

With a Little Help from My Friends:[†] Forty Years of Fruitful Chemical Collaborations

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S Supporting Information

ABSTRACT: Over the past 40 years, much of the author's research, both computational and experimental, has involved collaborations. This Perspective describes some of the author's collaborative research in eight different areas of organic and theoretical chemistry: (1) hydrocarbons containing unsaturatively, 1,3-bridged cyclobutane rings, (2) the use of orbital topology for predicting the ground states of diradicals, (3) violations of Hund's rule, (4) the chemistry of phenylnitrenes, (5) tunneling by carbon in organic reactions, (6) the Cope rearrangement and the effect of substituents on it, (7) pyramidalized alkenes, dehydrocubanes, cubyl cation, and octanitrocubane, and (8) the effects of geminal fluorine substitution at C-2 of 1,3-diradicals. Highlighted in this Perspective are the synergism between calculations and experiments in the author's research and the many different roles that serendipity has played in the collaborations that are described herein.

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A former colleague of mine at the University of Washington once told me, only half-jokingly, "You do a lot of collaborative research, and I think the reason for its success is that you are brave enough to choose as your collaborators people who are better chemists than you." Looking back over the past 40 years of my career, I have, indeed, had an unusually large number of research collaborations, and they have, in fact, been successful, largely because my collaborators have all been talented chemists who had expertise that I lacked.

These collaborations have come about in several ways. In some cases, an experimentalist has asked my research group to perform calculations. On other occasions, I have sought collaborators outside of my own research group when I needed help, usually experimental but sometimes computational, in testing a prediction. I have also had research collaborations begin when I was on sabbatical or when Professors from other universities spent sabbaticals in my research group, usually with the goal of learning how to do electronic structure calculations.

This Perspective allows me to thank at least a few of my many collaborators over the past 40 years by recounting how their contributions made it possible for me to do research that I probably would not have been able to do on my own. This Perspective also gives me the opportunity to give some examples of the synergism between theory and experiments in my research and to acknowledge the important role that serendipity has played throughout my career, but particularly in the collaborative projects that are the focus of this Perspective. I have been lucky in having had puzzling experimental and computational results brought to my attention at times when I had the knowledge and/or computational resources that were necessary in order to

explain those results. I have also been very fortunate in knowing experimentalists and theoreticians who were willing to collaborate with me on experiments and calculations that were of interest to me, but which I could not have readily done on my own.

Serendipity has also played a different kind of role in my research. When I have been working on finding the solution to a specific problem, my research has frequently led me to the solution of a problem of much broader scope. I attribute my good fortune, at least in part, to my compulsive habit of persistently asking myself the question, "Why is that?" when I am presented with an experimental or computational result that I do not understand.

I have divided this Perspective into eight major sections, each of which describes a different area of my research during the past 40 years, in which collaborations have played an important role. Rather than reading this Perspective in its entirety, some readers may prefer to be selective and peruse just a few of the eight sections. The sections cover my collaborative research on (1) hydrocarbons containing unsaturatively 1,3-bridged cyclobutane rings, (2) the use of orbital topology for predicting the ground states of diradicals, (3) violations of Hund's rule, (4) the chemistry of phenylnitrenes, (5) tunneling by carbon in organic reactions, (6) the Cope rearrangement and the effect of substituents on it, (7) pyramidalized alkenes, dehydrocubanes, cubyl cation, and octanitrocubane, and (8) the effects of geminal fluorine substitution at C-2 of 1,3-diradicals.

Unfortunately, I have had to be selective in both the areas of research that I covered in this Perspective and the depth in which

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I covered each of them. In order to make myself feel a little better about having had to omit from this Perspective descriptions of so many other rewarding research collaborations, I have provided in the Supporting Information a chronological list of the papers, including titles, that I have published with senior collaborators during the past 40 years. In preparing this list, I was amazed to discover that nearly half of my publications over the course of my career have come from collaborative research.

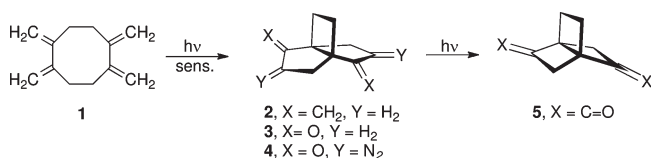
1. THE CHEMICAL CONSEQUENCES OF ORBITAL INTERACTIONS IN MOLECULES CONTAINING UNSATURATIVELY 1,3-BRIDGED CYCLOBUTANE RINGS

The story of how, in the early 1970s, I serendipitously came to study the chemical consequences of orbital interactions between four-membered rings and unsaturated bridges starts with a brief description of some of my research at the time. After completing my Ph.D. under the direction of E. J. Corey in 1968, I began my independent academic career at Harvard by going into the family business of making molecules. However, unlike E. J., I was interested in making unnatural, rather than natural, products.

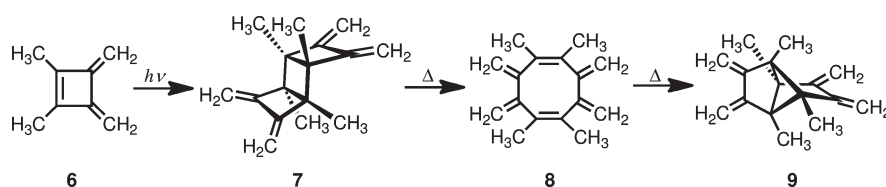
“Synthesis and Study of Theoretically Interesting Molecules” was not only the title of my first successful NSF proposal, but this phrase also described accurately the majority of my research group’s activities during the five years that I was on the Faculty of the Chemistry Department at Harvard. After I moved to the University of Washington in 1973 and until I left UW for the University of North Texas in 2004, the research in my group continued to have a large synthetic component.

One of the first projects that my research group at Harvard undertook was a synthesis of [2.2.2]propellane by the route shown in Scheme 1. Sensitized photolysis of 1,2-dimethylenecyclobutane led to the formation of the three expected dimers, all of which underwent pyrolysis to form 1,2,5,6-tetramethylenecyclooctane (**1**).^{1a,c} As I had hoped, upon sensitized photolysis, **1** underwent transannular ring closure to form 2,6-dimethylene-[3.3.2]propellane (**2**), which could be ozonized to afford the corresponding diketone (**3**).^{1b,c} The plan was then to form bis- α -diazoketone **4**, which I hoped, upon photolysis, would undergo contraction of both 5-membered rings, thus providing an entry into the [2.2.2]propellane skeleton via bis-ketene **5**.

Scheme 1



Scheme 2

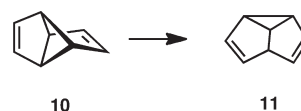


While Dr. Ieva Lazdins Reich, a postdoc in my group, was working on transforming **3** into **4**, Phil Eaton informed me of his successful synthesis of a derivative of [2.2.2]propellane.² Being scooped by Phil actually turned out to be very fortunate, because it led me to abandon my own [2.2.2]propellane synthesis in order to begin a new project. Serendipitously, the new experimental project led me to some theoretical insights into the chemical consequences of orbital interactions between cyclobutane rings and unsaturated 1,3-bridging groups.

Dr. Avram Gold’s Serendipitous Discovery Leads to a Qualitative Theory. The new project was a spin-off of my group’s research on the sensitized photodimerization of 1,2-dimethylenecyclobutane.¹ We decided to investigate the same type of reaction with 1,2-dimethyl-3,4-dimethylenecyclobutane (**6**). Sensitized photodimerization of **6** occurred only at the endocyclic double bonds, and the resulting dimer (**7**) could be pyrolyzed to afford 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenecycloocta-1,5-diene (**8**).³

However, my postdoc, Dr. Avram Gold, found that another compound was formed from **8** in increasing amounts as the pyrolysis temperature was raised. The NMR spectrum of this isomer of **8** clearly identified it as 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**9**).³

Formation, under pyrolytic conditions, of the four-membered ring in **9** from “2 + 2” cycloaddition of the two endocyclic double bonds in **8** was totally unexpected. What made this transformation even more surprising was the then-recent finding that tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**10**) undergoes rapid rearrangement at very low temperatures to semibullvalene (**11**).⁴ Taken together, these results suggest that, if a molecule contains a cyclobutane ring, bridged across C-1 and C-3 and across C-2 and C-4 with butadienes, as in **9**, the molecule is stabilized thermodynamically. However, when the bridging groups are double bonds, as in **10**, the molecule is destabilized, both kinetically and thermodynamically.



At the time that my group discovered the thermal rearrangement of **8** to **9**, the impact of the Woodward–Hoffmann rules⁵ had made physical–organic chemists very much aware of the change in the symmetries of the HOMO and LUMO that occur on replacing ethylene by butadiene. In addition, Roald Hoffmann had recently published a paper on the Walsh orbitals for cyclobutane.⁶ Therefore, I knew that the HOMO of the puckered four-membered ring in **9** and in **10** consists of a degenerate pair of orbitals of e symmetry. One of these ring orbitals can mix with the π HOMO of the etheno group that bridges C1 and C3 of the four-membered ring in **9**, while the other e orbital can mix with

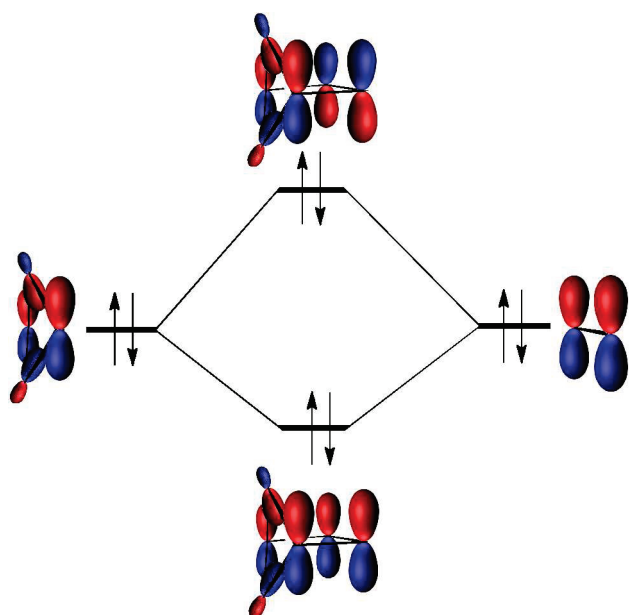


Figure 1. Orbital interaction diagram for mixing of one of the degenerate ϵ MOs of the cyclobutane ring with the bonding π orbital of one of the double bonds in **10**.

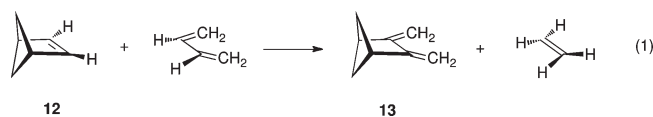
the π HOMO of the etheno group that bridges C2 and C4.⁶ One of these orbital interactions is shown in Figure 1.

Since the interaction between two-filled MOs results in net antibonding between them, the interaction between the degenerate HOMOs of the four-membered ring and the etheno bridges of **10** should destabilize this molecule,^{7a} thus explaining the very facile rearrangement of **10** to **11** by a symmetry-forbidden reaction.^{5,8} On the other hand, replacing the etheno bridging groups in **10** with the butadieno bridging groups in **9** would allow the degenerate HOMOs of the cyclobutane ring to mix with the LUMOs of the butadieno bridges, resulting in stabilizing orbital interactions and thus rationalizing the formation of **9** from **8**.^{7a}

I wanted to obtain some computational confirmation that my explanation of the experimental results,^{3,4} based on the interactions of the degenerate HOMOs of the cyclobutane ring with the HOMOs and LUMOs of the unsaturated bridges in **9** and **10**, was correct. This desire led to my first collaboration.

Bill Jorgensen Carries Out EH Calculations. These days I could ask anyone in my research group to carry out *ab initio* or DFT calculations to see if the computational results supported my explanation of the difference in stabilities between **9** and **10**. However, 40 years ago, my options were much more limited. Fortunately, I learned that Bill Jorgensen, who was then a graduate student in the Harvard Chemistry Department, had written an Extended Hückel (EH) program that ran on Harvard University's PDP-10 computer. Bill was obviously interested in MO theory,⁹ so I asked him if he would be willing to collaborate with me and to perform EH calculations in order to verify whether my frontier-orbital explanations for the relative stabilities of **9** and **10** had any merit. Luckily for me, Bill agreed. I could not have found a better collaborator for this project than Bill, and our collaboration turned into a friendship that has endured for the past 40 years.

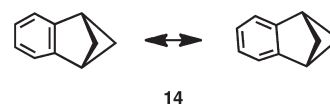
Bill computed the energy of the reaction shown in eq 1, in which butadieno replaces etheno as the 1,3-cyclobutane bridging group in bicyclo[2.1.1]hexene (**12**). Bill's EH calculations found this reaction to be energetically favorable by 17 kcal/mol.^{7a} Shortening the C2–C3 bond in both butadiene and in the butadiene bridge in **13** to the length of the C=C bond in **12** changed the energy by only 3 kcal/mol, thus indicating that ring strain in **12** is not responsible for the energetic favorability of the reaction in eq 1.



Bill also computed the π bond orders between the bridgehead carbons and the unsaturated carbons to which they are attached in **12** and **13**. Consistent with the frontier orbital analysis, the π bond order in **12** was actually found to be slightly negative, whereas that in **13** was computed to be positive and 11 times larger in magnitude.^{7a}

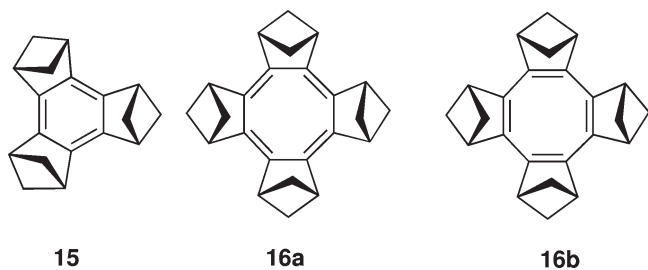
Had Bill been able to use EH calculations to optimize geometries, instead of just to compute bond orders, we would have compared the lengths of the C–C bonds between the four-membered rings and the bridges in **12** and **13**. Nearly 40 years after Bill did his EH calculations, Dr. Xiaoguang Bao, who is currently a postdoc in my research group, did the geometry optimizations that I wish I could have asked Bill Jorgensen to do 40 years ago. Consistent with the difference between the calculated π bond orders between the bridgehead carbons and the unsaturated carbons to which they are attached, Xiaoguang's B3LYP calculations¹¹ with the 6-31G* basis set¹² found that the bonds that join these pairs of carbons are nearly 0.02 Å longer in **12** than in **13**.¹³

Bill and I also used EH calculations to compute the effect of replacing butadiene in eq 1 with benzene. We reasoned that one of the two resonance structures for the benzene ring of benzobicyclo[2.1.1]hexene (**14**) has a double bond bridging the four-membered ring, so the effect of replacing butadiene with benzene in eq 1 would be to reduce the energetic favorability of this reaction. Actually, Bill found that replacing butadiene with benzene on both sides of eq 1 reduces the EH energy for this reaction by more than two-thirds, from $\Delta E = -17$ kcal/mol to $\Delta E = -5$ kcal/mol.^{7a,14}



Had Bill and I been able to optimize the geometry of benzobicyclo[2.1.1]hexene (**14**), we would have found something very interesting. Xiaoguang's B3LYP/6-31G*-optimized geometry for **14** reveals that the bridged four-membered ring tends to cause the bond lengths in the benzo bridging group to alternate in such a way that they resemble those of the butadieno bridging group in **13** more than those of the etheno bridging group in **12**.¹³ This finding makes perfect sense, since the energy computed for the reaction in eq 1 shows that a 1,3-bridged cyclobutane ring much prefers a butadieno to an etheno bridging group.

