along the SRP; the notation $\omega_\perp(r)$ is thus appropriate.[5a] To see how this might affect the reaction picture, we follow Lee and Hynes[5b] and consider a rate-like expression $k(r)$ defined at each point (r, s) on the SRP:

$$k(r) = \frac{k_B T}{h} \frac{Q_\perp(r)}{Q_\parallel^R Q_\perp^R} \exp\left[-\frac{G^{SRP}(r) - G_R}{k_B T} \right] \qquad (4.13)$$

Here $Q_\parallel^R$ and $Q_\perp^R$ are, respectively, the functions associated with the two normal modes parallel and perpendicular to the SRP at the reactant state, and $Q_\perp(r)$ is the partition function for the transverse mode at a point (r, s) on the SRP. The corresponding free energies are G_R and $G^{SRP}(r)$, respectively.[50] In the nonlinear variational transition-state theory,[5] the reaction rate is determined by the minimum value of $k(r)$. (This is strictly analogous to the procedure carried out in gas-phase variational TST studies.[9–11]) Because of the inhomogeneity in $\omega_\perp(r)$ and the associated entropy effect, this minimum may not occur at the saddle point (r^*, s^*) on the free energy surface; it rather could be shifted to a different r value owing to the competition between G^{SRP}, which favors the standard transition state, and entropic contributions associated with $\omega_\perp(r)$, which favor a displaced transition state. To explore this possibility, we have numerically scanned the local region near the saddle point following the SRP and have calculated $k(r)$, evaluating the partition functions classically. Figure 8 shows the result, as well as the local behavior of $\omega_\perp(r)$, for CH_3CN. The r range was ±0.08 Å so that $G^{SRP}(r)$ was within $\sim k_B T$ of the saddle point, and the step size was 1×10^{-5} Å. $\omega_\perp(r)$ increases with r in the saddle point region because of the increasing angle of the SRP relative to the r axis (cf. Figure 1a). This results in more of a contribution from the higher frequency r motion, although clearly the s contribution is dominant. It can be seen from Figure 8 that although $\omega_\perp(r)$ is not constant, the minimum in $k(r)$ corresponds to the same saddle point value that we have employed heretofore. Thus as for the potential of mean force and $\omega_s(r)$, the inhomogeneity in $\omega_\perp(r)$ plays no significant role, a conclusion consistent with that of ref 5a. In particular, the transition-state location is not sensitive at room temperature to the entropic contributions because of the moderate variation of $\omega_\perp(r)$; this is in contrast[5a] to high-temperature gas-phase reactions where analogous frequency variations can lead to marked variational transition-state shifts,[9,11] a reflection of the greater importance of entropy at higher temperatures. This ensures that the transmission coefficient obtained from eq 4.1 is indeed a valid measure for the deviation from the conventional equilibrium solvation theory.

5. Concluding Remarks

In this paper, we have used the electronic structure-based two-dimensional free energy formulation of part 1 to find that there is significant deviation from the equilibrium solvation path for a model of the *t*-BuCl S_N1 ionization in solution. This deviation arises from a solvent lag as the system crosses the transition state, as indicated by the disparity between the solution reaction path and the equilibrium solvation path. This lag occurs despite the strong solute–solvent coupling, proportional to the change of the S_N1 solute ionic character with the nuclear separation.

With the aid of linear and nonlinear variational transition-state theory, we have predicted that these nonequilibrium solvation effects can lead to marked departures of the rate constant from its equilibrium solvation transition-state theory approximation, especially for more polar solvents. This leads to a solvent polarity dependence of the rate over and above that due to the true activation free energy. In addition to their intrinsic interest as indicators of dynamic solvent-induced transition-state recrossing and deviations from the equilibrium solvation path, such departures which depend on the solvent polarity, can contribute factors of ≈ 1 kcal/mol to the apparent free energy of activation. This is not an insignificant effect in terms of the detailed level of activation free energy analysis often presented in the literature for S_N1 reactions.[34,35]

We expect that reaction path and rate features similar to those that we have found will also arise in other reaction classes such as twisted intramolecular charge transfer[51,52] and photoionizations,[53] where significant charge variation occurs along nuclear coordinates due to electronic mixing involving ionic states.

