mixture of products, but no hydrogen evolution was detected.

Experimental Section

General. W-2 Raney nickel was prepared according to ref 31. Raney nickel (ready for use in water) and hypophosphorous acid (50% wt in water) were purchased from Fluka. THF was distilled from sodium benzophenone ketyl. Other reagents were obtained commercially and used without further purification. Infrared (IR) spectra were measured on a Perkin-Elmer PE 682 spectrophotometer; ^1H NMR spectra were measured in $CDCl_3$ at 90 MHz on a Varian EM 390 instrument; chemical shifts are reported in δ units using Me_4Si as internal standard. Capillary gas chromatography (GLC) was performed on Carlo Erba HRGC 5300 Mega series apparatus using the following columns: OV1 (0.1-μm diameter, 15-m length); Carbowax 20M (0.4 μm, 20 m); and SE 52 (0.1 μm, 25 m).

The $Et_3NH^+H_2PO_2^-\cdot nH_2O$ Reagent. H_3PO_2 (54.5 mL, 66 g (50% wt in water from Fluka) was placed in a flask immersed in an ice bath; then 69.7 mL (50.6 g) of Et_3N was slowly added and the mixture shaken after each addition until a homogeneous solution was obtained, whereupon water was removed by distillation in two ways: (a) At 40–50 °C under 15 mmHg after 30 min, about 17 g of H_2O was removed, leaving 96.3 g of liquid $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ in the flask; and after 1 h, 21 g of water was removed and 91 g of $Et_3NH^+H_2PO_2^-\cdot H_2O$ remained. (b) At 65 °C under 0.2 mmHg for 3 h, not only water but also Et_3N was removed (about 42 g), leaving 69 g of dry $Et_3NH^+H_2PO_2^-$ reagent.

A. Reduction of Nitriles to Aldehydes by the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney Nickel System. Moist Raney nickel (5 g) (Fluka) was placed into a flask containing 10 mL of THF and 5 mL of EtOH, 95%, at 0 °C, then 4 mL of the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ reagent was added all at once, and immediately an evolution of hydrogen was observed. The reaction was exothermic, and the temperature rose to 8–10 °C. When the temperature began to fall, 0.01 mol of nitrile was added, and the solution was kept at 2–3 °C for 2 h. In the cases in which conversion was not complete (Table II, experiments 10–12), the solution was cooled to 0 °C, 1 g of Raney nickel was added, and then 1 mL of $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ was added. The addition of reagent can be repeated until conversion is complete (determined by GLC and compared with authentic samples). The solution was then stirred at 2–3 °C for 4–5 h. Finally, the products were extracted three times with 20 mL of ether, washed three times with 25 mL of water, and dried over $MgSO_4$. After solvent evaporation, the aldehydes were found from IR and NMR spectra to be sufficiently pure, and after the products were chromatographed over a short column of silica gel with ether/hexane as eluant, their boiling points were in agreement with those found in the literature (Table II).

B. Reduction of Ketones to Alcohols by the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O/RuCl_2(PPh_3)_3$ System. The ketone (0.006 mol) and 4 mL of the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ were mixed in a flask under a nitrogen atmosphere at room temperature and stirred until a homogeneous solution was obtained. Then 6×10^{-5} mol of $RuCl_2(PPh_3)_3$ was added to the solution, and immediately hydrogen was evolved (after 2 h, if 70% conversion was not achieved, determined by GLC, another 0.5 mL of $Et_3N^+H_2PO_2^-\cdot 1.5H_2O$ and 0.020 g of $RuCl_2(PPh_3)_3$ were added). The solution was stirred overnight, then 20 mL of water was added, and the products were extracted three times with 20 mL of ether or CH_2Cl_2. Finally the solution was washed with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was analyzed by IR and ^1H NMR spectra and GLC by comparison with authentic samples (Table III).

Registry No. $Et_3NH^+H_2PO_2^-$, 117872-98-7; $RuCl_2(PPh_3)_3$, 15529-49-4; Raney nickel, 7440-02-0; nitrobenzene, 98-95-3; cyclohexanone oxime, 100-64-1; 1-nitro-1-cyclohexene, 2562-37-0; *p*-chloroacetophenone, 99-91-2; ethyl *trans*-3-(*p*-chlorophenyl)-2-propenoate, 24393-52-0; benzaldehyde, 100-52-7; 2-furonitrile, 617-90-3; 2-thiophenecarbonitrile, 1003-31-2; benzonitrile, 100-47-0; phenylacetonitrile, 140-29-4; valeronitrile, 110-59-8; 5-chlorovaleronitrile, 6280-87-1; aniline, 62-53-3; cyclohexanone, 108-94-1; ethyl 3-(*p*-chlorophenyl)propanoate, 7116-36-1; benzyl alcohol, 100-51-6; furfural, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; phenylacetaldehyde, 122-78-1; valeraldehyde, 110-62-3; 5-chlorovaleraldehyde, 20074-80-0; acetophenone, 98-86-2; propiophenone, 93-55-0; *p*-methylacetophenone, 122-00-9; *p*-nitroacetophenone, 100-19-6; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; camphor, 76-22-2; 2-octanone, 111-13-7; ethyl acetoacetate, 141-97-9; 6-methyl-5-hepten-2-one, 110-93-0; 1-phenylethanol, 98-85-1; 1-phenylpropanol, 93-54-9; 1-(*p*-tolyl)ethanol, 536-50-5; 1-(*p*-nitrophenyl)ethanol, 6531-13-1; 1-(*p*-chlorophenyl)ethanol, 3391-10-4; cyclohexanol, 108-93-0; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *cis*-2-methylcyclohexanol, 7443-70-1; borneol, 507-70-0; 2-octanol, 123-96-6; ethyl 3-hydroxybutyrate, 5405-41-4; 6-methyl-5-hepten-2-ol, 1569-60-4.