Unfortunately, in 1973, neither Bill or I guessed that the bridged four-membered ring in **14** might tend to induce alternation of the C–C bond lengths in the benzo bridging group. It was not until almost 20 years later that Kim Baldrige and Jay Siegel published the results of calculations which predicted that the three 1,3-bridged cyclobutane rings in **15** would almost completely localize the π bonds in the benzene ring, so that each cyclobutane ring has a butadieno, rather than an etheno bridge.^{15a} Three years later, this prediction was confirmed experimentally by Jay, Kim, their student Natia Frank, and their Swiss collaborators.^{15b,c} Another two years passed before Ken Houk and Paul Schleyer suggested that the bond alternation in the benzene ring of **15** has its origin in the same types of orbital interactions^{15d} as those that Bill and I had discussed in **12** and **13** nearly 25 years earlier.⁷



There is ample experimental evidence that Bill's EH calculations were correct in predicting that the interaction between the π orbital of the etheno bridging group and the orbitals of the 1,3-bridged cyclobutane ring in bicyclo[2.1.1]hexene (**12**) is destabilizing. For example, Ken Wiberg's measurements found that hydration of **12** is more exothermic than that of cyclopentene by 14.9 kcal/mol.¹⁶ In addition, Kim and Jay predicted computationally,^{17a} and Koichi Komatsu confirmed experimentally^{17b} that when cyclooctatetraene is annelated by four 1,3-bridged cyclobutane rings, the double bonds localize as shown in **16a**, not as in **16b**.¹⁸

Rolf Gleiter Suggests a Project. When I sent Roald Hoffmann a preprint of Bill Jorgensen's and my 1973 paper on the chemical consequences of the orbital interactions in molecules containing unsaturatively 1,3-bridged cyclobutane rings,^{7a} Roald suggested that I also send a copy to his former postdoc, Rolf Gleiter. Rolf was studying the orbital interactions in etheno-bridged cyclobutane rings⁸ using photoelectron spectroscopy.¹⁹ Although Rolf and I exchanged letters in 1973 (email, of course, being unknown at that time), it was not until 20 years later that we first met at a conference at Cornell University. Our meeting resulted in Rolf's applying for a Humboldt Senior Scientist Award for me, and thanks to Rolf and the Humboldt Foundation, I wound up spending three, 3-month sabbaticals in Heidelberg.²¹

My three sabbaticals in Heidelberg led to Rolf's and my collaborating on calculations on some Cope rearrangements that his group had discovered²² and on trying to predict whether or not (CO)₄ has a triplet ground state,²³ a question that Rolf had previously addressed²⁴ and my group has continued to explore.^{24c} However, my most recent collaborative project with Rolf²⁵ took us back to the subject that had first introduced us to each other—orbital interactions in molecules containing unsaturatively 1,3-bridged cyclobutane rings.

In 1978, Rolf had published a paper on through-bond interactions in tricyclo[4.4.0.0^{2,7}]deca-3,8-dien-5,10-diyl (**19**).²⁶ He

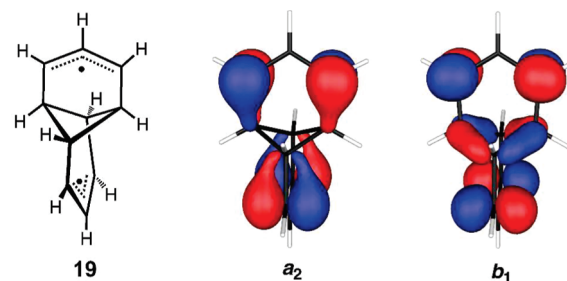
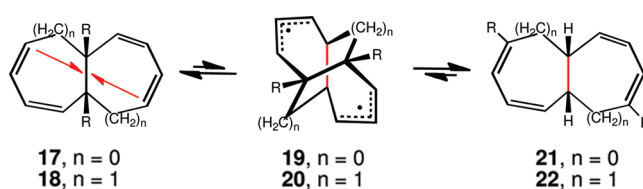


Figure 2. a_2 and b_1 CASCF nonbonding MOs of **19**. In the singlet ground state of **19**, two electrons occupy the lower energy a_2 MO.

showed that the in-phase (b_1) combination of allylic nonbonding (NB)MOs in **19** is destabilized by mixing with the filled b_1 orbital of the bridged four-membered ring. In contrast, the out-of-phase (a_2) combination of allylic nonbonding (NB)MOs does not interact with any filled ring orbitals but only with an unfilled, antibonding, ring orbital. Therefore, the a_2 combination of allylic nonbonding (NB)MOs in **19** is slightly stabilized by its interaction with the bridged four membered ring. The a_2 and b_1 CASCF MOs of diradical **19** are depicted in Figure 2.

Rolf had asked my group to compute the singlet–triplet energy difference in **19**. However, as Rolf pointed out to me, the electronic structure of **19** is of more than just theoretical interest, because **19** actually appears to be an intermediate in the degenerate rearrangements of 9,10-dihydronaphthalenes (**17**).²⁷ Paquette and co-workers had measured the barrier to this rearrangement to be $\Delta H^\ddagger = 25$ kcal/mol in two derivatives of **17**.^{27a}



A similar degenerate rearrangement occurs in a derivative of **18**,²⁸ which is a bis-homologue of **17**. The diradical intermediate (**20**) that is formed from **18** contains a six-membered ring, bridged by two allylic radicals, rather than the four membered ring that is present in **19**. Given the large expected difference between the strain energies of the four-membered ring in **19** and the six-membered ring in **20**, it is quite surprising that the value of $\Delta H^\ddagger = 21$ kcal/mol for the rearrangement of **18**²⁸ is only 4 kcal/mol lower than $\Delta H^\ddagger = 25$ kcal/mol^{27a} for the rearrangement of **17**.

In the absence of substituents that might affect the energies of diradicals **19** and **20**, the computed enthalpy difference of $\Delta H = 25.6$ kcal/mol between **17** and **19** ($R = H$) is only 1.7 kcal/mol higher than the enthalpy difference between **18** and **20** ($R = H$).²⁵ Why does formation of the four-membered ring in **17** \rightarrow **19** not involve a much larger enthalpy change than formation of the six-membered ring in **18** \rightarrow **20**?

The calculations of ΔE_{ST} in **19**, suggested by Rolf, provided us with the impetus also to compute ΔE_{ST} in **20**. Comparison of the CASPT2 values of, respectively, $\Delta E_{ST} = 25.5$ kcal/mol in **19** and $\Delta E_{ST} = 2.4$ kcal/mol in **20** then solved the riddle of why the enthalpy changes for formation of both *singlet* diradicals are nearly the same.²⁵

Formation of the triplet state of **19** from **17** is computed to require a $1.7 + (25.5 - 2.4) = 24.8$ kcal/mol larger increase in enthalpy than formation of triplet **20** from **18**. This is about the size of the enthalpy difference between these two reactions that might be expected, based on the difference between the sizes of the doubly bridged rings that these diradicals contain. The reason that the enthalpy difference between singlet **19** and **17** is about the same size as the enthalpy difference between singlet **20** and **18** must be then that the difference between the strain energies of **19** and **20**, seen in the relative enthalpies for formation of the triplet diradicals, is approximately canceled by the much greater electronic destabilization of singlet **20**, relative to singlet **19**.

Unlike the case in **19**, in **20** both symmetry combinations of allylic NBMOs are destabilized by interactions with filled orbitals of the six-membered ring.²⁵ Since the pair of nonbonding electrons in singlet **20** have to occupy an MO that is destabilized by antibonding orbital interactions between the six-membered ring and the two allylic radical bridges, the electronic interactions between the ring and the bridges are much less destabilizing in singlet **19** than in singlet **20**.

This project is typical of many of the collaborations in which my group has been asked to do calculations. Rolf requested that my group compute ΔE_{ST} in **19**. However, by the time that the calculations were done, we had been led to ask a question that neither Rolf or I had previously considered—why do the rearrangements of **17** and **18** have nearly the same activation enthalpies? Rolf's previous analysis of the orbital interactions between the cyclobutane ring and the unsaturated bridges in **19**²⁶ and our calculations of ΔE_{ST} in **19** and **20** provided us with the answer to this question.²⁵

2. PREDICTING THE GROUND STATES OF DIRADICALS FROM NBMO TOPOLOGY

I spent 1964–65, the year after I received my B.A. from Harvard College, in Cambridge, England. At the suggestion of E. J. Corey, from whom I had taken an undergraduate chemistry course and who would subsequently become my Ph.D. Adviser, I had applied for and won a Fulbright Fellowship to study theoretical chemistry with Professor H. C. Longuet-Higgins.

While I was studying with Professor Longuet-Higgins in Cambridge,²⁹ in order to develop my understanding of how to include the effects of electron repulsion in MO calculations, I used Pariser–Parr–Pople (PPP) theory to carry out back-of-the-envelope calculations on some unsaturated organic molecules. Included in the molecules on which I performed PPP calculations were two diradicals, trimethylenemethane and square cyclobutadiene. A decade later, the results of those calculations serendipitously provided me with the foundation for the development of a simple rule for predicting the ground states of diradicals, based on the topology of their nonbonding (NB)MOs.

Lionel Salem Asks a Question. In 1972, Lionel Salem was on sabbatical at Harvard and writing *The Organic Chemist's Book of Orbitals*¹⁰ with Bill Jorgensen. I was more than a little impressed by Lionel,³⁰ so when he asked me a question, I was very flattered. I was also very happy that, thanks to the PPP calculations I had done during the previous decade in Cambridge, I knew the answer to Lionel's question.

Lionel asked me about the effects of electron repulsion in singlet trimethylenemethane (TMM) and their relevance to the results of calculations on TMM that had recently been published

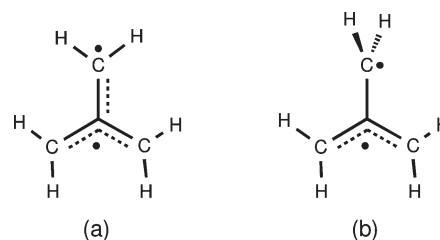


Figure 3. (a) Planar D_{3h} and (b) twisted C_{2v} geometries for TMM.

by Professor Michael J. S. Dewar.³¹ In agreement with the experiments of Paul Dowd on triplet TMM,³² Dewar's calculations found that the triplet has a planar, D_{3h} geometry. However, in agreement with the experiments of Bill Doering on singlet TMM,³³ Dewar's calculations found that the singlet prefers the C_{2v} geometry, shown in Figure 3, with one CH_2 group twisted out of conjugation.

When Lionel asked me about Dewar's results, I had already knew from my PPP calculations that the nonbonding (NB)MOs in Figure 4b for twisted TMM give a much lower electron repulsion energy for singlet TMM than do the D_{3h} Hückel NBMOs in Figure 4a, which are optimal for planar triplet TMM.³⁴ My PPP calculations had also found that, like TMM, cyclopentadienyl cation (CPDC) and benzene dianion (BDA) are each calculated to have a triplet ground state.³⁵ However, in contrast, my PPP calculations on square cyclobutadiene (CBD) had found that the lowest singlet and triplet states have nearly the same energies.³⁵

By drawing the MOs for these open-shell molecules, I had realized that in planar TMM, CPDC, and BDA, the partially filled MOs have atoms in common. This is shown in Figure 4a for the degenerate, nonbonding (NB)MOs of D_{3h} TMM. In contrast, as shown in Figure 4b, in twisted TMM the NBMOs have no atoms in common, and as illustrated in Figure 4c, in square CBD the degenerate NBMOs can be chosen so that they too have no atoms in common.

The triplet is the ground state of TMM, CPDC, and BDA because, in the triplet, the Pauli exclusion principle prevents the electrons of the same spin from simultaneously occupying the AOs that the singly occupied MOs have in common. However, in square CBD the pair of electrons that singly occupy the two NBMOs shown in Figure 4c are confined to different regions of space, irrespective of their spins. That is the reason why the lowest singlet and triplet states of square CBD are calculated to have nearly the same energies.³⁵

Localization of the pair of nonbonding electrons in different regions of space is also the reason why the NBMOs for twisted TMM in Figure 4b, consisting of an allyl NBMO plus a 2p AO on the unique CH_2 group, provide a lower energy for singlet TMM than do the D_{3h} NBMOs in Figure 4a.³⁶ The NBMOs in Figure 4a have atoms in common, whereas the NBMOs in Figure 4b do not. Therefore, the mutual Coulombic repulsion energy between electrons of opposite spin, one in each NBMO, is much lower for the NBMOs in Figure 4b than for the NBMOs in Figure 4a. Thus, the difference between the topologies of the NBMOs in parts a and b of Figure 4 provides a simple explanation for the otherwise puzzling pair of experimental observations, namely that triplet TMM has the planar, D_{3h} geometry shown in Figure 3a,³² but that singlet TMM prefers the twisted C_{2v} geometry in Figure 3b.³³

Lionel thought that both the results of my PPP calculations on TMM and CBD and my explanations of these results were worth

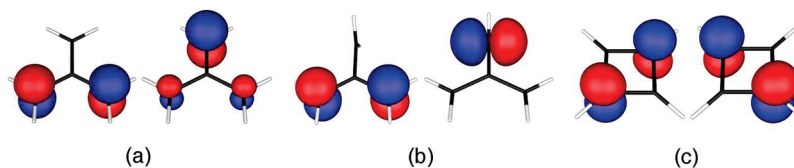


Figure 4. Singly occupied nonbonding MOs for (a) D_{3h} TMM, (b) twisted TMM, and (c) square (D_{4h}) CBD.

publishing, so I offered to draft a manuscript. Lionel read my draft, and he promptly rewrote it. Lionel's revised version, which was the one that we published,³⁶ focused much more than my draft had on the explanation of the PPP results, rather than on the details of the calculations. This experience taught me a valuable lesson. Although describing the details of calculations and the results obtained from them is certainly important, it is even more important to write a clear, physical explanation of the results.³⁷

Fritz Schaefer Answers a Question. In our paper, Lionel and I explained that singlet TMM prefers the C_{2v} geometry in Figure 3b, with one CH_2 group twisted out of conjugation, because in this geometry the NBMOs are those in Figure 4b, which are confined to different sets of carbons. I assumed that a planar geometry for singlet TMM must have a much higher Coulombic repulsion energy than the twisted C_{2v} geometry because I believed that the planar singlet must use the D_{3h} MOs in Figure 4a that are used by the triplet.

I held to this belief, that a planar geometry for singlet TMM must have a much higher energy than the twisted C_{2v} geometry, even though Bill Doering reminded me of the results of his experiments on the thermal rearrangement of an optically active methylenecyclopropane.³³ Although Bill's experiments showed that singlet TMM prefers a geometry with one CH_2 group twisted out of conjugation, his experiments also showed that a planar geometry for the singlet is only slightly higher in energy than the twisted geometry.

I came to the realization that Bill's experiments were right and that I was wrong when I read a paper about TMM by Fritz Schaefer.³⁸ In it, he made the somewhat cryptic statement that the energy of *planar* singlet TMM is much lower if the MOs are allowed to have C_{2v} symmetry, rather than if D_{3h} symmetry is imposed upon them. I immediately realized what Fritz's statement meant. The optimal SCF wave function for planar singlet TMM does *not* use the same D_{3h} MOs as the planar triplet. Instead, the wave function for the planar singlet uses the same C_{2v} MOs as the wave function for the twisted singlet—MOs that can be described as those for an allyl radical plus a 2p AO on the unique CH_2 group.³⁹

I wrote to Fritz to ask him to look at the C_{2v} MOs for the planar singlet to see if I was right. Fritz was kind enough to send me the coefficients of the AOs in these MOs. As I had guessed, the MOs turned out to be those for an allyl radical plus a 2p AO on the unique carbon.

As an organic chemist, I was accustomed to Hückel calculations, in which there is just one set of MOs for a molecule. The results of Fritz's calculations demonstrated that different electronic states of the same molecule can have different sets of MO's, even at exactly the same geometry. Many theoretical chemists might have known this fact, but until I read Fritz's paper,³⁸ I did not.