Finally, many of the features described here are confirmed in an application of a variant of our formulation to a microscopic level molecular dynamics simulation of a model of the *t*-BuCl S_N1 ionization in water.[7]

Registry No. *t*-BuCl, 507-20-0.

(50) Since the SRP is a single-valued curve in (r, s) coordinates, the r value completely specifies a location on the SRP.

(51) Barbara, P. F.; Kang, T. J.; Jarzeba, W.; Fonseca, T. In *Perspectives in Photosynthesis*; Jortner, J., Pullman, B., Eds.; Kluwer: Dordrecht, 1990. Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(52) Kim, H. J.; Hynes, J. T. *Solute Electronic Structure and Solvation in Time-Dependent Fluorescence: I. Formulation and Application to a Two-State Model*, to be submitted for publication. Kim, H. J.; Simon, J. D.; Hynes, J. T. *Solute Electronic Structure and Solvation in Time-Dependent Fluorescence: II. Three-State Model*, to be submitted for publication.

(53) See, for example: Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. Spears, K. G.; Gray, T. H.; Huang, D.-Y. *J. Phys. Chem.* **1986**, *90*, 779.

Spin Preferences of Conjugated Polyradicals: The Disjoint NBMO Analysis

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Abstract: The concept of disjoint nonbonding molecular orbitals (NBMOs) has been extended from its original application to biradicals to molecules with more than two NBMOs. It is shown how the disjointness of NBMOs in polyradicals can be related to their spin preferences. Ab initio molecular orbital calculations are reported which demonstrate the validity of the disjoint NBMO analysis.

In 1977 Borden and Davidson introduced the concept of disjoint nonbonding molecular orbitals (NBMOs) and showed how this concept can be used to rationalize the ground-state spin preferences of conjugated biradicals—molecules possessing two NBMOs

occupied by two electrons.[1] In this paper, it is demonstrated how the concept can be generalized to molecules with more than two NBMOs. We also report the result of molecular orbital calculations which confirm the validity of the generalized concept.

The Borden–Davidson analysis is best illustrated by considering a few examples. Trimethylenemethane (TMM) is the prototypical conjugated biradical having a triplet ground state.[2]


TMM
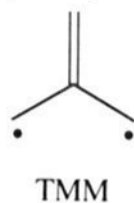
Its NBMOs are usually represented as shown below.

In this representation, or in any other, the NBMOs span common atoms; they are not disjoint. If the two electrons occupying the NBMOs have the same spin, their motions are correlated to prevent them from occupying the same region of space simultaneously—a consequence of the Pauli principle. On the other hand, if the electrons have opposite spins, no such correlation exist. There is a greater probability of the two electrons being closer to each other, resulting in greater electron–electron repulsion. As a consequence, the singlet state is destabilized relative to the triplet, and the triplet becomes the ground state. The Pauli principle is embodied in the exchange integral K.[3] For electrons in nondisjoint NBMOs, K is substantial, and the electrons "prefer" to have the same spin.

As the opposite example, consider tetramethyleneethane (TME).[4,5]

TME
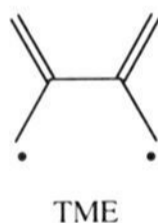
Like TMM, it has two NBMOs, but in this case they can be localized to different sets of atoms.

They are disjoint. The exchange integral is small, and to a first approximation the two nonbonding electrons have no spin preference. The singlet and triplet states become essentially degenerate. In fact, the ground state of TME is still a controversy. There are experiments which indicate a triplet ground state,[4] while high quality ab initio calculations predict a singlet ground state.[5] In any case, it is apparent that whichever state has the lowest energy, the other is not far above it.

Borden and Davidson also pointed out the connection between the disjointness of the NBMOs and the topology of the molecules.[1] Both TMM and TME are alternant hydrocarbons (AHs), which means their (carbon) atoms can be labeled as "starred" and "unstarred", such that starred atoms are bonded only to unstarred atoms, and likewise unstarred atoms are bonded only to starred atoms. Usually, the atoms are labeled such that the number of starred atoms, n_s, is greater than or equal to the number of un-

starred atoms, n_u. The number of NMBOs of an AH and their nature can be determined from its adjacency matrix $\mathbf{A}$.[1,6] In constructing this matrix, it is preferable to enumerate the starred atoms first, followed by the unstarred atoms. This causes a natural partitioning of the adjacency matrix into four blocks, two of which are identically zero.

