabicyclo[2.1.1]hexene system for which we had developed a synthetic route. In practice, however, the synthesis of 12 proved to be quite challenging, requiring the development of several new synthesis technologies.^{21,22} Once the synthesis hurdle was overcome, we found that biradical 11 was especially amenable to spectroscopic characterization.²² EPR studies con-

(19) For relevant reviews, see: (a) Dowd, P. *Acc. Chem. Res.* 1972, 5, 242-248. (b) Berson, J. A. *Acc. Chem. Res.* 1978, 11, 446-453. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 151-194. (c) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 195-258. (d) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* 1981, 14, 69-76. (e) Michl, J.; Bonacic-Koutecký, V. *Tetrahedron* 1988, 44, 7559-7585. (f) Berson, J. S. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, pp 455-536. (g) Breslow, R. *Mol. Cryst. Liq. Cryst.* 1989, 176, 199-210.

(20) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp 232-233.

(21) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* 1985, 107, 1774-1775.

(22) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* 1989, 111, 3927-3942.

firmed that the structure has a triplet ground state. Hyperfine coupling was again clearly evident, and it provided values for the spin densities at the methine and methylene carbons (where, to first order, all spin density should lie). The spin densities seen are not consistent with those predicted by Hückel theory, but instead indicate substantial spin polarization effects. Subsequent to our findings, Dowd prepared 11 from an alternative precursor and confirmed its triplet ground state by EPR studies.²³

The reason 11 has a triplet ground state can be ascertained from inspection of the NBMOs (Table I). Like the p orbitals on atomic C, they are very much coextensive in space.²⁴ Thus, exchange repulsions are large, and a T ground state is observed. The same holds for TMM and *m*-xylylene (9). However, the NBMOs of square cyclobutadiene (8) are *disjoint*: they do not span any common atoms.²⁴ This minimizes exchange repulsions, and computationally, at least, a S ground state results even at the square geometry. The NBMOs of tetramethylethane (10) are also "geographically isolated",^{25a} and theory predicts that S lies below T.²⁶ However, experimentally T seems to be the ground state,²⁵ a conflict that is, at present, unresolved. As a guide to designing high-spin structures, it seems safe to assume that simple topologies that produce clearly nondisjoint (i.e., coextensive) NBMOs (such as TMM, 9, and 11) will be "robust" triplets: T will lie well below S, and the high-spin preference will survive significant structural perturbations (angle changes, heteroatom substitutions, ...). Systems with disjoint NBMOs, however, can have S lying below T or T lying below S, and generally the intrinsic preference will be small.

As our studies of 11 progressed, we were surprised to find that concentrated, frozen solutions of this structure were visibly orange.²² This benzene isomer absorbs visible light, with $\lambda_{\max} = 506$ nm. It fluoresces with an intense green color. Using magnetophotoselection we were able to assign the optical transition as ${}^3B_{2u} \rightarrow {}^3B_{1g}$, as had been anticipated computationally.²⁷ Magnetophotoselection also led to a full assignment of the zfs levels for triplet 11.

Photolysis of 11 at 500 nm cleanly produces the covalent isomer 2,4-dimethylenebicyclo[1.1.0]butane (13). Diene 13 is a highly strained benzene isomer that displays a remarkable chemistry of its own.²⁸ One interesting feature is that sensitized photolysis of 13 converts it back to 11. Thus, the 11/13 pair serves as a prototype for magneto-optical switching of organic materials. That is, one can use 500-nm light to convert a colored, "paramagnetic" structure (11) to a colorless, "diamagnetic" molecule (13) and light of a different wavelength to reverse the process. Note that current magneto-optical devices do not at all use a process such as this; the laser in the "write" step is essentially a heat source, not the activator of a photoswitch. Of course,

(23) Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* 1986, 108, 2788-2790.

(24) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1977, 99, 4587-4594.

(25) (a) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* 1986, 108, 7416-7417. (b) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* 1987, 109, 5284-5285. (c) Roth, W. R.; Kowalczyk, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1285-1287.

(26) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* 1987, 109, 930-931.

(27) Pranata, J.; Dougherty, D. A. *J. Am. Chem. Soc.* 1987, 109, 1621-1627.

(28) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* 1989, 111, 3942-3954.

structures such as **11** and **13** are far too exotic for any practical applications. They do establish, however, the potential of organic materials for displaying novel properties that would be quite difficult to realize with conventional metals and alloys.