As discussed in section 4 of this Perspective, the lesson I learned from planar singlet TMM—that the NBMOs for a singlet diradical may differ from those of the triplet, by tending to

localize the nonbonding electrons of opposite spin to different regions of space—was to prove very useful again 17 years later in interpreting the results of calculations on the lowest singlet and triplet states of phenylnitrene (PhN).⁴⁰

CI Calculations on TMM: My Collaboration with Ernest Davidson Begins. At D_{3h} geometries, singlet TMM prefers a C_{2v} allyl plus 2p, wave function, but at D_{3h} geometries the correct TMM MOs really must have D_{3h} symmetry. This paradox led me to investigate how the optimal MOs for D_{3h} singlet TMM can turn out to have only C_{2v} symmetry, as the results of Fritz Schaefer's calculations had shown.³⁸

I realized that the answer to this question about symmetry breaking in singlet D_{3h} TMM would be of very little interest to organic chemists, and that is why I have put the answer in the Supporting Information for this Perspective, rather than in the text. However, I thought that Ernest Davidson, an eminent theoretical chemist at UW, might be interested in my answer. Therefore, I gave Ernest a preprint of my paper on configuration interaction (CI) as a formalism for understanding symmetry breaking in planar singlet TMM.⁴¹

As it turned out, Ernest was interested in my paper. He too was working on some problems concerned with symmetry breaking, both real and artifactual, and 7 years later, we actually wound up coauthoring a review article on this subject.⁴²

Ernest's interest in symmetry breaking and, hence, in my paper was very fortunate for me, because it led to a collaboration that continued for another 30 years and resulted in the publication of more than 40 coauthored papers. Our collaboration began with Ernest's offering to do some *ab initio* CI calculations on singlet TMM, using his program MELD.

Ernest's ability to use MELD to do full π CI calculations on TMM (albeit with the STO-3G basis set) came as a revelation to me. By the time that work on Ernest's and my manuscript on *ab initio* CI calculations on D_{3h} TMM had been completed,⁴³ my previous skepticism about the usefulness of *ab initio* calculations for understanding chemistry had vanished forever.⁴⁴ Therefore, I suggested to Ernest that, as our next project, we should use CI calculations in order to explore the entire potential energy surface (PES) for singlet TMM.

This time, Ernest actually allowed me to do the MELD CI calculations myself, using a small deck of computer punch cards that he gave me. For each calculation I added 10 cards, which I punched myself, that specified the Cartesian coordinates of each atom in TMM for that calculation. I also wrote the first draft of the paper, describing our results, which showed that the PES for planar singlet TMM can be completely understood in terms of the interplay between first-order and second-order Jahn–Teller Effects.^{45,46}

Diradicals with Disjoint and Non-Disjoint MOs. My next paper with Ernest expanded upon the Communication that I had published with Lionel Salem,³⁶ and this paper with Ernest has turned out to be my most cited publication.⁴⁷ It showed why attachment of CH_2^\bullet to the central carbon of allyl radical, to form

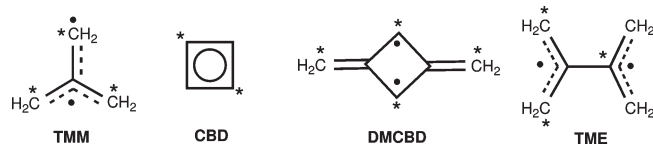


Figure 5. Four alternant hydrocarbon (AH) diradicals, showing the starred and unstarred atoms in each diradical.

TMM, gives rise to a pair of π NBMOs that have atoms in common (Figure 4a), whereas attachment of CH^* to both terminal carbons of allyl, to form **CBD**, gives rise to a degenerate pair of π MOs that have no atoms in common (Figure 4c).

In our paper, Ernest and I reiterated that the differences between these two types of diradicals are as follows: (a) Diradicals, whose NBMOs have atoms in common, have a triplet ground state, and the optimal wave functions for the lowest singlet states of such a diradical use MOs that are different from those for the triplet. (b) In contrast, a diradical whose NBMOs have no atoms in common (i.e., whose NBMOs are disjoint)⁴⁸ is likely to have a singlet ground state, and the lowest singlet and triplet will use nearly identical sets of MOs.

Thanks to Ernest, we were able to carry out calculations with MELD to confirm that these conclusions are valid not only for **TMM** and **CBD** but also for 2,4-dimethylenecyclobutane-1,3-diyl (**DMCBD**) and for tetramethylethane (**TME**). The NBMOs of **DMCBD** have atoms in common; those of **TME** do not. Better calculations and subsequent experiments have confirmed the predictions of a triplet ground state for **DMCBD** and a singlet ground state for **TME**.⁴⁹

As shown in Figure 5, **TMM**, **CBD**, **DMCBD**, and **TME** are all alternant hydrocarbons (AHs), molecules in which the carbons can be divided into two sets, starred and unstarred, such that two atoms of the same set are not nearest neighbors.⁵⁰ Ernest and I noted that in AH diradicals, such as **TMM** and **DMCBD**, in which the number of starred exceeds the number of unstarred atoms by two, both NBMOs are confined only to the more numerous set of atoms. Thus, these NBMOs do, in general, have atoms in common. In contrast, in AH diradicals, such as **CBD** and **TME**, in which the number of starred and unstarred atoms is the same, the NBMOs can be chosen so that one NBMO is confined to just the starred set of atoms and the other to the unstarred set. In an appendix to our paper, Ernest proved mathematically that this is, indeed, the case.⁴⁷

Therefore, simply by counting the number of starred and unstarred carbons in an AH diradical, one can determine whether the NBMOs of the diradical do or do not have atoms in common. Thus, by counting the number of starred and unstarred carbons, it is very easy to predict the ground state of an AH diradical, without actually doing any calculations.⁵¹

3. VIOLATIONS OF HUND'S RULE IN MOLECULES WITH DISJOINT NBMOs

In diradicals, such as square **CBD** and **TME**, that have disjoint NBMOs, the lowest singlet and triplet states have, at least to a first approximation, the same energy. However, the nonuniform distribution of electron spin in the pair of disjoint NBMOs in the singlet state,⁵² leads to it being computed to fall below the triplet state in energy in both **CBD**⁵³ and in **TME**.⁵⁴ Thus, both of these molecules are predicted to violate Hund's rule.⁵⁵

My Group Does Calculations and Jerry Berson Does Experiments on TMB. As shown in Figure 6a, 1,2,4,5-tetramethylenebenzene (**TMB**) has an equal number of starred and unstarred atoms. Therefore, the NBMOs of **TMB** can be chosen to be disjoint. The disjoint NBMOs of **TMB** are shown in Figure 6b.

In **TME**, the dihedral angle between the two allylic radicals, of which **TME** is comprised, is predicted to be different in the singlet and triplet states,⁵⁴ and this conformational flexibility complicates the determination of whether the singlet is lower in energy than the triplet at the equilibrium geometry of the triplet state. **TMB** lacks this conformational flexibility because the pair of pentadienyl radicals, of which **TMB** is comprised, are joined by two bonds. Therefore, **TMB** is really a more convenient disjoint diradical than **TME** in which to investigate experimentally the existence of a violation of Hund's rule.

Jerry Berson was interested in determining the ground state of **TMB** experimentally, and he asked my group to compute the singlet–triplet energy difference in **TMB** at geometries that had been optimized with inclusion of correlation between the π electrons.^{57a} Inclusion of correlation between all 10 π electrons in calculations on **TMB** results in the prediction of weak π bonding between the two pentadienyl radical fragments in the singlet state, due, in part, to dynamic spin polarization.⁵² Our calculations found that the bond distance between the nodal carbons of the two pentadienyl fragments in **TMB** is ca. 0.01 Å shorter in the singlet than in the triplet state, and we calculated a value of $\Delta E_{\text{ST}} \approx -5$ kcal/mol in this diradical, with the singlet lower in energy.⁵⁷

The first experiments, designed to test the prediction of a singlet ground state for **TMB**, were published by the late Wolfgang Roth and co-workers, and unfortunately, these experiments seemed to show that our prediction of a singlet ground state for **TMB** was wrong.⁵⁸ The experiments found that matrix-isolated **TMB** had a triplet EPR signal, and the intensity of the signal followed the Curie–Weiss law, thus indicating that **TMB** has a triplet ground state. In addition, the UV–vis spectrum that was observed by Roth and co-workers resembled more closely the spectrum that had been predicted for the triplet, rather than for the singlet, state of **TMB**.^{57a}

However, subsequent experiments by Jerry Berson's group showed that the EPR signal in matrix-isolated **TMB** did not belong to **TMB**.⁵⁹ The UV–vis spectrum of **TMB** could be photobleached, but the EPR signal persisted, undiminished in intensity. Jerry and his co-workers also succeeded in obtaining a ¹³C NMR spectrum of ¹³C-enriched **TMB**, and the sharpness of the NMR spectrum was inconsistent with a triplet ground state for **TMB**.^{59c}

Roth's experimental results not only stimulated experiments in Jerry's research group but also more calculations in mine. My long-time collaborator, Dave Hrovat, recalculated the UV–vis spectrum of **TMB**, this time including the effects of dynamic correlation⁶⁰ between the π and the σ electrons, using Roos' CASPT2 method.⁶¹ Dave's CASPT2 calculations predicted a UV–vis spectrum for the singlet^{57b} that was in good agreement with the observed spectrum of matrix-isolated **TMB**. The new calculations were also able to account for the vibrational structure in the long-wavelength band in the UV–vis absorption spectrum of **TMB**, which had been observed by both the Roth and Berson groups.^{58,59} Jerry's experiments⁵⁹ and Dave Hrovat's CASPT2 calculations^{57b} left little or no doubt that **TMB** has a singlet ground state.^{55a}

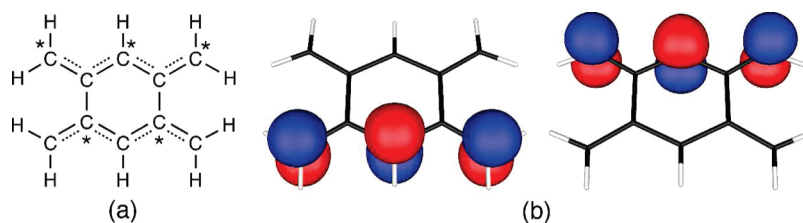


Figure 6. (a) Starred and unstarred carbons of TMB and (b) disjoint NBMOs.

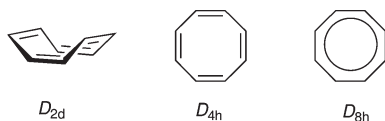


Figure 7. D_{2d} equilibrium geometry of COT, the D_{4h} transition structure for ring inversion, and the D_{8h} transition structure for bond shifting. The equilibrium geometry of triplet COT also has D_{8h} symmetry.

TMB is certainly a diradical with a singlet ground state, but does it really violate Hund's rule? In TMB, the in-phase combination of the two, disjoint, pentadienyl NBMOs in Figure 6b is lower in energy than the out-of-phase combination, and this difference in orbital energies is a contributor to making the singlet the ground state of TMB.⁵⁷ Since Hund's rule was devised for atoms, in which the partially filled AOs have *exactly* the same energy,^{55b} the nondegeneracy of the NBMOs of TMB means that TMB cannot be claimed to be a diradical that violates the strictest version of Hund's rule.

Paul Wenthold and Carl Lineberger Do Transition-State Spectroscopy on the Radical Anion of Cyclooctatetraene ($\text{COT}^{\bullet-}$). In order for a violation of the strictest version of Hund's rule to be claimed in a molecule, the singly occupied MOs must be degenerate by symmetry. At $D_{(4m)h}$ geometries, $(\text{CH})_{4m}$ annulenes do have half-filled shells of disjoint NBMOs that are degenerate by symmetry. Unfortunately the $D_{(4m)h}$ geometries of $(\text{CH})_{4m}$ annulenes are the transition structures (TSs) for bond shifting in, for example, CBD ($m = 1$) and COT ($m = 2$). However, negative ion photoelectron spectroscopy (NIPES) can be used to access TS geometries and to provide information about the energies of TSs and even about the frequencies of some of the vibrations in them.⁶²

At a Gordon Conference in the summer of 1995, I sought out Paul Wenthold, who was a postdoc in Carl Lineberger's group at the time, I suggested that he and Carl attempt to obtain the NIPE spectrum of $\text{COT}^{\bullet-}$. The detailed reasoning in designing this experiment was as follows.

Although neutral COT is tub-shaped, COT radical anion ($\text{COT}^{\bullet-}$) is planar.⁶³ Therefore, photodetachment of an electron from $\text{COT}^{\bullet-}$ should initially generate planar COT, and the triplet state of neutral COT is predicted⁶⁴ to have a planar D_{8h} geometry.⁶⁵

However, a planar D_{4h} geometry is the TS for ring inversion in singlet COT.⁶⁴ Nevertheless, I hoped that in the NIPE spectrum of $\text{COT}^{\bullet-}$, the peak for formation of this TS in neutral COT would be sharp enough so that its energy, relative to that of the peak for formation of the D_{8h} triplet, could be measured (Figure 7).

Of course, the singlet TS, whose energy we needed to know in order to confirm the prediction of a violation of the strictest form

of Hund's rule in COT, was not the D_{4h} TS for ring inversion, but the D_{8h} TS for bond shifting. Fortunately, previous NMR studies had found that bond shifting in COT requires 3–4 kcal/mol more energy than ring inversion.⁶⁶ Therefore, I was confident that, by measuring the energy difference between the D_{4h} TS for ring inversion and the D_{8h} triplet from the NIPE spectrum of $\text{COT}^{\bullet-}$ and subtracting 3–4 kcal/mol from this measured value, Paul and Carl would be able to obtain ΔE_{ST} between the D_{8h} singlet TS for bond shifting in COT and the D_{8h} triplet equilibrium geometry.

The experiment was done the week after I proposed it to Paul, and the experiment turned out even better than I had expected.⁶⁷ In the NIPE spectrum of $\text{COT}^{\bullet-}$ the first band in the vibrational progression for bond alternation in singlet COT was split into a doublet at 1370 and 1670 cm^{-1} . Carl provided the explanation for this unexpected splitting and pointed out that it confirmed the approximate energy of the transition state for bond shifting.⁶⁸

Taking the energy of the transition state for bond shifting as being about 4 kcal/mol higher than the energy of the bond-alternated but planar D_{4h} transition structure for ring inversion, the NIPE spectrum showed that the D_{8h} transition state for bond shifting in singlet COT is 8–9 kcal/mol below the energy of the D_{8h} equilibrium geometry of the triplet state.⁶⁷ This value is in reasonable agreement with the value of ΔE_{ST} for COT that is predicted by CASPT2 calculations.^{55c,d}

The experimentally confirmed violation of the strictest version of Hund's rule in D_{8h} COT has the same origin as the predicted violation in D_{4h} CBD.⁵³ Because the two NBMOs of D_{8h} COT can be confined to disjoint sets of atoms, to a first approximation the lowest singlet and triplet states have the same energy.^{35,36,47} Dynamic spin polarization selectively stabilizes the nonuniform distribution of electron spin in the NBMOs of D_{8h} singlet COT,⁵² making the singlet the ground state.

4. PHENYLCARBENE AND PHENYLNITRENE

Phenylcarbene (PhCH) and phenylnitrene (PhN) are iso-electronic. However, as pointed out in a review, written by Matt Platz, the chemistries of PhCH and PhN are very different.⁶⁹ For example, singlet PhCH and singlet PhN both undergo intramolecular cyclization, followed by electrocyclic ring-opening to give a seven-membered cumulene, but the cyclization reaction has a much higher barrier in singlet PhCH than in singlet PhN. Consequently, unrearranged singlet PhCH survives long enough to undergo intermolecular reactions, whereas singlet PhN rearranges too fast to allow intermolecular trapping to compete with rearrangement. Paradoxically, singlet PhCH seems to be much more reactive than singlet PhN toward intermolecular addition reactions.