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{ss} & \mathbf{A}_{su} \\ \mathbf{A}_{us} & \mathbf{A}_{uu} \end{pmatrix} = \begin{pmatrix} 0 & \mathbf{A}_{su} \\ \mathbf{A}_{us} & 0 \end{pmatrix}$$

Let r be the rank (i.e., the number of linearly independent rows or columns) of the $\mathbf{A}_{su}$ submatrix. There will be $(n_s - r)$ NBMOs confined to starred atoms (i.e., they have nonzero coefficients only on the starred atoms), and $(n_u - r)$ NBMOs confined to unstarred atoms. For TMM, there are two NBMOs confined to starred atoms and none confined to unstarred atoms. Thus, the NBMOs are confined to the same set and, in this case, they are not disjoint. For TME, there is one NBMO confined to starred atoms and one confined to unstarred atoms. The confinement to different sets makes the NBMOs necessarily disjoint.

While confinement of two NBMOs to different sets of atoms guarantees disjointness, confinement to the same set does *not* ensure nondisjointness. A particular example is pentamethylenepropane (PMP).[1,7]

PMP
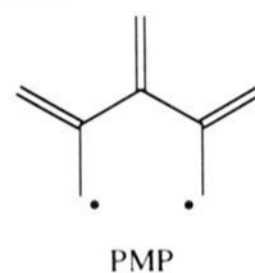
Its two NBMOs are confined to starred atoms, yet they can be localized to disjointness.
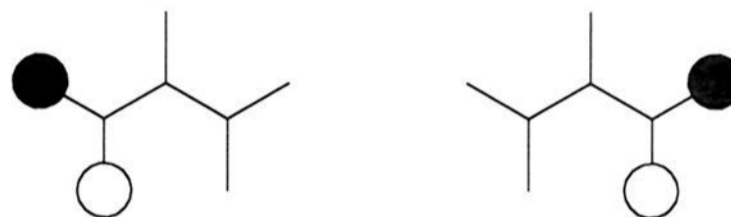
The Borden–Davidson analysis therefore predicts nearly degenerate singlet and triplet states for PMP.

Extension to Higher Spin Systems

We have extended the Borden–Davidson analysis to molecules with more than two NBMOs. To some extent, this extension has been foreshadowed by the work of Klein and Alexander,[9,10] who pointed out that molecules with three disjoint NMBOs should possess a doublet ground state, while with three nondisjoint NBMOs the molecule should have a quartet ground state. However, the situation is not quite so simple, as described below.

Consider the following molecule, which, by analogy with TMM, TME, and PMP, we will call tetramethylenepropane.[11] We will subsequently refer to this molecule as 4M3; the first integer referring to the number of methylene "substituents", and the second to the "main chain". This nomenclature will also be used

(1) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
(2) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.
(3) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.
(4) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416. Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.
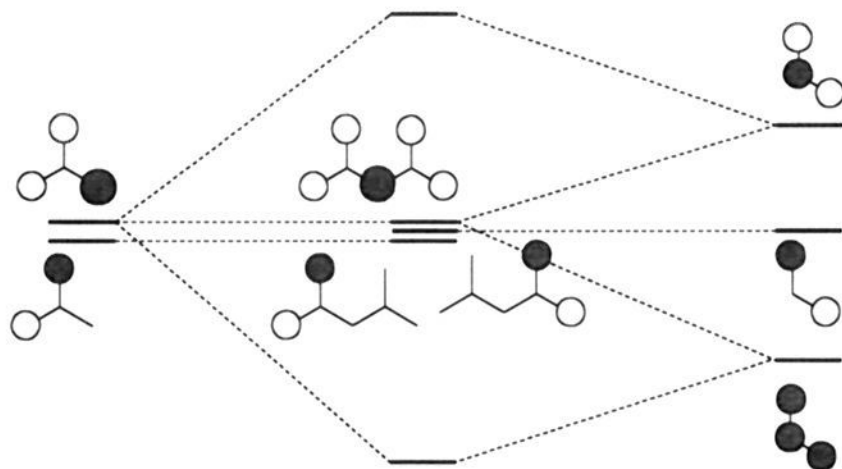(5) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930.