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(31) Mozingo, R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 181.

Design of Concerted Multicenter Reactions

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The transition state of a one-step "allowed" reaction is stabilized by charge alternation at the four union sites. In order to promote such bizwitterionic character, the "observer" σ-bonds must be weak and, hence, polarizable. It is argued that the fine balance between a one-step "allowed" and a two-step mechanism involving diradical intermediates is determined by the σ-bonds of reacting polyenes, and specific illustrations, using data drawn from the literature, are presented. The message for the experimentalist is as follows: To enforce a concerted "allowed" reaction, make the "observer" bonds weak by replacing first row atoms by their heavier congeners, e.g., C by Si, etc.

The pioneer work of Hueckel[1] and the pivotal contribution of Heilbronner regarding the Hueckel–Moebius distinction[2] provide an answer to the following question: Given a cyclic array of *m* orbitals containing *n* electrons, what is the dependence of the stabilization energy on the number of orbital phase changes, odd versus even, one encounters in travelling around the ring? The answer is

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(1) (a) Hueckel, E. *Z. Physik.* **1930**, *60*, 423. (b) Heilbronner, E.; Bock, H. *Das HMO-Modell und Seine Anwendung*; Verlag Chemie, Gmbh: Weinheim, 1968.

(2) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923.

0022-3263/89/1954-0953$01.50/0

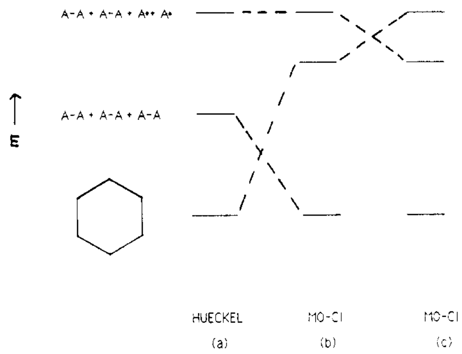


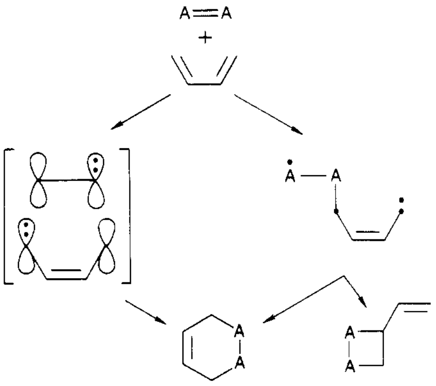
Figure 1. Illustration of the Hueckel prediction of maximal aggregation (A_6 hexagon is lowest energy form) and the prediction of minimal aggregation at a higher level of theory. Depending on how favorable correlated electron motion is, the diradical species (2 A–A + A$^\bullet$ + A$^\bullet$) may lie either above or below the "aromatic" A_6 complex. A is a one-electron/one-orbital atom.

that even number of phase changes produce the more stable system when $n = 4N + 2$ while odd phase changes produce the more stable system when $n = 4N$, where N is an integer. Systems that meet these conditions are called "aromatic". The implications of these rules for chemical reactions were independently recognized by many investigators[3] but always within the context of Hueckel MO (HMO) theory insofar as interpretation was concerned. By this statement, we mean that even if the theoretical formalism used for computing reaction pathways or for analyzing the origin of stereoselection was SCFMO, SCFMO–CI, MCSCF, VB, or some other theory higher than HMO, the final argument was based on Hueckel theory and standard notions of overlap bonding, at least in the vast majority of cases. So, it has always been assumed that high-level theory paints the same picture of multicenter reaction stereoselection as HMO theory. In this paper, we will attack this position.

The most thorough interpretation of the stereochemistry of multicenter reactions was presented in the form of the so-called Woodward–Hoffmann rules.[4] It was argued that, if a multicenter reaction were to occur in a concerted, one-step fashion, its stereochemical outcome could be predicted by reference to the rules stated above. Of course, this left unanswered the key question: When is a multicenter reaction expected to be concerted? Hueckel theory gives a very direct answer: A cyclic "aromatic" complex has much lower energy than the corresponding diradical, which is expected to be formed in the course of a stepwise reaction, as the A_6 example of Figure 1a illustrates.[5] This led people, including this author, to surmise that an "allowed" path is intrinsically favored over a stepwise path.