The results of calculations, intended only to compute the singlet–triplet energy gap in PhN,^{40,70} turned out, serendipitously,

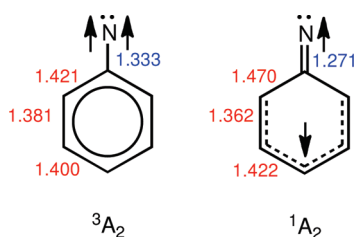


Figure 8. Calculated bond lengths (Å) in the triplet ground state (3A_2) and the lowest energy singlet state (1A_2) of PhN. The most recently published values are given.^{70c}

to provide the explanations for not only these differences in reactivities between PhN and PhCH but also for the many other differences between this nitrene and the isoelectronic carbene.⁷¹ Our calculations^{40,71} led to a very fruitful collaboration with Matt Platz's research group involving new calculations by my research group and new experiments by his.

Matt Platz Is Polite but Persistent. Our first calculations on PhN were the result of polite but persistent prodding by Matt. Based on his experiments,⁶⁹ Matt thought that the experimental value of the singlet–triplet energy difference in PhN that had been published by John Brauman⁷² was too small. Consequently, whenever I saw Matt at a conference in the early 1990s, he would invariably ask me, very politely, when I was going to keep my promise to compute ΔE_{ST} in PhN. Finally, I acceded to Matt's repeated requests. Had I known what the calculations would reveal, I would have done the calculations years earlier.

In singlet PhCH both nonbonding electrons occupy the same hybridized AO on the carbene carbon.⁷³ However, calculations performed independently by Fritz Schaefer's group^{70a} and by my own⁴⁰ found that in PhN the lowest singlet state has the same orbital occupancy as the triplet. One nonbonding electron occupies the $2p_x$ AO on nitrogen, which lies in the plane of the benzene ring, and the other nonbonding electron occupies the $2p_y$ AO on nitrogen, which is aligned with the π orbitals of the benzene ring.

In the singlet these electrons have opposite spin, so their localization on the nitrogen atom would give rise to high energy ionic terms in the singlet wave function. Consequently, as is the case in singlet TMM (discussed in section 2),³⁹ the MOs for the lowest singlet state of PhN (1A_2) are different from the MOs for the triplet ground state (3A_2).⁴⁰

The difference between the MOs for these two states of PhN is reflected in the differences between the optimized bond lengths in these two states. The bond lengths are given in Figure 8. In particular, in the 1A_2 state the short C–N bond length and the alternation of the lengths of the C–C bonds in the benzene ring indicate that, in the lowest singlet state of PhN, the electron in the $2p_y$ AO is largely delocalized into the benzene ring.

The delocalization of one of the nonbonding electrons in singlet PhN results in the Coulombic repulsion between the electrons of opposite spin in the $2p_x$ and $2p_y$ AOs on N being much smaller in singlet PhN than in singlet HN or singlet CH₃N. In the latter pair of nitrenes, both NBMOs are either completely or largely localized on nitrogen. This difference between PhN and both HN and CH₃N is responsible for the calculated values of $\Delta E_{ST} = 15\text{--}18$ kcal/mol in PhN^{40,70} being much lower than those measured in HN ($\Delta E_{ST} = 36.5 \pm 0.4$ kcal/mol)⁷⁴ and CH₃N ($\Delta E_{ST} = 31.2 \pm 0.3$ kcal/mol).^{75,76} The calculated values of ΔE_{ST} in PhN are in excellent agreement with the values that were subsequently measured by three different research groups.⁷⁷

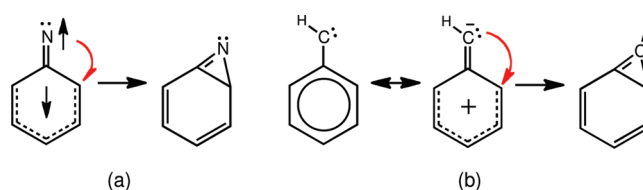


Figure 9. Schematic depiction of the cyclization of (a) the open-shell, 1A_2 , state of PhN to an aziridine and (b) the closed-shell, 1A_1 , state of PhCH to a cyclopropene.

The open-shell wave function (1A_2) of the lowest singlet state of PhN^{40,70} and the closed-shell (1A_1) wave function of the lowest singlet state of PhCH⁷³ are depicted schematically in Figure 9. Dr. Bill Karney, a postdoc in my group, showed that the difference between these two types of wave functions is responsible for the difference between the heights of the barriers to the intramolecular cyclization reactions of PhN and PhCH.⁷¹

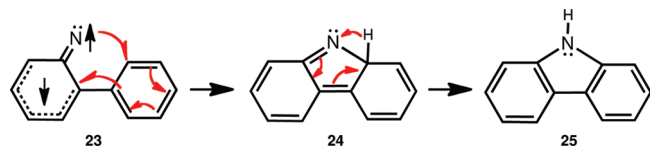
Ring closure in the lowest singlet state of PhN requires only a small amount of bending of the nitrogen out of the plane of the benzene ring, so that the singly occupied AO on nitrogen can begin to overlap with the singly occupied π MO of the six-membered ring. In contrast, the intramolecular cyclization of PhCH requires increasing the contribution of the ionic resonance structure in Figure 9b, in which a pair of π electrons is delocalized from the benzene ring into the formally empty $2p_y$ AO on carbon. Calculations have confirmed that in the transition structure for cyclization of PhCH there is a greater negative charge on the carbenic carbon than in the reactant.^{78a}

The cyclization of singlet PhN is really an intramolecular radical coupling reaction between an electron in the $2p_x$ AO on N and an electron of opposite spin in the NBMO of the pentadienyl radical in the six-membered ring. This realization allows one to predict that steric effects, involving *ortho* substituents on the benzene ring, are likely to be more important than electronic effects in this reaction. This expectation leads to the prediction that, when a single *ortho* substituent is present, cyclization at the unsubstituted *ortho* carbon will, in general, be preferred. This prediction was confirmed by calculations in my group, performed by Bill Karney,⁷⁹ and subsequently by experiments carried out in Matt's group.⁸⁰

An exception to the generalization that steric effects on PhN cyclizations are more important than electronic effects is provided by cyano substituents. A cyano group stabilizes a radical center at the carbon to which the cyano group is attached. Therefore, a cyano group in the *para* position of the benzene ring in PhN should deplete the unpaired spin density at the *ortho* positions, thus retarding the rate of the cyclization reaction. On the other hand, being linear, cyano is a rather sterically undemanding substituent, and its ability to stabilize an adjacent radical center might be expected to favor cyclization at a cyano-substituted *ortho* carbon, in preference to an unsubstituted *ortho* carbon. These two qualitative expectations were both confirmed by Bill Karney's calculations and by Matt's group's experiments.⁸¹

As the grand finale to the collaboration between Matt's group and mine, together we investigated the competition between the three different cyclization modes that are possible in *o*-biphenyl nitrene (**23**).⁸² In this case, attack of nitrogen on the *ortho* carbon of the phenyl substituent can lead to isocarbazole (**24**), which can, in turn, undergo a 1,5-hydrogen shift to form carbazole (**25**). Of course, cyclization of **23** can also occur at either the substituted or unsubstituted *ortho* carbon of the benzene ring

to which the nitrogen is attached, and the resulting pair of aziridenes can each undergo electrocyclic ring-opening to a different cyclic ketenimine. Calculations by my group located the important transition structures on the PES for singlet **23**, and to my amazement, Matt's group was able to measure the rate of passage over each of them.⁸²



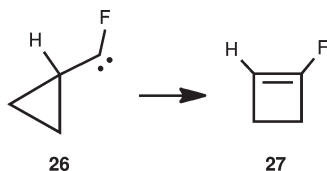
The *o*-biphenyl nitrene project was the last in a very successful collaboration between Matt's group and mine. The collaboration really began with Matt's asking me to compute ΔE_{ST} in PhN, and our research on PhN extended over more than a decade. Before our collaboration ended, Matt and I had coauthored several reviews, describing what we had learned about the chemistry of aryl nitrenes from our collaborative research.⁷⁸

5. TUNNELING BY CARBON IN ORGANIC REACTIONS

At an International Symposium on Reactive Intermediates and Unusual Molecules (ISRIUM) in Hawaii in December 2000, I heard a lecture on rearrangements of alkylhalocarbenes. The lecturer claimed that these reactions have very low barriers and very low *A* factors; and I wondered whether tunneling might be involved.

Matt Platz and Bob Moss were also in the audience, and since they both know much more about carbene chemistry than I, I asked them about the very low *A* factors that the speaker had reported. They confirmed that low *A* factors are commonly observed in rearrangements of alkylhalocarbenes. Bob referred me to a 1992 paper of his which had reported $A = 10^8 - 10^9 \text{ s}^{-1}$ ($\Delta S^\ddagger = -20$ to -24 eu) for the rearrangements of a variety of alkylhalocarbenes, by 1,2-shifts.⁸³

Professor Alan Goren was on sabbatical in my research group at the time, and when I returned from Hawaii, I asked him to do some (10/10)CASSCF and CASPT2 calculations on the ring expansion of fluorocyclopropylcarbene (**26**) to 1-fluorocyclobutene (**27**), one of the reactions that Bob had studied experimentally. Alan calculated $\Delta H^\ddagger = 14.7$ kcal/mol and $\Delta S^\ddagger = -2.7$ eu at the (10/10)CASPT2/cc-pVTZ//((10/10)CASSCF/6-31G* level of theory.⁸⁴ Bob Moss and his co-workers had measured $\Delta H^\ddagger = 3.6$ kcal/mol and $\Delta S^\ddagger = -22.5$ eu for this reaction.⁸³ There is obviously a significant difference between the calculated and observed activation parameters for the rearrangement of **26** to **27**.



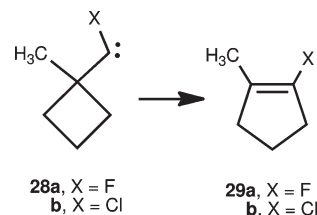
Don Truhlar Does More Calculations, Bob Moss Does More Experiments, and the Results Still Do Not Agree. The much higher values of ΔH^\ddagger and ΔS^\ddagger that Alan calculated for the ring expansion of **26** to **27**, by passage over the reaction barrier,

provided evidence that tunneling through the barrier might be responsible for the much lower activation parameters that Bob Moss had measured for this reaction.⁸³ Barry Carpenter reminded me that Don Truhlar had created a program called POLYRATE for calculating rate constants with inclusion of corrections for multidimensional tunneling. Therefore, I asked Don if he was interested in carrying out POLYRATE calculations to see if tunneling was responsible for the low values of ΔH^\ddagger and ΔS^\ddagger that Bob Moss had measured for the ring expansion of **26**. Don agreed, and several months later he sent me the first draft of a comprehensive manuscript on 1,2-shifts in carbenes.⁸⁴

The manuscript reflected a huge amount of very careful work that Don and his co-workers had put into calculations on these reactions. They had calculated rate constants for four different types of carbene 1,2-shifts, each at several different levels of theory and with inclusion of both solvent effects and corrections for tunneling. These calculations found that, at the temperatures at which Bob Moss had measured the rate constants for ring expansion of **26** to **27**, tunneling contributes very little to the rate of reaction.⁸⁴

When I informed Bob of Don's computational results, Bob was concerned that they might indicate that there was a problem with his experiments. Therefore, Bob repeated his experiments and obtained $E_a = 5.1 \pm 1.1$ kcal/mol and $\log A = 9.2 \pm 0.9 \text{ s}^{-1}$,⁸⁴ values that are close to those that he had previously published.⁸³ Clearly, there was and there still is a major disagreement between the results of Don's calculations and Bob's experiments because, to date, neither Don, nor Bob, nor I have been able to think of a way to reconcile the conflicting results.

Bob Sheridan Enlists Don Truhlar and Me in a Collaboration on Tunneling in a Carbene Rearrangement. Although the 16-page paper that was coauthored by Don, Bob, and me was unsuccessful in identifying the reason for the large difference between the calculated and experimental activation parameters for ring expansion of **26**,⁸⁴ this paper did, fortuitously, lead to a very successful collaboration between Don, Bob Sheridan, and me on another carbene ring-expansion reaction. Bob Sheridan had been doing experiments at 8 K on the rearrangement of 1-methylcyclobutylhalocarbenes (**28**) to 1-halo-2-methylcyclopentenes (**29**). Even at 8 K the ring expansion reaction of chlorocarbene **28b** was too fast to allow Bob Sheridan and his co-worker, Peter Zuev, to observe **28b**. However, they were able to observe fluorocarbene **28a** and to measure the rate of rearrangement of **28a** to **29a**.



Any reaction that occurs rapidly at 8 K must involve tunneling. However, carbon, rather than hydrogen, migrates in the ring expansion of **28** to **29**, and because of the heavier mass of carbon, carbon is much less likely than hydrogen to tunnel. Therefore, Bob and Peter had discovered a rare example of a reaction in which carbon tunnels rapidly. Having read the paper about calculations of the tunneling rates in the ring expansion of **26** to **27**,⁸⁴ Bob Sheridan asked me, and I asked Don Truhlar to

compute the rates of the ring expansion reactions of **28a** and **28b** by tunneling at 8 K, in order to investigate why carbon apparently tunnels rapidly in these reactions.

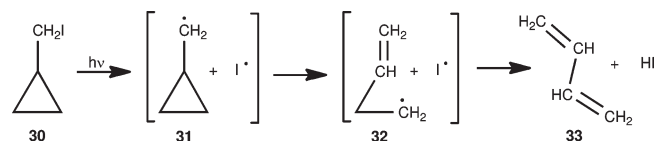
The tunneling rates, calculated by Don and his postdoc, Titus Albu, were in excellent agreement with Peter Zuev's and Bob Sheridan's experiments.⁸⁵ The calculations predicted that the rate of tunneling by the chlorocarbene would be so fast that **28b** would not be observable under Bob and Peter's reaction conditions. However, due to the stabilization of **28a** by donation of a fluorine lone pair to the empty 2p AO on the carbenic carbon, the rearrangement of **28a** was computed to be slow enough to make the carbene observable. In fact, the calculated rate of rearrangement of **28a** to **29a** at 8 K, by tunneling from the lowest vibrational level of **28a**, was within a factor of 5 of the measured rate.

The calculations also revealed the reason why the rearrangement of **28** to **29** is very rapid. Despite the fact that a CH₂ group, rather than a hydrogen atom, migrates to the carbenic center in this reaction, the small distance that the CH₂ group has to move makes the calculated barrier to this reaction very narrow.⁸⁵ The small width of the barrier compensates for the high mass of the group that tunnels through it.⁸⁶

The Collaboration with Don Truhlar and Bob Sheridan Results in a New Area of Research for My Group. The success of Don and Titus' POLYRATE calculations in replicating Bob Sheridan's experimental tunneling rates in the ring expansion of **28** to **29** made me decide to start doing POLYRATE calculations on tunneling in my own research group. Don and Titus were both very helpful in answering the questions asked by me and by my long-time collaborator, Dave Hrovat about using POLYRATE, and when Dave and I moved from UW to UNT in 2004, we began performing POLYRATE calculations on reactions that we thought were likely to involve tunneling.