(6) Lounget-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.
(7) This molecule has been studied using PPP-CI calculations.[8] A triplet ground state is predicted with a small singlet–triplet gap (0.02 eV = 0.46 kcal/mol), consistent with the present analysis. Döhnert, D.; Koutecký, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789.
(8) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466. Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.
(9) Klein, D. J.; Alexander, S. A. In *Graph Theory and Topology in Chemistry*; King, R. B., Rouvray, D. H., Eds.; Elsevier: Amsterdam, 1987; pp 404–419.
(10) Klein, D. J.; Alexander, S. A.; Randic, M. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 109.
(11) This molecule was among the many listed by Klein and co-workers in their paper on high-spin hydrocarbons (Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101). It was also mentioned in ref 9.

Figure 1. Orbital interaction diagram for the PMO analysis of 4M3 as the union of TMM and an allyl radical.

Figure 2. Orbital interaction diagram for the PMO analysis of 5M4 as the union of TME and an allyl radical.

for the subsequent examples below. (With this nomenclature, trimethylenemethane and tetramethyleneethane would be abbreviated 3M1 and 4M2, respectively, but we will continue to refer to them as TMM and TME since these abbreviations are well established in the literature.) From the adjacency matrix, we


4M3
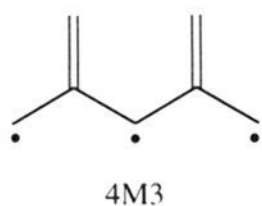
can determine that for 4M3 $n_s = 5$, $n_u = 2$, and $r = 2$, so 4M3 has three NBMOs confined to starred atoms. Alternatively, one can perform a Hückel calculation to obtain the NBMOs. But perhaps it would be most instructive to use a perturbational molecular orbital (PMO) approach to obtain the NBMOs of 4M3.[12]

Figure 1 shows the orbital interaction diagram between TMM and an allyl radical to form 4M3. The union between these two fragments occur at a node of the NBMO of the allyl radical, thus the allyl NBMO is unaffected by the union. Similarly, one of the TMM NBMOs has a node at the union site, and it is also unaffected by the union. The only interactions are between the other TMM NBMO and the bonding and antibonding orbitals of the allyl radical. At the Hückel level, these allyl orbitals are equally spaced above and below the nonbonding energy level, and their coefficients have the same magnitude—by virtue of the pairing theorem.[6] Thus, the interaction between these three orbitals leaves one MO at the nonbonding level.

Regardless of how one obtains the NBMOs of 4M3, it is clear that they are nondisjoint. While the first two NBMOs can be localized to different atoms, the third spans atoms used by both. By extension of the Borden–Davidson analysis, the electrons in the first and third NBMOs prefer to have the same spin; so do those in the second and third NBMOs. Thus, all three electrons prefer to have the same spin. Put in another way, there is a substantial exchange interaction between the electrons in the first and third NBMOs and also between the electrons in the second and third NBMOs, provided that these electrons have the same spin. These exchange interactions stabilize the high-spin state. Thus, the disjoint NBMO analysis predicts a definite preference for a quartet ground state for 4M3.

Next, consider pentamethylenebutane (5M4).[13]

5M4

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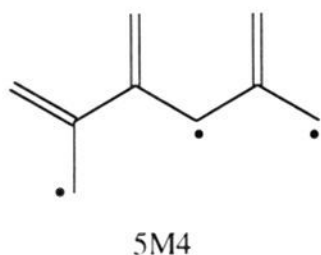
(12) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Chapter 3.