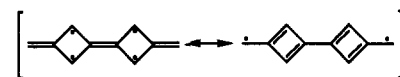
We believe that studies on biradicals and related structures suggest that *the critical factor in determining the S-T gap in organic molecules is the extent to which the NBMOs overlap in space, not their relative energies.* A precise NBMO degeneracy can only exist in molecules of high symmetry, and there are many examples of molecules that cannot have degenerate NBMOs yet still have T lying far below S. Conversely, there is at least one case—square cyclobutadiene—where a true NBMO degeneracy still gives rise to S lying below T. Of course, there are limits to how large the NBMO gap can be and still have T lying below S, but it would appear that quite substantial nondegeneracies can be tolerated in the proper systems. On the other hand, in systems with topologies that produce only weak exchange repulsions, and thus small intrinsic S-T gaps, it has been argued that maintaining an exact NBMO degeneracy is critical to obtaining T lying below S.²⁹

Extensions to Higher Spin Systems

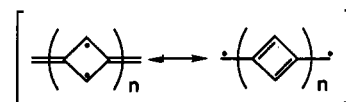
To build materials with interesting bulk magnetic behaviors, one needs many more than two spins, and many workers have been investigating a variety of approaches to very high spin molecules and materials. Our own interest in organic structures with $S > 1$ began in 1979, with spiroconjugated tetraradical **14** as a target.³⁰ Qualitative MO arguments suggested to us that **14** might be a quite stable molecule, as tetraradicals go, and subsequent experimental studies indicated that **14** is a viable reactive intermediate under conventional conditions. High-quality theoretical studies,^{30b} however, predicted a *singlet* ground state for tetraradical **14**, for reasons that can be understood within the context of the above discussions: **14** is essentially a three-dimensional cyclobutadiene.

Our studies of non-Kekulé benzene (**11**) provoked the question, "What is non-Kekulé naphthalene?" The answer is **15**, a $C_{10}H_8$, 10- π -electron system. In fact, one can envision a whole series of structures **16**, which we have called the non-Kekulé acenes.²⁷ Theoretical studies point out many distinctions between the classical acenes (benzene, naphthalene, ...; **17**) and the non-Kekulé acenes. When n is odd in a non-Kekulé acene (as in **11**), there are $n + 1$ singly occupied NBMOs, two of which are nondisjoint, and a triplet ground state is predicted. When n is even, there are n , completely disjoint NBMOs, and S and T (and higher spin states) are essentially degenerate. The larger non-Kekulé acenes should be fascinating molecules, and efforts to prepare such structures are underway in our lab.

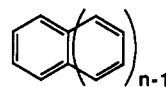
In the limit of an infinitely large non-Kekulé acene, the effect of the end groups (CH_2 's) will be negligible, leaving poly(cyclobutadiene) (**18**). This polymer is



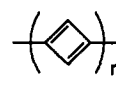
15



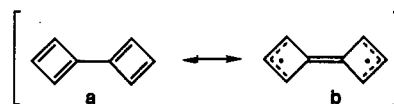
16



17



18



19



20



21

predicted^{27,31} to be a very interesting material that, depending on its exact structure, could be an organic metal even in an undoped state. We have also studied (computationally) the lower homologues, such as bi(cyclobutadienyl) (**19**), the cyclobutadiene analogue of biphenyl.³¹ Unlike biphenyl, **19** shows a strong preference for a planar structure. It is best thought of as a biradical (**19b**) with a true double bond between the rings. Similarly, the terphenyl and tetraphenyl analogues, structures **20**, and **21**, are best thought of as tetraradicals.

The non-Kekulé acenes and the poly(cyclobutadienes) contain large numbers of unpaired spins. However, their topologies mandate that the spins are weakly coupled at best, with antiferromagnetic interactions appearing to dominate. Most interesting magnetic behaviors require ferromagnetic interactions of spins. Thus as a guide to the design of new structures, we have developed the schematic of Figure 3.³² We divide a very high spin structure into two building blocks. The first is simply a structure that contains a permanent magnetic moment. It could be a free radical, (triplet) biradical, radical ion, transition metal, etc. There are, in fact, many stable, spin-containing (SC) structures that could be considered. At present we consider the second fragment, the ferromagnetic coupling (FC) unit, to be the critical design element. As such, we are developing strategies to test the generality of potential FC units. From the outset it should be appreciated that, in large systems, the distinction between SC and FC units can become blurred and that, in certain situations, their roles could be interchanged.

One way to test the generality of potential FC units is illustrated by structure **22**. By linking two triplets through a FC unit, one now has a molecule with four unpaired electrons occupying four (nearly) degenerate



22

(29) See, for example: ref 19g. Dixon, D. A.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 211-228.

(30) (a) McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 4722-4724. (b) McElwee-White, L.; Goddard, W. A., III; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3461-3466. (c) McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3466-3474.

(31) Pranata, J.; Marudaran, V. S.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2026-2030.

(32) (a) Dougherty, D. A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 25-32. (b) Dougherty, D. A.; Kaisaki, D. A. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 71-79.