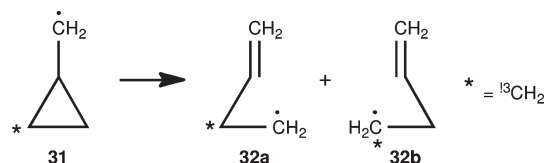
To date, my group has used POLYRATE to carry out calculations on tunneling by hydrogen atoms in the following reactions: (a) the 1,5-hydrogen shift in 5-methyl-1,3-cyclopentadiene,^{88a,b} (b) the reductive elimination of methane from (R₃P)₂Pt(CH₃)H,^{88c,89} and (c) the degenerate hydrogen atom exchange between hydroxylamines and nitroxyl radicals.^{88d,90} We have investigated tunneling by carbon in (d) the ring-opening of cyclopropylcarbinyl radical^{91a-c} and (e) the degenerate Cope rearrangement of semibullvalene.^{90d}

Professor Wolfram Sander agreed to test my group's POLYRATE prediction that cyclopropylcarbinyl radical (**31**) should undergo ring-opening to the homoallyl radical (**32**) in less than a minute at cryogenic temperatures.^{90a} Although photolysis of **30** in matrix isolation did lead to a ring opened product, 1,3-butadiene (**33**), Wolfram was unable to detect the putative cyclopropylcarbinyl radical (**31**) as an intermediate in this reaction.⁹¹ Therefore, this experiment, unfortunately, provided no information as to whether our POLYRATE prediction is right or wrong.



Dan Singleton and Ollie Gonzalez-James Give Me a Present. Another possible way of testing experimentally our

prediction of a large role for tunneling in the ring-opening of **31** to **32** would be to measure the ¹²C/¹³C or CH₂/CD₂ kinetic isotope effects (KIEs) on this reaction and to compare the measured KIEs with those calculated with and without tunneling. The effect of mass on tunneling rate means that the presence of ¹³C or D₂ at one of the methylene ring carbons of **31** should disfavor cleavage of the bond to that carbon. Consequently, rather than measuring the individual ¹²C/¹³C or CH₂/CD₂ KIEs at C-3 and C-4 of **31**, it would be sufficient to obtain their ratio by measuring the distribution of ¹³C or CD₂ at C-2 and C-1 in the product that is formed by chemically trapping **32a** and **b**. Therefore, we performed POLYRATE calculations, in order to predict the ratios of **32a** (¹³C or D₂ at C-2) to **32b** (¹³C at or D₂ at C-1) in the ring-opening of **31**.^{90b}



In a lecture at the Gordon Conference on Isotope Effects in the winter of 2010, I described my group's calculations on tunneling in the ring-opening of cyclopropylcarbinyl radical (**31**) and showed the predicted intramolecular KIEs at 8 K that we had computed. The following evening, Dan Singleton's student, Ollie Gonzalez-James, reported that she had measured the intramolecular ¹²C/¹³C KIEs on the ring-opening of **31** in solution at higher temperatures, using ¹³C in natural abundance. The results of her measurements are shown in Figure 10.⁹² Also shown are the predicted ratios, with and without inclusion of tunneling corrections, which Ollie obtained from POLYRATE calculations. Obviously, the intramolecular ¹²C/¹³C KIEs that she measured fit much better those predicted by her CVT + SCT calculations, which include contributions to the rate constants by tunneling, than by her CVT calculations, in which tunneling is not included.⁹²

Even without making comparisons between the KIEs that Ollie measured and those that she computed, the Arrhenius plot of Ollie's experimental KIEs in Figure 10 is, by itself, indicative of the occurrence of tunneling in the ring-opening of **31**.⁹³ The Arrhenius plot of the intramolecular ¹²C/¹³C KIEs that she measured is not linear but curved, and it is curved in exactly the manner expected for a greater contribution to tunneling when the bond to ¹²C, rather than to ¹³C is broken in the ring-opening of **31**.⁹²

What a fine present it was for me to have made a prediction about the importance of tunneling in the ring-opening of **31** at a conference one night and the next night to have Ollie report that she had confirmed the prediction! For a theoretical chemist, life does not get much better than this.

6. THE COPE REARRANGEMENT

When I was an Assistant Professor at Harvard, unlike most of my colleagues in the Chemistry Department, Bill Doering seemed genuinely interested in talking about chemistry with me. One day Bill asked me a question about the Cope rearrangement that took me nearly 30 years to answer to Bill's satisfaction.

Bill Doering's Question about the Cope Rearrangement. Bill asked whether I thought that there are two distinct pathways

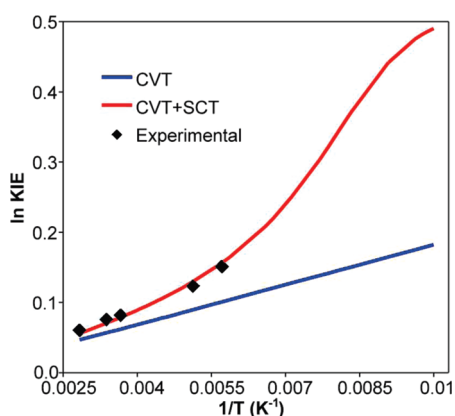


Figure 10. Arrhenius plot of the measured ratios of the products formed from 32a and 32b (* = ^{13}C) in the ring-opening of 31. Also shown are the Arrhenius plots of the ratios computed with (CVT+SCT) and without (CVT) tunneling corrections.

for the Cope rearrangement, one of which proceeds via cyclohexane-1,4-diyl and the other by a transition structure (TS) that resembles two allyl radicals? Or did I think that there is a variable TS for the Cope rearrangement, whose nature can be changed by substituents at C-2 and C-5 and/or by substituents at C-1, C-3, C-4, and C-6? Many years later, Bill posed the same question in print, using Doeringesque terms that are vividly descriptive. Bill asked whether the Cope transition structure is “centauric” or “chameleonic”.⁹⁴

In 1973, when Bill first asked me to speculate on the nature of the Cope TS, Michael J. S. Dewar had just published the results of experiments which showed that substituents at either C-2 and C-5 or at C-1, C-3, C-4, and C-6 can lower the barrier to the Cope rearrangement, and Michael had come down on the side of two different pathways for this reaction.⁹⁵ However, as I pointed out to Bill, it is possible to show that, provided one takes account of through-bond interactions between the radical centers in cyclohexane-1,4-diyl and through-space interactions between the radical centers in two allyl radicals, the MOs in one representation of the Cope TS correlate with the MOs in the other.⁹⁶ Therefore, as indicated in Figure 11, these two limiting structures can be considered to be resonance contributors to the Cope TS, and their relative contributions will depend on the interallylic distance (R) in the TS. Thus, I told Bill that I believed there is a variable TS for the Cope rearrangement, which can be stabilized by substituents in two different ways.

Bill encouraged me to publish my thoughts on this subject; so I prepared a manuscript and submitted it to the *Journal of the American Chemical Society* as a Communication. My manuscript was rejected. One reviewer, who identified himself as Howard Zimmerman, said that there was nothing wrong with the science in my manuscript, but that it would be a mistake for me to pick a fight with Michael Dewar. The second “anonymous” reviewer wrote, “Publication of this manuscript would only serve to provide the gladiatorial spectacle of Borden being torn to shreds in print.”

Collaborations with Keiji Morokuma and Ernest Davidson on (6/6)CASSCF Calculations on the Cope Rearrangement. A decade after an “anonymous” reviewer wrote this sentence, I had the good fortune to get a Guggenheim Fellowship to spend four months at the Institute for Molecular Science (IMS) in Okazaki, Japan, working with Keiji Morokuma.⁹⁷ Working in Keiji’s group

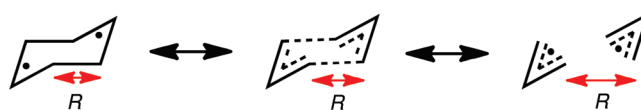


Figure 11. Possible transition structures for the chair Cope rearrangement of 1,5-hexa-diene. The limiting structures are cyclohexane-1,4-diyl at small interallylic distances (R) and two weakly interacting allyl radicals at large R . At intermediate values of R , bond making and bond breaking are synchronous, and the transition structure can be considered to be a resonance hybrid of the two diradical extreme structures.

at IMS allowed me to begin working on trying to do CASSCF calculations on the Cope rearrangement, a project that I continued when I returned to UW.

In a review that I published, describing the experimental and computational research on the Cope rearrangement,⁹⁸ I have recounted the story of how, with the help of David Feller (a postdoc at UW, whom I shared with Ernest Davidson) and two postdocs from Keiji’s group, Keiji, Ernest, and I were able to simulate the results of (6/6)CASSCF/3-21G calculations, which provided correlation for all six of the electrons that are “active” in the Cope TS. The calculations found that the Cope TS involves synchronous bond making and bond breaking.⁹⁹

Subsequently, Keiji acquired sufficient computing power at IMS to be able to perform real (6/6)CASSCF/3-21G calculations. The results of those calculations, including the computed value of $R = 2.023 \text{ \AA}$ in the chair Cope TS,¹⁰⁰ confirmed our previous finding that bond making and bond breaking in the Cope rearrangement are synchronous.

Ken Houk and I Coauthor a Review Article on Synchronicity. Michael Dewar had published a paper boldly titled, “Multibond Reactions Cannot, in General, Be Synchronous”.¹⁰¹ However, Ken Houk’s calculations on the Diels–Alder reaction and my calculations with Keiji and Ernest on the Cope rearrangement led Ken and me to the conclusion that, “Multibond reactions cannot only be synchronous, but they often are.”¹⁰²

About the time that Ken and I published our review, Michael Dewar was making two, related claims about the methodology for doing calculations on pericyclic reactions, particularly the Cope rearrangement.¹⁰³ First, Michael claimed that (6/6)-CASSCF/3-21G calculations were probably not accurate enough to give a correct description of the potential energy surface (PES) for the Cope rearrangement. Second, Michael claimed that his semiempirical calculations described the Cope PES properly. As it turned out, Michael’s first claim was correct.

Ernest Davidson Appears To Prove that Michael Dewar Was Right. Soon after publication of Ken’s and my review, Ernest acquired sufficient computer resources at the University of Indiana (where he had moved from UW) to perform (6/6)-CASSCF calculations with the larger 6-31G* basis set. The Cope PES that Ernest obtained was different from Keiji’s (6/6)-CASSCF/3-21G PES, and to the horror of Keiji, Ernest, Ken, and me, Ernest’s (6/6)CASSCF/6-31G* calculations gave a Cope PES very similar to that found by Michael Dewar’s semiempirical calculations.¹⁰⁴ This was, indeed, a bitter pill that Ernest’s (6/6)CASSCF/6-31G* results forced Ernest, Keiji, Ken, and me to swallow.

The only good news about Ernest’s (6/6)CASSCF/6-31G* calculations was that they gave a value of ΔH^\ddagger for the Cope rearrangement that was about 12 kcal/mol higher than Bill Doering’s experimental value of $\Delta H^\ddagger = 33.5 \text{ kcal/mol}$.¹⁰⁵ Clearly, Michael Dewar had been right about the (6/6)CASSCF

methodology that Ernest, Keiji, and I had been using, something important was still missing from these calculations.

The Importance of Including Dynamic Electron Correlation. Although the (6/6)CASSCF calculations included correlation among the six electrons that are active in the Cope rearrangement, these calculations did not include any correlation between the six active electrons and the remaining 26 valence electrons. Fortunately, about the time that I realized that inclusion of this latter type of “dynamic” correlation was probably going to be necessary, in order to compute an accurate value of ΔH^\ddagger for the Cope rearrangement, Björn Roos and his co-workers had already published the CASPT2 method, which uses second-order perturbation theory to add dynamic electron correlation to a CASSCF wave function.⁶¹ Even better, they incorporated this method into their program, MOLCAS.

When Dave Hrovat used MOLCAS to carry out (6/6)-CASPT2 calculations on the Cope rearrangement, he obtained a PES with a single TS, in which bond making and bond breaking are synchronous.¹⁰⁶ The value of ΔH^\ddagger that Dave obtained with a large basis set was within about 1 kcal/mol of Bill Doering's experimental value of $\Delta H^\ddagger = 33.5$ kcal/mol.

Ernest, too, had come to the conclusion that inclusion of dynamic electron correlation was necessary, in order to obtain an adequate description of the Cope PES, but he decided to use his own version of the CASPT2 method.¹⁰⁷ Therefore, Ernest's paper, reporting the results of his calculations on the Cope rearrangement, with inclusion of dynamic electron correlation,¹⁰⁸ appeared after the paper published by Dave, Keiji, and me.¹⁰⁶ Ernest's results agreed with ours, but his computer code allowed him to show that, including dynamic electron correlation selectively stabilizes the lowest energy configuration in the (6/6)-CASSCF wave function.¹⁰⁸ Therefore, with inclusion of dynamic electron correlation, calculations on the Cope rearrangement give a TS that more closely resembles the TS obtained with a one-configuration SCF wave function than with a multiconfigurational (6/6)CASSCF wave function.

Partly as a result of our experience with the Cope rearrangement, Ernest and I decided to coauthor a review about the importance, for many different molecules and reactions, of adding dynamic electron correlation to CASSCF wave functions.⁶⁰ This review has been widely cited. Therefore, it would not be incorrect to say that Bill Doering's question about the nature of the Cope TS in the early 70s led, serendipitously, to an increased recognition among computational chemists of the importance of dynamic electron correlation a quarter of a century later.

Bill Doering Assigns Ken Houk and Me the Same Project. The *ab initio* calculations, carried out by Dave Hrovat¹⁰⁶ and by Ernest¹⁰⁸, revealed that the PES for the Cope rearrangement of unsubstituted 1,5-hexadiene has a single TS in which bond making and bond breaking are synchronous. However, this finding did not address Bill Doering's question about how the Cope TS responds to the presence of radical-stabilizing substituents, such as cyano and phenyl groups. Bill still wanted to find the answer to this question, so he asked Ken Houk and me each to address this problem computationally.¹⁰⁹

Using CASPT2 calculations to determine the effects of multiple substituents on the Cope rearrangement would not have been possible. However, soon after I published the results of Dave Hrovat's CASPT2 calculations,¹⁰⁶ Ken and Paul Schleyer both found that B3LYP/6-31G* calculations almost duplicate the CASPT2 PES for the parent reaction.¹¹⁰ Therefore, Ken and I

were able to use B3LYP/6-31G* calculations to attempt to answer Bill's question about the effect of substituents on the Cope rearrangement.

Since the findings made by Ken's and my collaborative research on the effect of substituents on the Cope rearrangement have been reviewed,⁹⁸ here I will only briefly summarize our results.¹¹¹ Our B3LYP/6-31G* calculations confirmed my conjecture, made 30 years earlier on the basis of a correlation diagram,⁹⁶ that the Cope TS is chameleonic. Four radical-stabilizing substituents, one each at C-1, C-3, C-4, and C-6 of 1,5-hexadiene, result in very long interallylic bond lengths (*R*) in the Cope TS, so it resembles the two weakly interacting allyl radicals that are shown on the right side of Figure 11. In contrast, a pair of radical stabilizing substituents at C-2 and C-5 cause *R* to shorten, so that the TS resembles cyclohexane-1,4-diyl, the diradical that is shown on the left side Figure 11.

Ken's and my calculations also showed that the effects of substituents on the Cope rearrangement can be either cooperative or competitive. For example, we calculated^{111b} that, as found experimentally,^{95,112a} a pair of phenyl substituents at C-2 and C-5 of 1,5-hexadiene provide about three times the TS stabilization as the single phenyl substituent in 2-phenyl-1,5-hexadiene.⁹⁵ Similarly, our calculations^{111b} reproduced the experimental finding that the four phenyl substituents in 1,3,4,6-tetraphenyl-1,5-hexadiene^{112b} lower the barrier height to Cope rearrangement by, not twice, but by about four times as much as the pair of phenyl substituents in either 1,3- or 1,4-diphenyl-1,5-hexadiene.^{112c}

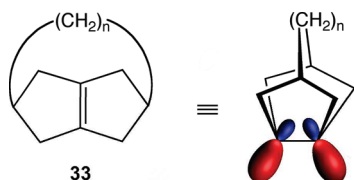
Ken's and my collaborative research showed that these cooperative substituent effects are due to the following: (a) substituents affect the interallylic distance (*R*) in the Cope TS; (b) the value of *R* affects the wave function at the TS geometry; and (c) the ability of substituents to stabilize the TS depends on its wave function. Thus, the effect of one phenyl group on the value of *R* in the Cope TS allows a second phenyl group that is placed at the same type of carbon as the first to stabilize the TS by more than the first Ph group does.