(13) This molecule was mentioned in ref 10 as having a doublet ground state.
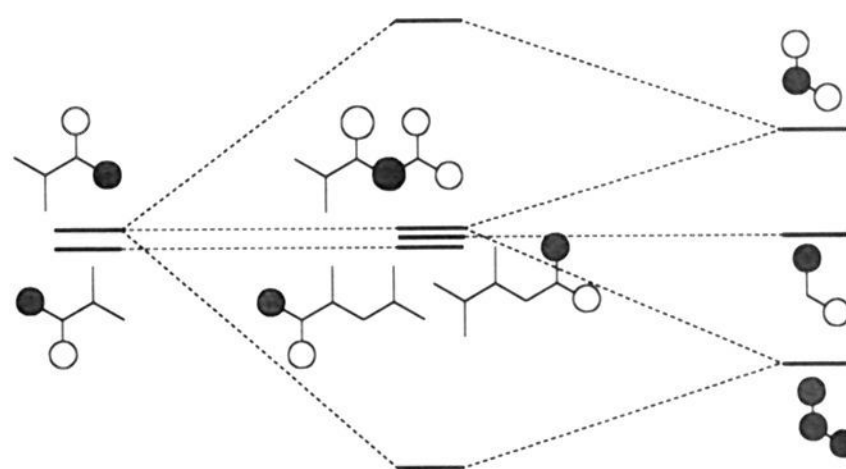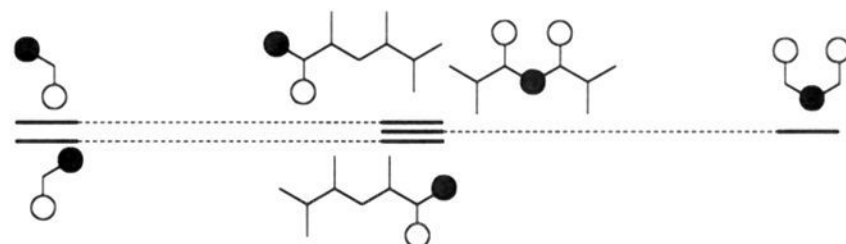
Figure 3. Orbital interaction diagram for the PMO analysis of 6M5 as the union of two allyl radicals and a pentadienyl radical.
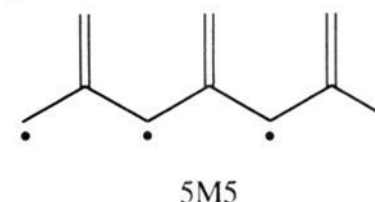
From the adjacency matrix we can determine that 5M4 has two NBMOs confined to starred atoms and one NBMO confined to unstarred atoms. A PMO analysis can also be performed on 5M4 as the union between TME and an allyl radical (Figure 2). As in 4M3, two NBMOs, one from the allyl radical and one from TME, are unaffected by the union. The only interactions are between the other NBMO of TME and the bonding and antibonding orbitals of the allyl radical, resulting in one new MO at the nonbonding level. The difference from 4M3 is that the NBMO originating from the TME fragment is disjoint from the other two NBMOs, which are nondisjoint. The electrons in these two disjoint NBMOs would prefer to have the same spin, while the third electron has no spin preference. Thus, the analysis predicts 5M4 to have essentially degenerate quartet and doublet states.

The next example is hexamethylenepentane (6M5).

6M5
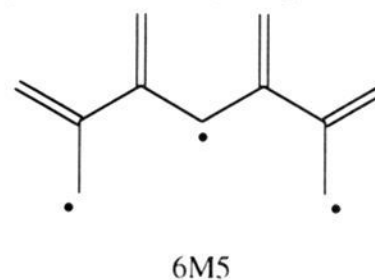
The PMO analysis is actually simpler in this case compared to 4M3 and 5M4. We can consider 6M5 as the union between two allyl radicals and a pentadienyl radical (Figure 3). All the union sites would then be located at the nodes of the fragments' NBMOs. There are no interactions between the orbitals, and all three NBMOs are unaffected by the union. In this case, the three NBMOs are totally disjoint from one another. One way to analyze the situation is to consider it as the union between a biradical and a monoradical. The biradical in this case has no spin preference; it can be a triplet or a singlet. The monoradical is of course a doublet. The union between a triplet and a doublet gives rise to two states, a quartet and a doublet. The singlet plus doublet combination results in another doublet. Thus, the three lowest lying states of 6M5 are nearly degenerate; these states consist of a quartet and two doublets.