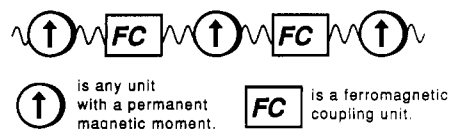
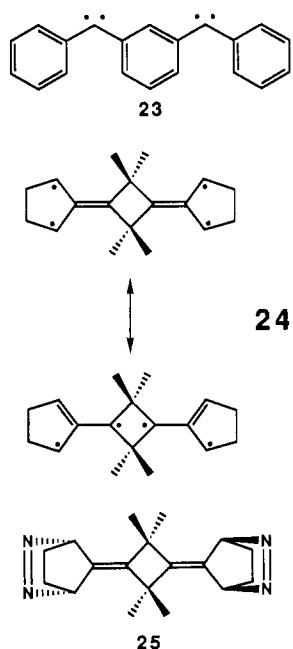


Figure 3. Schematic of an approach to very high spin structures.

NBMOs. The complexity of the problem increases substantially. There are 70 different ways to put four electrons into four orbitals, and these 70 configurations break down into 36 states: 20 singlets, 15 triplets and one quintet (Q). The problem can be simplified by ensuring that the two building blocks have strong, intrinsic triplet preferences ("robust" triplets). Then one has exclusively a T + T coupling, which produces $3 \times 3 = 9$ configurations, and three states: S, T, and Q. Clearly, Q corresponds to the ferromagnetic coupling of the triplet building blocks, and S results from anti-ferromagnetic coupling. Such an analysis is not new and, of course, lies at the heart of the famous quintet hydrocarbon **23**, first prepared in 1967 by Itoh and by Wasserman.³³ In this structure, *m*-phenylene is the FC,



and diphenylcarbene is the SC. This work has been extended to an elegant series of poly(carbenes) with very high spin states.³⁴ These results, and others, suggest that *m*-phenylene is a general FC unit, at least for one-center spin systems (carbenes, radicals).

We have designed several structures meant to test the limits of such reasoning. One such target is tetradical **24**.³⁵ This simple, symmetrical molecule contains two robust triplets (TMM derivatives^{19b}) that are completely insulated from one another in the conventional sense. Their primary interaction is, in effect, an exchange coupling across the cyclobutane, which, based on our cyclobutanediyl work, should be ferromagnetic.

(33) (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.

(34) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368–371. * Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147–2156.

(35) Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618–7619.

Bis(diazene) precursor **25** was efficiently synthesized, and photolysis led to sequential loss of 2 equiv of N₂ and production of tetradical **24**. EPR studies clearly indicated a Q ground state. The molecule is more stable than simple cyclobutanediyls, and intense, long-lived EPR signals can easily be generated at liquid nitrogen temperatures (77 K). It has long been appreciated that magnetism, unlike conductivity, does not require delocalization, but **24** is the first organic realization of this concept.

Using this molecular approach, one can envision a wide array of very high spin structures, and we are now extending these results in several directions. We are continuing to search for new FCs and new topologies, and we are also attempting to build room-temperature-stable, very high spin molecules.

Conclusions and Outlook

The past 10–15 years have seen considerable advances in our understanding of the forces that control spin-coupling mechanisms in organic molecules. From a personal perspective, when we started in this field we were unsure whether we would ever see a triplet, and our first successes were cause for celebration. Now, we can rationally design, with a high probability of success, hydrocarbon triplets, quintets, and, no doubt, even higher spin states. We have much to learn about these structures. There is still no general way to determine the energy gaps separating the S, T, Q, ... levels of such systems. This is a great impediment to the development of a *quantitative* understanding of spin-coupling mechanisms. In addition, very little is known about the reactivity of, for example, hydrocarbon quintets, and the intrinsic spectroscopy of such species is a wide open area for future exploration. Nevertheless, the field has come a long way in a short time.

The next design/synthesis frontier is clearly the development of very large arrays of spins, and there is much effort worldwide toward the development of molecular magnetic materials.³⁶ As stated at the outset, bulk magnetic behaviors require ferromagnetic couplings of the type described here *in three dimensions* throughout a solid-state material. Certainly, the lessons learned from small molecule studies will be invaluable aids to the rational design of higher order systems. We believe that the next decade will see the development of a large number of organic materials with novel magnetic behaviors and that these will greatly expand our understanding of electronic structure theory and the physics of magnetism.

I have been fortunate to have an outstanding group of graduate students and postdoctoral fellows as colleagues, and I gratefully acknowledge their substantial intellectual and experimental contributions to this work. I also thank the National Science Foundation for consistent support of our biradical projects and, more recently, the Office of Naval Research and the Caltech Consortium in Chemistry and Chemical Engineering (founding members: E. I. du Pont de Nemours and Co., Inc.; Eastman Kodak Company; and Minnesota Mining and Manufacturing Company) for support.

(36) For a recent overview, see: *Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials*; 197th National Meeting of the American Chemical Society, Dallas, TX. Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1–562.