A corollary of this explanation of the cooperative Ph substituent effects on the energy of the Cope TS is that radical stabilizing substituents which are placed at different types of carbons in the Cope TS have opposite effects on *R*. Therefore, this substitution pattern should give rise to competitive, rather than cooperative substituent effects.¹¹¹ Indeed, the lowering of the Cope rearrangement barrier height, provided by the three phenyl substituents in 1,3,5-triphenyl-1,5-hexadiene, was both calculated^{111b} and experimentally found^{112c} to be less than the sum of the TS stabilizations provided by the pair of phenyl groups in 1,3-diphenyl-1,5-hexadiene^{112c} and the lone phenyl group in 2-phenyl-1,5-hexadiene.⁹⁵

A simple mathematical model¹¹³ quantitatively duplicated the cooperative and competitive phenyl substituents effects that Ken and I had calculated¹¹¹ and that Michael Dewar⁹⁵ and Bill Doering¹¹² had measured for the Cope rearrangement. The success of this mathematical model showed that cooperative and competitive substituent effects on a reaction will be observed if the amount of stabilization provided to the transition structure by the substituents depends on the bond lengths in the transition structure. Thus, this collaborative project with Ken, the initial goal of which was just to answer Bill Doering's question about whether the Cope TS is chameleonic or centauric, wound up providing a general insight into the features that can make substituent effects on a reaction either cooperative or competitive.

7. PYRAMIDALIZED ALKENES, DEHYDROCUBANES, AND OTHER DERIVATIVES OF CUBANE

One of the projects I began as a Harvard Assistant Professor was the synthesis and study of the members of the homologous series of 3,7-bridged bicyclo[3.3.0]oct-1(5)-enes (**33**). As the number of methylene groups in the bridge is reduced, the carbons forming the double bond are forced to pyramidalize.¹¹⁴ Therefore, we were able to systematically investigate the effect of pyramidalization on the reactivity and spectroscopy of the C=C double bonds in this series of alkenes.¹¹⁵



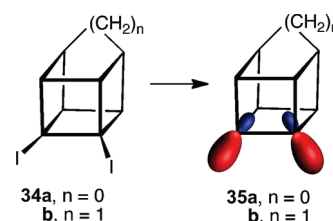
It took my research group nearly 25 years to complete our work in this area, and another 10 years passed before Thanasis Nicolaidis, one of my former graduate students, answered the final question about why we had been unable to isolate the $(\text{Ph}_3\text{P})_2\text{Pt}$ complex of the most strained member of this series, **33**, $n = 0$.¹¹⁶ My group's research on pyramidalized alkenes could not have been completed without the help of the senior investigators, Jon Clardy, Josef Michl, Michael Allen, and Leo Paquette, who collaborated with us on different aspects of this project.

Since a comprehensive review of my group's research in this area has been published,¹¹⁵ I will not describe here the many highlights of these collaborations. However, I will relate how my group's research on pyramidalized alkenes led me to predict to Phil Eaton that he would be successful if he attempted the synthesis of cubene from 1,2-diiodocubane. This prediction proved to be correct,¹¹⁷ and it was followed by subsequent collaborations between Phil and me on 1,4-dehydrocubane,¹¹⁸ cubyl cation,¹¹⁹ and octanitrocubane.^{120,121}

Dave Hrovat Confirms His Own Prediction. Although my first contact with Phil Eaton came through the competing efforts of his research group and mine to prepare [2.2.2]propellane by different routes,^{1,2} his successful synthesis of cubene¹¹⁷ and ours of homocubene¹²² were not the result of a competition. Calculations in my group by Dave Hrovat predicted, somewhat surprisingly, that cubene (**35a**) and homocubene (**35b**) both have an olefin strain energy comparable to that of **33**, $n = 1$,¹²³ a pyramidalized alkene that George Renzoni in my group had successfully prepared and trapped by reduction of the corresponding diiodide in solution.^{124a} Thus, Dave's calculations predicted that the same type of reaction could be used to generate **35a** and **35b** from, respectively, diiodides **34a** and **34b**.¹²³

In testing this prediction, Dave actually found it easier to prepare the bromiodide, rather than diiodide **34b**, as the precursor of homocubene (**35b**), and he was successful in generating **35b** from the bromiodide. In the meantime, I had informed Phil Eaton about Dave's prediction, in the hope that Phil would prepare **34a** and attempt to generate cubene (**35a**) from it. However, as it turned out, Phil was already working on

this synthesis of **35a**, and like Dave's synthesis of **35b**, Phil's synthesis of **35a** was successful.

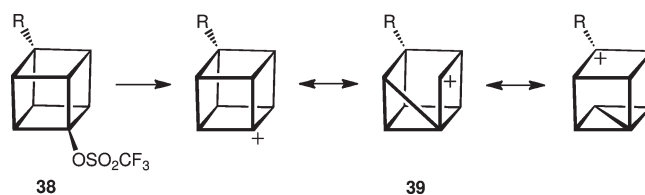


Phil's synthesis of **35a** and Dave's of **35b** were published as back-to-back Communications.^{117,122} The reactions of **35a** and **35b** were both found to be consistent with predictions^{123,125} that pyramidalized double bonds have very low-lying LUMOs. This prediction was also confirmed by the spectroscopy¹²⁶ and the chemistry¹²⁷ of members of the homologous series of pyramidalized alkenes **33**, $n = 0-3$.¹¹⁵

Phil Eaton Asks My Group To Perform Calculations on 1,4-Dehydrocubane and on Cubyl Cation. Following my contacting Phil to inform him of Dave's prediction that a synthesis of **35a** from **34a** would be successful,¹²³ Phil returned the favor and contacted me to suggest to me that my group perform calculations on 1,4-dehydrocubane (**37**). Phil had evidence that his group had successfully generated **37**,^{118c} and he was curious as to whether there is any significant bonding between C1 and C4 in the singlet state of this molecule.

The relative energies that we calculated for 1,2-, 1,3-, and 1,4-dehydrocubane were qualitatively in the order expected, with $E(\mathbf{37}) > E(\mathbf{36}) > E(\mathbf{35a})$.^{118b} However, a wholly unexpected finding was that **37** is calculated to have a singlet ground state, which is stabilized, relative to the triplet, by a strong bonding interaction between the radical centers at C1 and C4.^{118b} Josef Michl, whose research group had also succeeded in generating **37**,^{118a} made the same discovery. Josef's and Dave Hrovat's calculations both found that the interaction between C1 and C4 in **37** occurs through the bonds of the cube, rather than directly through space (Figure 12).^{118a,b}

I believe that the computational results on **37** convinced Phil that electronic structure calculations can provide experimentalists with useful information, and that is why Phil asked my group to undertake another project, calculations on cubyl cation (**39**). The Eaton and Moriarty research groups both found that cubyl cation (**39**) can be generated by solvolysis of cubyltriflate (**38**).^{119a,c} The bridgehead carbocation is formed at a rate that is ca. 10^{15} faster than that predicted on the basis of the strain energy of **39**.^{119d} Interestingly, placing π electron donor groups, such as $\text{R} = \text{Cl}$ and CH_3 , at C4 of **38** does not accelerate the rate of formation of **39**, as might have been expected, but actually retards it. Phil asked my group to perform calculations, in order try to explain both the rapid formation of **39** and the puzzling effect of electron-donating, C-4 substituents on the rate of this reaction.



Consistent with Phil's experimental rate studies, our MP2 calculations predicted formation of **39** from cubane requires

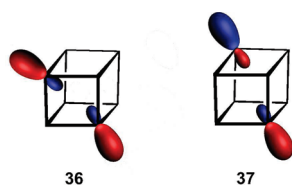


Figure 12. Schematic depiction of the HOMOs of 1,3- and 1,4-dehydrocubane. The out-of-phase combination of the AOs at C-1 and C-4 is the HOMO of 37 because the dominant interaction between these AOs is through the cubyl C–C bonds, rather than through space.^{119a,b}

7.3 kcal/mol less energy than formation of 1-norbornyl cation from norbornane.^{119b} Our calculations indicated that 39 is a nonclassical carbocation, which is stabilized by electron delocalization, as depicted in the resonance structures shown for 39. This type of stabilization has been suggested for other carbocations containing four-membered rings,¹²⁸ including homocubyl cation;^{128d} and the resonance structures for 39 explain why much more positive charge is calculated to be found at the α and γ carbons of 39 than at the β carbons.¹²⁹

The LUMO of 39, like the formally unoccupied AO at C-1, has cylindrical symmetry. Consequently, π electron-donor substituents, R, at C4 are incapable of stabilizing 39, because the π orbital of the donor substituent is orthogonal to the LUMO of 39.^{119b} Because the C-4 substituents studied, including R = CH₃, are all more electronegative than hydrogen, they destabilize the positive charge in 39 inductively, thus explaining the rate retarding effects of π electron-donating substituents at C-4, found by Eaton and by Moriarity.^{119a,c} Phil's subsequent experiments found, as our subsequent calculations had predicted, that σ electron-donating C-4 substituents, such as R = (CH₃)₃Si, do, in fact, accelerate the rate of solvolysis of 38.^{119d}

Bart Kahr Helps To Answer Two Questions about Octanitrocubane. Although Phil Eaton and I collaborated on several projects around 1990,^{117–119} Phil and I did not actually publish a paper together until 2001.¹²⁰ In the spring of 2000, Phil gave a seminar at UW, in which he described his successful synthesis of octanitrocubane (ONC).¹³⁰ After the seminar, I asked Phil how he thought the eight nitro groups in ONC pack themselves around the carbon cube and whether there is a large barrier to nitro group rotation. He suggested that my group should do calculations to find the answers to these two questions.

I was able to interest Bart Kahr, one of my colleagues at UW, in investigating the conformations and dynamics of the nitro groups in ONC. Bart was a former student of Kurt Mislow's and, hence, knew more about rotational dynamics and gearing than Phil, Dave Hrovat, and me combined. Therefore, Bart actually took the lead in this collaborative research project.

Dave did several different types of electronic structure calculations on ONC, and all of them predicted the barrier to nitro group rotation in ONC to be essentially nonexistent.¹²⁰ The understanding of the results of Dave's computational modeling was greatly assisted by a physical model, which Bart constructed from one of his son Aden's toy blocks (to represent the carbon skeleton) and 8 butterfly screws (to represent the nitro groups). Together, the two types of models revealed that the eight nitro groups in ONC undergo dynamical gearing. The nitro groups at C-1, C-3, C-5, and C-7 undergo simultaneous rotation in one direction, while those at C-2, C-4, C-6, and C-8 undergo simultaneous rotation in the opposite direction.¹²⁰

Although simultaneous rotation of the eight nitro groups in ONC is calculated to be nearly barrierless, our subsequent calculations on rotation of eight CX₃ groups (X = H, Cl, and Br), attached to the carbons of cubane, found that coupled rotation of all eight CX₃ groups has a much higher barrier than rotation of just one of them.¹³¹ The difference between the rotations of the substituents in ONC and in (C-CX₃)₈ resides in the symmetry of the rotors. In ONC NO₂ rotors, which have a 2-fold axis of symmetry, are attached to the cubyl carbons, which each have a 3-fold axis of symmetry. In contrast, in (C-CX₃)₈ both the CX₃ rotors and the cubyl carbons, to which they are attached, have 3-fold axes of symmetry. When a 2-fold rotor is attached to a stator with 3-fold symmetry, the barrier to rotation is very small; whereas, when the rotor and the stator both have 3-fold symmetry, the barrier to rotation is usually much larger.¹³²

8. EFFECTS OF GEMINAL FLUORINES AT C-2 OF 1,3-DIRADICALS

Based on the apparent ability of the σ^* orbital of a C–F bond to delocalize a pair of electrons in a C–H bond at an adjacent carbon,¹³³ I reasoned that a pair of C–F σ^* orbitals at C-2 of a 1,3-diradical should be able to delocalize a pair of electrons that occupy the in-phase combination of the 2p- π AOs at C-1 and C-3.¹³⁶ This conjecture was confirmed by the results of *ab initio* calculations.¹³⁷ The further conjecture that this type of stabilizing interaction would be enhanced by the presence of electron donating alkyl groups at C-1 and C-3 of 2,2-difluoropropane-1,3-diyl was also validated computationally.¹³⁷

I put these two facts to use in designing two experiments, each of which was performed with the help of collaborators. However, in order to understand the significance of the experiments—one on the stereomutation of optically active *cis*- and *trans*-1,1-difluoro-2-ethyl-3-methylcyclopropane¹³⁸ and the other on establishing the ground state of a derivative of 1,3-diphenyl-2,2-difluorocyclopentane-1,3-diyl¹³⁹—it is necessary to put each of these experiments into context by providing a little background.

Roald Hoffmann Makes a Prediction that Experimentalists Fail To Confirm. In one of the first papers Roald Hoffmann published after he joined the Faculty at Cornell, he reported his prediction, based on the results of Extended Hückel (EH) calculations, that cyclopropane should preferentially undergo conrotatory ring-opening and ring closure.¹⁴⁰

Such was Roald's post-Woodward–Hoffmann stature among organic chemists that many experimentalists rushed to test his prediction. However, none of the experimental tests found any indication that Roald's prediction was correct.¹⁴¹ Then Jerry Berson then did an elegant experiment that avoided the need for substituents on the cyclopropane ring, other than deuteria.

Jerry Berson's and John Baldwin's Elegant Experiments. Jerry measured the relative rates of *cis*–*trans* isomerization versus racemization of optically active *trans*-cyclopropane-1,2-*d*₂.¹⁴² Interpretation of these experiments required Jerry to guess the size of the secondary H/D isotope effect on which C–C bond preferentially breaks in the ring-opening of cyclopropane-1,2-*d*₂. With the seemingly reasonable guess of $k_H/k_D = 1.10$, Jerry's analysis of his experimental results found that coupled methylene rotation was favored over single methylene rotation by a factor of about 50, although Jerry's experiment did not allow him to conclude whether the coupled methylene rotation was con- or disrotatory. However, his finding that, "The double rotation mechanism predominates by a considerable factor,"¹⁴²

was at least consistent with Roald's prediction¹⁴⁰ that coupled (con)rotation should be preferred over rotation of a single methylene group in the stereomutation of cyclopropane.

For about 15 years, the case for coupled methylene rotation in the ring-opening of cyclopropane seemed settled. Then, in 1991, John Baldwin studied the stereomutation of cyclopropane-1,2,3-*d*₃, made optically active by the incorporation of ¹³C at one carbon.¹⁴³ In one sense, John's experiment was even more elegant than Jerry's because, with a deuterium at every carbon, John did not have to assume a size for the H/D KIE on which bond broke. From analysis of his results, John concluded, "the double rotation mechanism does *not* predominate by a substantial factor".¹⁴³ John attributed this difference between his results and Jerry's to Jerry's having made "some reasonable but nevertheless erroneous assumptions about kinetic isotope effects...".¹⁴³

My Group Collaborates with Ernest Davidson and Barry Carpenter in Performing Calculations on Cyclopropane Stereomutations. Motivated by the conflicting experimental results that had been obtained by Jerry¹⁴² and by John¹⁴³ and by John's rather cryptic explanation of the origin of this difference, Steve Getty, a postdoc in my research group, set about computing not only the (2/2)CASSCF/6-31G* potential energy surface (PES) for ring-opening of cyclopropane but also the H/D KIEs on ring-opening. Ernest Davidson was considering doing the same types of calculations, but he decided to collaborate with us instead.