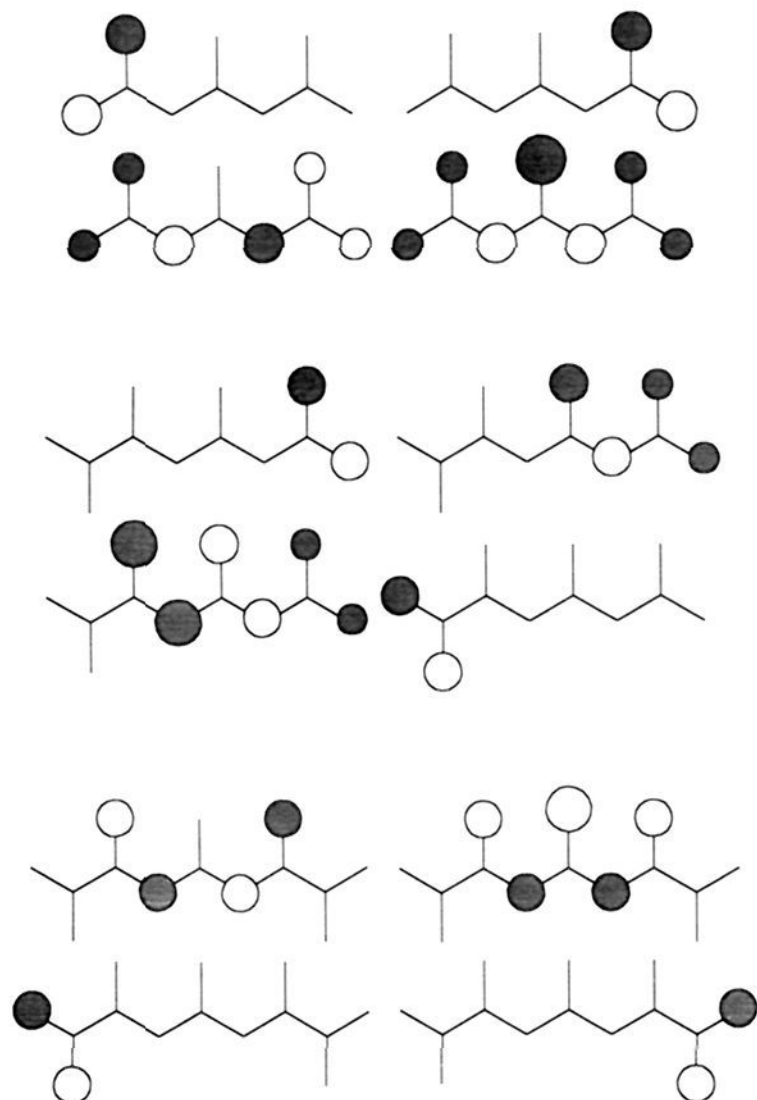Next we consider systems with four NBMOs. The first of these is pentamethylenepentane (5M5).[14]

5M5

Figure 4. NBMOs of 5M5, 6M6, and 7M7.

Table I. Relative Energies (kcal/mol) from CASSCF/STO-3G Calculations[a]

TMM	triplet	0.0	6M6	triplet	0.0
	singlet	20.48		quintet	0.096
4M3	quartet	0.0		triplet	12.92
	doublet	20.37	PMP	singlet	0.0
5M5	quintet	0.0		*triplet*	0.045
	triplet	6.07		singlet	147.83
TME	singlet	0.0	6M5	doublet	0.0
	triplet	0.17		doublet	0.15
	singlet	132.30		quartet	0.23
5M4	doublet	0.0		doublet	118.70
	quartet	0.10	7M7	singlet	0.0
	doublet	16.44		triplet	0.073
				triplet	0.14
				quintet	0.21
				triplet	11.45

[a] Total energies of the ground states (hartrees): TMM −152.968 758; TME −228.876 883; PMP −304.785 144; 4M3 −266.849 034; 5M4 −342.763 762; 6M5 −418.674 222; 5M5 −380.728 978; 6M6 −456.642 074; 7M7 −532.554 164.

Regardless of how we obtain them, the NBMOs for 5M5 (and for the next two examples) are shown in Figure 4. There are four NBMOs which are nondisjoint. We therefore would expect all four electrons occupying these NBMOs to have the same spin. A quintet ground state is expected.
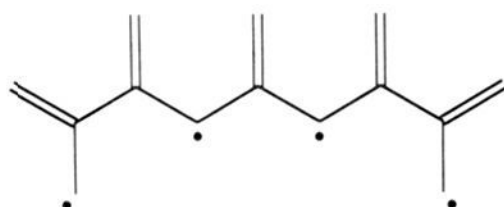
For hexamethylenehexane (6M6),
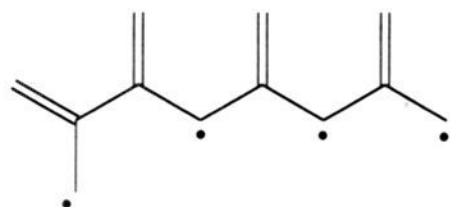
6M6

there are three NBMOs which are nondisjoint and a fourth one which is disjoint (Figure 4). This situation would give rise to nearly degenerate quintet and triplet states.

Finally, for heptamethyleneheptane (7M7),

7M7

there are two nondisjoint NBMOs and two more which are disjoint (Figure 4). We analyze the situation as the union of two biradicals. The first biradical has to be a triplet; the other can be a triplet or a singlet. The triplet plus triplet combination gives rise to three states; a quintet, a triplet and a singlet. The triplet plus singlet combination gives rise to another triplet. Thus, this

molecule would have, as its four lowest lying states, a quintet, two triplets, and a singlet. These four states are expected to be nearly degenerate.

It is easy to see how this sequence can be extended to even larger molecules. In fact, the extensions of 4M3 and 5M5 would ultimately lead to the "ferromagnetic polymer" suggested by Ovchinnikov.[15,11]

As we can see, the disjoint NBMO analysis predicts different results for molecules which at first look quite similar. We will now discuss our efforts to confirm these fascinating results using molecular orbital calculations.

Computations

The objective of our computations is to confirm the analysis described in the previous section. They are *not* intended to provide a definitive prediction of the ground states in the molecules discussed or to accurately calculate the energy gaps between the various spin states. Our calculations were performed at a level which should provide qualitatively correct descriptions of the electronic states of these molecules.

A proper and balanced description of biradicals requires at least a restricted open-shell Hartree–Fock (ROHF) wave function for the triplet state and a two-configuration self-consistent field (TCSCF) wave function for the lowest singlet states.[16] Most discussions of biradicals have focused on these two states and have largely neglected the presence of two other singlet states—justifiably so, because these states tend to be much higher in energy. In fact, these four states, one triplet and three singlets, are the states obtained by a multiconfiguration self-consistent field (MCSCF) calculation which allows all possible occupancies of the two NBMOs by the two nonbonding electrons. This is commonly known as a 2 × 2 CAS (complete active space)SCF calculation.[17]

For the triradicals, a comparable treatment requires a 3 × 3 CASSCF calculation. This involves nine distinct configurations, giving rise to one quartet and eight doublet states. For the tetraradicals, a 4 × 4 CASSCF calculation is needed, involving 36 distinct configurations, resulting in one quintet, fifteen triplet, and twenty singlet states.

In our calculations, we have only calculated the energies of the ensemble of states which are predicted by the disjoint NBMO analysis to be nearly degenerate, plus the energy of the next highest state, regardless of spin. In this way we seek to confirm that the states predicted to be nearly degenerate do in fact have similar energies, while other states have considerably higher energies.

In our calculations, the molecules are constrained to be planar. The geometry was otherwise optimized for the highest spin state (triplet for the biradicals, quartet for the triradicals, and quintet for the tetraradicals) using the AM1 semiempirical method,[18] as implemented in the MOPAC program.[19] These geometries were used for ab initio CASSCF calculations with the minimum basis set STO-3G.[20,21] The CASSCF

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(14) PPP-CI calculations on this molecule predict a quintet ground state, with the triplet state 0.16 eV (3.7 kcal/mol) and the singlet state 0.21 eV (4.8 kcal/mol) above it (Koutecký, J.; Döhnert, D.; Wormer, P. E. S.; Paldus, J.; Clzek, J. *J. Chem. Phys.* **1984**, *80*, 2244). It was also mentioned in refs 9 and 10.

(15) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(16) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(17) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.

(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(19) Stewart, J. J. P. MOPAC 6.10, *QCPE 455*; Indiana University, Bloomington, IN 47405, 1990.

calculations were performed using the TX90 program.[22] All computations were performed on Silicon Graphics Indigo workstations in our laboratory. The results are summarized in Table I.

Discussion

The results of the molecular orbital calculations (Table I) confirm the validity of the disjoint NBMO analysis, at least at this relatively low level of theory. There is at least an order of magnitude difference between the energy gaps within the ensemble of states predicted to be nearly degenerate and the energy gaps between these and other, higher lying states.

As we emphasized above, these calculations are not expected to be quantitatively accurate. Borden and Davidson have pointed out that this level of calculations are not appropriate for conjugated biradicals.[23] However, their greatest concern was the tendency of the calculations to converge to incorrect geometries. Our concern in this paper is not geometry optimization. We simply want to obtain a rough estimate of the energy gaps between the states, and we feel that our calculations are sufficient for this purpose.