Steve's findings¹⁴⁴ were as follows: (a) The difference in deuterium substitution in the cyclopropanes studied by Jerry and John could not reconcile the difference between their experimental results, (b) Jerry's assumption of $k_{\text{H}}/k_{\text{D}} = 1.10$ on which bond cleaved was in good agreement with the KIE of $k_{\text{H}}/k_{\text{D}} = 1.13$ that Steve computed, and (c) The PES that Steve computed predicted a preference of about a factor of 3 for double over single rotations.

In collaboration with the group of Fritz Schaefer, John Baldwin computed a very similar PES, but John came to the conclusion that the surface predicted close to equal amounts of double and single rotations.¹⁴⁵ How could two very similar PESs lead to two different conclusions?

In analyzing Steve's results, we had assumed that a molecule which undergoes ring-opening by con- or disrotation will undergo ring closure by the same type of pathway.¹⁴⁴ In contrast, John assumed that the mode by which a molecule undergoes ring-opening will have no effect on the mode by which it undergoes ring closure.¹⁴⁵ Since ring-opening by one mode of coupled rotation (e.g., conrotation), followed by ring closure by the opposite mode (e.g., disrotation) has the net effect of a single rotation, John's analysis predicted much more single rotation than our analysis did.

Which type of analysis is correct? The answer to this question depends on whether, in a diradical that passes over the TS for ring-opening by one mode of coupled rotation, the kinetic energy in that rotational mode becomes randomized before the diradical passes over one of the two possible TSs for ring closure by coupled rotation. If the energy does become randomized, then John's analysis, based on a statistical distribution of energy in the diradical, is correct.

However, my own physical intuition was that, after passing over the first TS, the diradical would have such a short lifetime that conservation of rotational angular momentum in the CH₂ groups would tend to favor ring closure by the same mode in which ring-opening had occurred. In other words, I was guessing

that there is a dynamical effect on cyclopropane ring closure, which is not captured by assuming a statistical distribution of energy in a diradical intermediate.

In order to test whether my assumption or John's was correct, I asked Barry Carpenter to collaborate with me on performing semiclassical trajectory calculations.¹⁴⁶ Dave Hrovat provided Barry with an analytical potential energy surface of reduced dimensionality, and on that surface conrotatory ring-opening was found to lead preferentially to conrotatory ring closure and disrotatory ring-opening to disrotatory ring closure.¹⁴⁷ A similar conclusion was reached by Chuck Doubleday and Bill Hase, who did direct dynamics on a full, 21-dimensional, potential energy surface.¹⁴⁸

The dynamics calculations provided support for Jerry Berson's experimental finding of a preference for coupled rotations in the stereomutation of cyclopropane-1,2-*d*₂.¹⁴² However, even if Jerry's experimental results are correct, they are, in a sense, incomplete, because Jerry's experiment could not address the question of whether the coupled rotation being observed was conrotation (as Roald had predicted),¹⁴⁰ disrotation, or a mixture of the two (as the dynamics calculations indicated).^{147,148}

A Computational Prediction Leads to a Collaboration with Bill Dolbier. I decided to use my group's computational findings about 2,2-difluoropropane-1,3-diyls^{137,149} to design an experiment that I thought would not only show that 1,1-difluorocyclopropane undergoes ring opening and ring closure by coupled rotations, but would also reveal that the preferred mode of coupling is disrotatory. I wanted to study the stereomutation of 1,1-difluoro-2-ethyl-3-methylcyclopropane (**40**), since both the *cis* and *trans* isomers could be made optically active. As shown in Figure 13, starting from the *cis* isomer (**40a**), disrotation leads to the *transoid,transoid* stereoisomer (**41a**) of the diradical intermediate, formed by ring-opening; whereas, starting from the *trans* isomer (**40b**), disrotation leads to diradical **41b**, in which one of the alkyl groups is *cisoid* in the diradical. Therefore, if, as predicted by our calculations,^{137,149} disrotatory ring-opening is preferred, the *cis* isomer (**40a**) should undergo ring-opening faster than the *trans* isomer (**40b**), whereas, if conrotatory ring-opening is favored, **40b** should undergo ring-opening faster than **40a**.

Our calculations predicted that this experiment should be successful in demonstrating that disrotatory ring-opening and ring closure are preferred in the stereomutations of both isomers of **40**. However, using calculations to predict the results of experiments is certainly not the same as actually doing the experiments. Therefore, I asked Scott Lewis, a graduate student in my research group, to prepare samples of optically active *cis*- and *trans*-1,1-difluoro-2-ethyl-3-methylcyclopropane (**40a** and **40b**). I also contacted Bill Dolbier, who had, many years before, measured the rates of interconversion of *cis*- and *trans*-1,1-difluoro-2,3-dimethylcyclopropane.¹⁵⁰ Bill agreed to let Scott come to his lab in Florida to measure the rates of racemization and *cis*-*trans* isomerization of optically active **40a** and **40b**.

Scott packed his clothes for the trip to Florida, and most unfortunately, in his suitcase he also packed his samples of the optically active **40a** and **40b**. When Scott arrived in Florida, he discovered that all of the glass tubes, in which the samples of optically active **40** had been stored, had broken, except for a small sample of optically active **40b**. Pyrolysis of this sample in Bill's lab did, in fact, show that racemization, by coupled rotation of the methylene groups, was much faster than isomerization to **40a**. However, the rate of racemization of **40a** still had to be measured

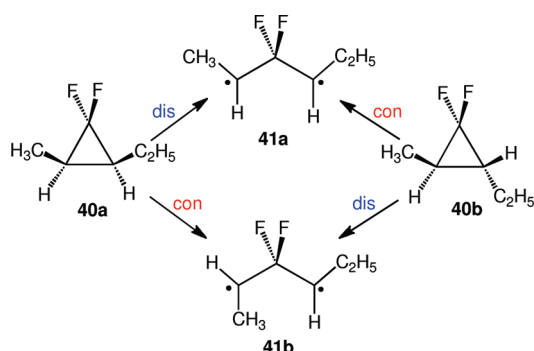


Figure 13. Stereochemistry of the diradicals (**41a** and **b**), formed by disrotatory and conrotatory ring-opening of the *cis* and *trans* isomers of 1,1-difluoro-2-ethyl-3-methylcyclopropane (**40a** and **b**).

before we could draw any conclusions about whether racemization of **40b** was occurring by con- or disrotation.

In choosing Bill Dolbier as my collaborator on this project, I was very fortunate for many reasons, but one of them was completely unanticipated by me. His name was Feng Tian. He was an extraordinarily talented graduate student in Bill's group, and Feng Tian was willing to complete work on Scott's project. Feng Tian not only repeated Scott's synthesis, he improved on it by using column chromatography at $-78\text{ }^{\circ}\text{C}$, rather than recrystallization, to effect the separation of the diastereomers that eventually led to the resolution of the enantiomers of **40a**.

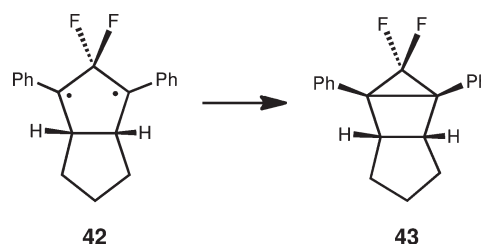
When Feng Tian carried out the kinetic studies on optically active **40a** and **40b**, he found that (a) racemization is much faster than *cis-trans* isomerization in both stereoisomers; and (b) racemization is considerably faster in **40a** than in **40b**.¹³⁸ Thus, we had experimental proof that, as predicted,^{136,137,149} (a) coupled rotation is much faster than single rotation in the ring-opening of both **40a** and **40b** and (b) the preferred mode of coupling is disrotation, rather than conrotation.¹³⁸

Another Prediction Leads to Collaborations with Waldemar Adam, Joggi Wirz, and Manabu Abe. Another computational prediction about the effect of geminal fluorines at C-2 of propane-1,3-diyls was that the fluorines would make the ground state of such diradicals a singlet.^{136,137} Many years before, Gerhard Closs and Steve Buchwalter had matrix isolated cyclopentane-1,3-diyl and showed that it had a triplet ground state.¹⁵¹ Subsequently, Dennis Dougherty, Waldemar Adam, Joggi Wirz, and their co-workers had studied derivatives of 1,3-diphenylcyclopentane-1,3-diyl and found that these diradicals too have triplet ground states.¹⁵²

Waldemar and Joggi agreed to undertake the experiments necessary to test my group's prediction that geminal fluorines at C2 should make the singlet the ground state of cyclopentane-1,3-diyl.¹⁵³ I sent Waldemar a sample, prepared by my graduate student, Heather Foster, of 2,2-difluoro-1,3-diphenylpropane-1,3-dione. This is the starting material for the synthesis of the azo precursor of diradical **42**, a derivative of 2,2-difluoro-1,3-diphenylcyclopentane-1,3-diyl.¹³⁹

Waldemar, Joggi, and their co-workers generated **42** by flash photolysis of its azo precursor. They found that **42** has a lifetime of only about 80 ns in solution.¹³⁹ However, they were able to isolate diradical **42** in a glass at low temperature and to measure the temperature dependence of its rate of ring closure to **43**. The value of $\log A = 12.8 \pm 0.4\text{ s}^{-1}$ that they measured is much larger

than the value of $\log A$ expected for intersystem crossing (ISC) in triplet **42**.¹⁵²



If **42** were a triplet diradical, ISC would be required for closure of **42** to **43**. Also, if **42** had a triplet ground state, it should be rapidly trapped by O_2 . Therefore, the insensitivity of **42** to the presence of O_2 ¹³⁹ provided further evidence that our calculations were correct in predicting singlet ground states for 2,2-difluoro-cyclopentane-1,3-diyls, such as **42**.¹⁵³

Thus, the experiments by Waldemar, Joggi, and their collaborators showed that **42** is apparently an example of a very rare species, a singlet diradical that lives long enough to be observed.¹³⁹

My invitation to Waldemar, to test experimentally our prediction that 2,2-difluoro-cyclopentane-1,3-diyls have singlet ground states,¹⁵³ was subsequently reciprocated. Waldemar and Joggi's collaborator, Dr. Manabu Abe, asked my group to perform calculations on how *para* substituents affect the singlet-triplet energy differences in 2,2-difluoro-1,3-diphenylcyclopentane-1,3-diyls¹⁵⁴ and on how different alkoxy groups alter ΔE_{ST} in 2,2-dialkoxy-1,3-diphenylcyclopentane-1,3-diyls.¹⁵⁵ There is no better evidence that a collaboration has been successful than when one's collaborators propose additional collaborative projects.

CONCLUSION

In this Perspective, I have attempted to describe the role that collaborations played in eight different areas of my research. The list in the Supporting Information of all my senior collaborators and the subjects on which we collaborated documents that I really have had to be very selective in choosing which collaborations to describe in this Perspective.

I am grateful to all of the chemists whose names appear on the list in the Supporting Information. Without them, not only would my publication list be much shorter, but doing research during the past 40 years would have been much less enjoyable. I have been blessed with collaborators who have not only been "better chemists than [I]" (as my former UW colleague was pleased to point out) but also people with whom I have thoroughly enjoyed working.

ASSOCIATED CONTENT

S Supporting Information. Publications of the author, based on collaborations, B3LYP/6-31G* energies of isodesmic reactions involving bicyclo[2.1.1]hex-2-ene, 2,3-dimethylenebicyclo[2.1.1]hexane, 1,2-dimethylenecyclopentane, cyclopentene, benzobicyclo[2.1.1]hex-2-ene, and benzocyclopentene, optimized geometries, energies, and vibrational frequencies for these molecules, and a brief description of a CI approach to

understanding symmetry breaking in TMM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

[†]“I get by with a little help from my friends.” From the chorus of “With a Little Help from My Friends” by John Lennon and Paul McCartney, *Sergeant Pepper's Lonely Heart's Club Band*, 1967.

ACKNOWLEDGMENT

I would like to thank all of my collaborators, but I want to single out three for special mention. Ernest Davidson not only taught me to appreciate the power of *ab initio* calculations but also how, at least occasionally, to think like a theoretical chemist. Jerry Berson inspired so many research projects in my group that I am convinced he has actually given me more projects to do than he has ever given to any one of his own graduate students or postdocs. Finally, for the past quarter of a century, Dave Hrovat has been my most indispensable collaborator. For example, for this manuscript, Dave conceived of and created the table of contents graphic; and he also did most of the work on the cover art. When Dave joined my group, he warned me that he was only going to stay for a year. Twenty-five years later he is still here, so I must assume that Dave has enjoyed collaborating with me as much as I have enjoyed collaborating with him. I am pleased to dedicate this Perspective to the memory of William von Eggers Doering, who passed away on January 3, 2011. Although I never published a paper with Bill, as this Perspective (especially section 6 on the Cope rearrangement) makes clear, he inspired a great deal of research in my group over the past 40 years. I greatly benefited from both his penetrating questions and his very high scientific standards. All of us who were fortunate enough to interact with Bill will miss him; he was an extraordinary chemist and a unique person. Finally, I would like to thank the National Science Foundation for supporting my research for the past 40 years and the Robert A. Welch Foundation for its support during the past 6 years through Grant B-0027. I also acknowledge the use of MacMolPlt¹⁵⁶ in creating the pictures of MOs in this Perspective and on the cover of this issue.

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- (21) In Heidelberg, not only did I learn a great deal of chemistry from Rolf and his group, but Rolf's wife Gertrud also introduced me to the pleasures of eating *spargel* (white asparagus), educated me about the importance of cream in German cuisine, and taught me that “no thank you” was not an acceptable answer to her offer of a second helping of anything that she had cooked (but especially her desserts). I was invited

to dinner at the Gleiter's home so frequently that I came to feel as though I was part of their family; and each of my stays in Heidelberg resulted in my gaining several pounds.

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(27) (a) Paquette, L. A.; Carmody, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 5841. (b) Alder, R. W.; Grimme, W. *Tetrahedron* **1981**, *37*, 1809. (c) Maier, G.; Wiegand, N. H.; Baum, S.; Wüllner, R.; Mayer, W.; Boese, R. *Chem. Ber* **1989**, *122*, 767.

(28) (a) Hafner, K.; Lindner, H. J.; Luo, W.; Meinhardt, K.-P.; Zink, T. *Pure Appl. Chem.* **1993**, *65*, 17. (b) Beno, B. R.; Fennen, J.; Houk, K. N.; Lindner, H. J.; Hafner, K. *J. Am. Chem. Soc.* **1998**, *120*, 10490.

(29) Professor Longuet-Higgins *might* have been the smartest person whom I have ever met, and he most definitely was the person who was least willing to suffer fools gladly. From the number of times he said to me in our weekly tutorial, "Weston, you are talking nonsense," I suspected that Professor Longuet-Higgins did not think that I had a bright future in theoretical chemistry. Many years later, I was reminded of both Professor Longuet-Higgins's blunt honesty as well as the low esteem in which he apparently held me by his reply to an email message I wrote to him, thanking him for helping me to learn electronic structure theory. I wrote that I was not sure that he would remember who I was, but he did; for he replied, "I remember you very well. You wrote that dreadful paper on the excited states of allene (Borden, W. T. *J. Chem. Phys.* **1966**, *45*, 2512), on which I refused to allow you to put my name."

(30) Lionel had gotten his Ph.D degree with H. C. Longuet-Higgins; I had the impression that Professor Longuet-Higgins had a great deal of respect for Lionel's intellect, which was not the way I would describe Longuet-Higgins' feelings about mine.²⁹ In addition, in 1962, when I was a Freshman and Lionel was an Instructor at Harvard, I had been invited to a party at his house by my roommate, who was doing undergraduate research with Lionel. I was very impressed that James Watson and Francis Crick were, purportedly, also attending Lionel's party. However, as an 18 year-old Freshman, I was even more impressed that many of the guests were gorgeous French women, all of whom seemed to be very good friends of Lionel's.

(31) Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1971**, *93*, 3081.