How accurate *are* the calculations? Higher level calculations have been performed for TMM and TME. For TMM, the singlet–triplet gap was calculated to be about 21–26 kcal/mol (T < S) for the planar structure.[24] The results of our CASSCF/STO-3G calculations compares quite favorably to this. For TME, the best computational estimate for the singlet–triplet gap is 2.8 kcal/mol (S < T) for the planar structure.[5] This is larger than the value we obtained, but our result is correct in predicting this energy gap to be small.

Neither our analysis nor computations consider higher order effects. In particular, we have neglected the correlation between the electrons in the NBMOs and those in the lower lying, doubly-occupied MOs. For biradicals with disjoint NBMOs, this type of correlation results in dynamic spin polarization (DSP) which usually stabilizes the singlet state.[25] The effect is small, and the resulting energy gaps are much smaller than those resulting from the nondisjointness of the NBMOs. We expect that similar interactions might preferentially stabilize the lower spin states of tri- and tetraradicals. Indeed, our calculations consistently predict the lower spin states to have the lower energies in the disjoint tri- and tetraradicals, although DSP is not explicitly taken into account. Explicit inclusion of this interaction, which can be done by expanding the active space of the CASSCF calculations, is expected to further stabilize the lower spin states. But we still expect this higher order effect to be small compared to the effect of having nondisjoint NBMOs.

Another assumption of our analysis is that the molecules are planar, and this assumption is included as a constraint in the calculations. This is necessary in order to limit our analysis to π-electrons; the concept of disjoint NBMOs, however, does not require planarity. The molecules are simply intended to illustrate our analysis. Real molecules may not be planar; calculations predict that the lowest singlet and triplet states of TME prefer nonplanar geometries.[5] The tri- and tetraradicals discussed in

this paper are also expected to be nonplanar, and this should be kept in mind if any attempt is made to observe them in the laboratory. It would be prudent to incorporate these structures into ring systems, as was done for TMM and TME,[2,4] to ensure near-planarity. For example, molecular models show that in the following structure, the 5M5 fragment does not deviate much from planarity.
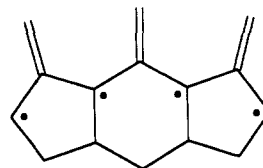
Another strategy is to design other topologies, which also result in multiple NBMOs with varying degrees of disjointness. For example, the anthracene-based tetraradical of Berson and co-workers is similar to 5M5 in having four NBMOs which are nondisjoint.[26]
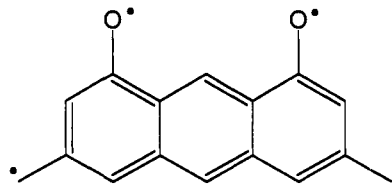
This molecule was found to have a quintet ground state, as expected.

Finally, we would like to comment on other qualitative methods of predicting the spin preference of polyradicals.[9–11] It is clear that classical structure theory, where one merely tries to maximize bonding and "count the remaining dots", is not applicable in many cases. Hund's rule, which predicts that all the nonbonding electrons would prefer to have the same spin, is also not universally applicable. Ovchinnikov, using a valence bond model, suggests that for alternant hydrocarbons the ground-state spin can be obtained by counting the difference between the number of starred and unstarred atoms ($S = |n_s - n_u|/2$).[15] In our analysis, this gives the spin of *one* of the states expected to be low-lying, but provides no information about other states. We would argue against indiscriminate reliance on Ovchinnikov's rule. Some organic molecules may really have several low-energy electronic states, and the presence of these states will certainly affect their properties. The disjoint NBMO analysis allows one to predict the existence of these states, and we feel that discovering their existence is more significant and interesting than finding the one definitive ground state, even if that state is high-spin.

Conclusions

The disjoint NBMO analysis, originally proposed to rationalize the spin preferences of biradicals, is shown to be applicable to other molecules possessing more than two NBMOs. Ab initio CASSCF calculations have been performed which confirm the predictions of the analysis for some selected molecules.

(20) We have also performed CASSCF calculations on the smaller molecules using the larger 3-21G basis set.[21] The results are consistent with those shown in Table I, e.g., a singlet–triplet gap of 18.7 kcal/mol is predicted for TMM and a doublet–quartet gap of 17.2 kcal/mol for 4M3.

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