(32) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

(33) Doering, W. von E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825.

(34) In fact, I had given this as a problem on an exam on PPP calculations in the course on MO theory that I taught at Harvard. However, until Lionel showed interest in this result, it did not occur to me that it might actually be worth publishing. Subsequently, I have become a little more confident that a result, which I find interesting and which has not been published by someone else, may actually turn out to be worth my publishing.

(35) Borden, W. T. *Chem. Commun.* **1969**, 881.

(36) Borden, W. T.; Salem, L. *J. Am. Chem. Soc.* **1973**, *95*, 932.

(37) This was also the lesson that I learned from the papers that Roald Hoffmann published in the late 1960s and early 1970s. Although it was well-known that the Extended Hückel (EH) method that Roald used was quantitatively unreliable, Roald provided such convincing qualitative explanations of his EH results that it always seemed to me Roald's EH results must be correct. Perhaps the tremendous increase in the accuracy of electronic structure calculations during the past 40 years has had the undesirable consequence that computational chemists feel less obliged to provide the kind of detailed physical explanations of their results than Roald routinely furnished 40 years ago.

(38) Yarkony, D. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1974**, *96*, 3754.

(39) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 2906.

(40) Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8698.

(41) Borden, W. T. *J. Am. Chem. Soc.* **1976**, *98*, 2695.

(42) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(43) Davidson, E. R.; Borden, W. T. *J. Chem. Phys.* **1976**, *64*, 663.

(44) Probably I had picked up some of the skepticism that my mentor, H. C. Longuet-Higgins, had about the use of "machine experiments" as a tool for understanding chemistry. See, for example: Jordan, P. H. C.; Longuet-Higgins, H. C. *Mol. Phys.* **1962**, *5*, 121.

(45) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053.

(46) I have to confess that, when I wrote the first draft of the paper, I was trying to impress Ernest and to convince him that his organic chemist collaborator knew enough theoretical chemistry to be an (almost) equal partner in our collaboration. I have described elsewhere some of the benefits that our very different backgrounds had for our collaboration, and I have also described some of the difficulties that these differences caused. [Borden, W. T. *Mol. Phys.* (special issue in honor of Ernest Davidson), **2002**, *100*, 337.] For example, my drawing a hexagon with a circle in the middle of it was insufficient for Ernest to recognize that the molecule I had drawn as benzene. Ernest used to say, "If I do a calculation on benzene, I have to put in the hydrogens; so you should include them in your drawings too."

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

(48) Soon after Ernest's and my paper appeared, I noticed that in his own papers Jerry Berson had begun calling NBMOs that have no atoms in common "disjoint". Since I thought this was an elegant term, in a phone conversation I asked Jerry for the reference to the first paper in which this term had been used. In a surprised tone of voice he replied, "You used the term 'disjoint' in the first line of the abstract of your paper with Davidson." I had, in fact, inserted this word into the abstract, just before I submitted the manuscript, and then I had totally forgotten that I had done so. I am grateful to Jerry for reintroducing me to this term and for helping to popularize its use.

(49) Reviews of the calculation and measurement of ΔE_{ST} in non-Kekulé hydrocarbons have been published: (a) Borden, W. T. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 61–102. (b) Lineberger, W. C.; Borden, W. T. *Phys. Chem., Chem. Phys.* **2011**, in press.

(50) (a) Coulson, C. A.; Rushbrooke, G. S. *Proc. Camb. Phil. Soc.* **1940**, *36*, 193. (b) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

(51) Subsequently, using valence bond (VB) theory, Ovchinnikov showed that, in general the spin quantum number, S , of the ground state of any AH can be predicted from $S = (n^* - n)/2$, where n^* and n are, respectively, the number of starred and unstarred atoms (Ovchinnikov, A. A. *Theor. Chim. Acta.* **1978**, *47*, 297). The advantages and disadvantages of the MO and VB approaches for predicting the ground states of diradicals have been discussed.^{49a}

(52) (a) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968. (b) The name "dynamic spin polarization" for the effect of the non-uniform distribution of electron spin in square singlet CBD was coined by: Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223.

(53) (a) Craig, D. P. *Proc. R. Soc. London, Ser. A* **1950**, *202*, 498. (b) Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354. (c) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583. (d) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388. (e) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.

(54) (a) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930. (b) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4743. (c) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 270. (d) Filatov, M.; Shaik, S. *J. Phys. Chem. A* **1999**, *103*, 8885. (e) Rodriguez, E.; Reguero, M.; Caballol, R. *J. Phys. Chem. A* **2000**, *104*, 6253.

(55) Reviews: (a) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 573. (c) Hrovat, D. A.; Borden, W. T. *THEOCHEM* **1997**, *398*, 211. (d) Hrovat, D. A.; Borden, W. T. In *Modern Electronic Structure Theory and Applications in Organic Chemistry*; Davidson, E. R., Ed.; World Scientific Publishing Company: Singapore, 1997; pp 171–195.

(56) Following the publication of my paper with Lionel,³⁶ every few months I would get a phone call from Jerry. He invariably began, “Hi, Wes, this is Jerry. Say, have you ever thought about...”. These phone calls usually led to my group undertaking a new computational project on the subject of After Jerry retired and the phone calls from him stopped, I realized how much Jerry had contributed to my group’s research on diradicals. Even though we only wound up publishing one paper^{57a} and one review article^{55a} together, next to Ernest, Jerry was really my closest senior collaborator.

(57) (a) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6327.

(58) (a) Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256. (b) Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitat, A.; Lennartz, H. W. *Chem. Ber* **1991**, *124*, 2752.

(59) (a) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 763. (b) Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 5866. (c) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.

(60) Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(61) (a) Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Chem. Phys.* **1990**, *94*, 5483. (b) Anderson, K.; Malmqvist, P. A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(62) Review: Neumark, D. M. *Acc. Chem. Res.* **1993**, *26*, 33.

(63) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.

(64) (a) Dewar, M. J. S.; Merz, K. M., Jr. *J. Phys. Chem.* **1985**, *89*, 4739. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(65) Josef Michl deserves credit for inspiring this experiment. The week before the Gordon Conference, I had been giving some lectures at the University of Colorado, when Josef told me of his unsuccessful attempt to observe triplet COT by photodetaching an electron from COT^{•-} in solution.

(66) (a) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671. (b) Anet, F. A. L.; Boum, A. J. P.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576. (c) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

(67) (a) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456. (b) Three weeks after my conversation with Paul Wenthold, Carl sent me the first draft of a manuscript describing their experimental results. However, it took Carl and me many more weeks and many more drafts to compromise on a version of the manuscript that had a suitable balance between TS spectroscopy and the violation of Hund’s rule in *D_{8h}* COT that it revealed. Consequently, when Carl and I quickly agreed on a version of a manuscript that described our next collaboration,⁶⁸ we were both greatly relieved. But then relief turned to dismay when we discovered that Carl and I had each created very different types of artwork to submit to *Angew. Chem.* as possible art for the cover. Fortunately, Carl’s former post-doc, Takatoshi Ichino, sent us his own draft of cover art for our manuscript, and it was so good that Carl and I immediately discarded our drafts. Carl and I are both very grateful to Takatoshi, not only for his artwork, which did, in fact, appear on the cover of *Angew. Chem.*, but also for saving Carl and me from having to work out a painful and time-consuming compromise between our first drafts of possible artwork for the cover.

(68) In a more recent collaboration with Carl, on measuring the singlet–triplet energy separation in oxyallyl, the NIPES spectrum again had an unexpected feature. Very broad lines for all the peaks

corresponding to the singlet but not the triplet state were observed. (a) Ichino, T.; Villano, S. M.; Gianola, A. J.; Goebbert, D. J.; Velarde, L.; Sanov, A.; Blanksby, S. J.; Zhou, X.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8509. (b) Ichino, T.; Villano, S. M.; Gianola, A. J.; Goebbert, D. J.; Velarde, L.; Sanov, A.; Blanksby, S. J.; Zhou, X.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *J. Phys. Chem. A* **2011** in press. This provided the first clue that singlet oxyallyl is actually the transition structure for ring opening and ring closure of cyclopropanone. Despite singlet oxyallyl’s being a transition structure, we were able to measure not only its energy, relative to that of the triplet, but also the C=O stretching frequency in the singlet. This is another good example of how useful NIPES can be for doing transition state spectroscopy.⁶²

(69) Review: Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

(70) (a) Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 5349. For more recent calculations, see: (b) Castell, O.; García, V. M.; Bo, C.; Caballol, R. *J. Comput. Chem.* **1996**, *17*, 42. (c) Winkler, M. J. *J. Phys. Chem. A* **2008**, *112*, 8649.

(71) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378.

(72) (a) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443. (b) Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285.

(73) (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (b) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F., III. *J. Org. Chem.* **1996**, *61*, 7030. (c) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.

(74) (a) Zezsch, C.; Stuhl, F. *Chem. Phys. Lett.* **1975**, *33*, 375. (b) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1976**, *65*, 4323.

(75) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Chem. Phys.* **1999**, *111*, 5349.

(76) Calculation and measurement of ΔE_{ST} in nitrenes and in methylene, as well as in non-Kekulé hydrocarbons and COT, have been reviewed recently.^{49b}

(77) (a) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 8699. (b) McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 10857. (c) Wijeratne, N. R.; Da Fonte, M.; Ronemus, A.; Wyss, P. J.; Tahmassebi, D.; Wenthold, P. G. *J. Phys. Chem. A* **2009**, *113*, 9467.

(78) Reviews: (a) Borden, W. T.; Gritsan, N. P.; Hadad, C. M.; Karney, W. L.; Kemnitz, C. R.; M. S. Platz, M. S. *Acc. Chem. Res.* **2000**, *33*, 765. (b) Gritsan, N. P.; Platz, M. S.; Borden, W. T. In *Theoretical Methods in Photochemistry*; Kutateladze, A., Ed.; Taylor and Francis: Boca Raton, FL, 2005. See also: (c) Karney, W. L.; Borden, W. T. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. 3, pp 206–251.

(79) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347.

(80) (a) Gritsan, N. P.; Gudmundsdottir, A. D.; Tigelaar, D.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 3458. (b) Gritsan, N. P.; Tigelaar, D.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 4465.

(81) Gritsan, N. P.; Likhovorik, I.; Tsao, M.-L.; Çelebi, N.; Platz, M. S.; Karney, W. L.; Kemnitz, C. R.; Borden, W. T. *J. Am. Chem. Soc.* **2001**, *123*, 1425.

(82) Tsao, M.-L.; Gritsan, N.; James, T. R.; Platz, M. S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2003**, *125*, 9343.

(83) Moss, R. A.; Ho, G.; Liu, W. *J. Am. Chem. Soc.* **1992**, *114*, 959.

(84) Albu, T. V.; Lynch, B. J.; Truhlar, D. G.; Moss, R. A.; Goren, A. C.; Hrovat, D. A.; Borden, W. T. *J. Phys. Chem. A* **2002**, *106*, 5323.

(85) (a) Zuev, P.; Sheridan, R. S.; Albu, T. V.; Truhlar, D. H.; Hrovat, D. A.; Borden, W. T. *Science* **2003**, *299*, 867. (b) While Don and I were polishing the manuscript for this *Science* paper, on several successive mornings at 1:30 AM in Seattle I found myself talking on the phone with Don, debating the best word to use in a particular sentence. Since 1:30 AM in Seattle is 3:30 AM in Minneapolis, I concluded that one reason for Don’s incredible productivity is that he apparently needs very little or no sleep.

(86) The first recognition of the importance of a very narrow barrier in facilitating tunneling by carbon appears to have been in: Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

- (87) (a) Shelton, G. R.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2007**, *129*, 164. (b) Shelton, G. R.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2007**, *129*, 16115. (c) Datta, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2008**, *130*, 2726. (d) Wu, A.; Mader, E. A.; Datta, A.; Hrovat, D. A.; Borden, W. T.; Mayer, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 11985.
- (88) I owe the idea for this project to a previous collaboration with Karen Goldberg, a former colleague at UW, on the differences between the mechanisms for reductive elimination of methane from Pt(II) and Pt(IV) complexes. (a) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456. (b) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *Organometallics* **2001**, *20*, 2669.
- (89) This project is one of several collaborations I have had with Jim Mayer, another former colleague at UW. I was very pleased that, even after I left UW, Jim continued to ask my group to do calculations to help interpret his group's experimental findings.
- (90) (a) Datta, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2008**, *130*, 6684. (b) Zhang, X.; Datta, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2009**, *131*, 16002. (c) Zhang, X.; Datta, A.; Hrovat, D. A.; Borden, W. T. *Org. Biomol. Chem.* **2011**, in press. (d) Zhang, X.; Hrovat, D. A.; Borden, W. T. *Org. Lett.* **2010**, *12*, 2798.
- (91) Sander, W. Unpublished results, communicated privately.
- (92) Gonzalez-James, O. M.; Zhang, X.; Datta, A.; Hrovat, D. A.; Borden, W. T.; Singleton, D. A. *J. Am. Chem. Soc.* **2010**, *132*, 12648.
- (93) In discussing the role of tunneling in the 1,5-hydrogen shift in *cis*-1,3-pentadiene, Bill Doering wrote, "The tunneling effect [in this reaction] is likely, in the opinion of some, to remain relegated to the virtual world of calculation." (Doering, W.; Von, E.; Zhao, X. *J. Am. Chem. Soc.* **2006**, *128*, 9080). It certainly matters less to experimentalists than to theoretical chemists whether one type of calculation (e.g., CVT + SCT) fits experimental data better than another type of calculation (e.g., CVT). Since I think that Bill made a valid point in this intentionally provocative passage, all of my group's calculations on tunneling have sought to predict phenomena (e.g., curved Arrhenius plots,^{87a,b} rapid reactions at cryogenic temperatures,^{91a,d} and anomalous KIEs^{87c,d,90b}), which, if observed experimentally, would, by themselves, indicate the importance of tunneling in a reaction.
- (94) Doering, W. v. E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10112.
- (95) (a) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1973**, *95*, 290. (b) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417.
- (96) (a) Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*; Prentice-Hall: Englewood Cliffs, NJ, 1975; pp 129–132. (b) Woodward and Hoffmann used a very similar orbital correlation diagram to show that in the Cope TS the interaction between C-2 and C-5 of 1,5-pentadiene is antibonding.⁵
- (97) While living in Okazaki, I contracted an acute case of Nipponophilia, which caused me to attempt to learn to speak Japanese, to study *ikebana* (flower arranging) and *chado* (tea ceremony), and to compulsively return to Japan whenever I could. I continue to suffer from this now-chronic affliction.
- (98) Borden, W. T. In *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C., Frenking, G., Kim, K., Scuseria, G., Eds; Elsevier, Oxford, 2005; pp 859–872.
- (99) Osamura, Y.; Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 3362.
- (100) Morokuma, K.; Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 4474.
- (101) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.
- (102) We made this claim in a review article titled, "Synchronicity in Multibond Reactions": Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213. Thanks to Ken, this review ended with an extended quote from the song "Synchronicity" by Sting. We claimed the existence of this song showed that the topic of synchronicity is of interest to more than just a small group of computational chemists. Members of the Houk group had T-shirts made with the words to the song "Synchronicity" emblazoned upon them.
- (103) See, for example: (a) Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* **1987**, *109*, 5893. (b) Dewar, M. J. S.; Jie, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1451.
- (104) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756.
- (105) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.
- (106) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.
- (107) Kozlowski, P. M.; Davidson, E. R. *J. Chem. Phys.* **1994**, *100*, 3672.
- (108) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.
- (109) Ken Houk and I believe that Bill Doering did not really trust either of us to work on this problem and/or to obtain the correct answer. That is why we think Bill asked us each separately to do calculations on the effect of substituents on the Cope TS, without telling us that he had also asked the other. When Ken and I discovered at a Reaction Mechanisms Conference that Bill had gotten both of us to start work on this project, we decided to collaborate on completing it.
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