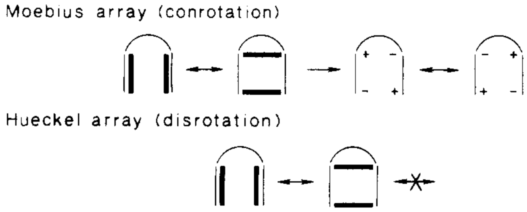
About 10 years ago, we abandoned one-electron theory as a qualitative tool for understanding chemical bonding, and we sought to develop a new theory based on a fusion of MO and VB concepts and without making assumptions that would ultimately restrict its applicability. The result has been the generation of new ideas, which are now founded on many-electron theory and which can be tested by high-level calculations.[6] What is important to stress is that the oft misused adjective "new" denotes not some more mathematically satisfying formulation of the problem but a view of molecular electronic structure that is very different from that offered by one-electron theory. Since the key concepts and their theoretical basis have been presented elsewhere, we summarize only the results pertinent to this paper:

Scheme I



(a) In a system made up of strong overlap binding atoms,[6g] typically H, C, N, O, and F, electron pair bonds due to "spin pairing" repel each other (overlap repulsion) even if they are part of a cyclic array with $4N + 2$ electrons ("aromatic" or "allowed" system). As a result, "aromatic" complexes are transition states rather than stable global minima.[6b–d,7]

(b) The difference between an "aromatic" and an "antiaromatic" complex lies in the fact that correlated electron motion is permitted by symmetry in the former but not in the latter.[6b–e] In resonance theoretic terms, this correlated electron motion is brought about by the interaction of Kekule and charge alternant structures as indicated below by reference to the thermal 1,3-butadiene electrocyclization to form cyclobutene. The charge alternant structure has each fragment in a zwitterionic form with the two interacting in a way that engenders Coulomb attraction. It is exactly this overlap-independent Coulomb attraction that stabilizes an "aromatic" cyclic system relative to a diradical species. We note parenthetically that yet another form of correlated electron motion, called relay electron transfer (RET), operates in the "aromatic" but not the "antiaromatic" complex, by symmetry.[6b,e]



(c) Systems made up of bonds other than the σ-bonds of typical hydrocarbons support correlated electron motion. This correlated electron motion becomes increasingly important as the constituent atoms become weaker overlap

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[3] Review: Epiotis, N. D.; Shaik, S.; Zander, W. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2.

[4] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1971.

[5] (a) Coulson, C. A.; Streitwieser, A. S., Jr. *Dictionary of Pi Electron Calculations*; Freeman: San Francisco, 1965. (b) Streitwieser, A. S., Jr.; Brauman, J. I. *Supplemental Tables of Molecular Orbital Calculations*; Pergamon Press: Oxford, 1965.

[6] (a) Epiotis, N. D. *Lect. Notes Chem.* **1982**, *29*, 1. (b) Epiotis, N. D. *Lect. Notes Chem.* **1983**, *34*, 1. (c) Epiotis, N. D. *Pure Appl. Chem.* **1983**, *55*, 229. (d) Epiotis, N. D. *Nouv. J. Chim.* **1983**, *8*, 11. (e) Epiotis, N. D. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinajstic, N., Eds.; Elsevier: Amsterdam, 1988. (f) Epiotis, N. D.; Larson, J. R.; Eaton, H. *Croatica Chem. Acta* **1984**, *57*, 1031. (g) Epiotis, N. D. *J. Mol. Struct. (THEOCHEM)* **1987**, *153*, 1. (h) Epiotis, N. D. *Pure Appl. Chem.* **1988**, *60*, 157. (i) Epiotis, N. D. *New J. Chem.* **1988**, *12*, 231 and 257. (j) Epiotis, N. D. *Top. Curr. Chem.*, in press.

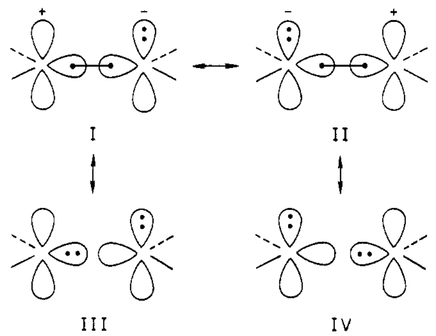
[7] Shaik, S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363.

binders[6b,g] and, hence, more polarizable.

(d) A combination of results (b) and (c) coupled with the recognition that carbon has low polarizability leads to the conclusion that concerted will be competitive with nonconcerted reaction paths.

In summary, our viewpoint differs from the Hueckel viewpoint in a fundamental way: The natural state of a system of bonds due to overlap is the one in which aggregation is minimized. Deviation from this state of affairs is attributed to strong, symmetry-allowed correlated electron motion. This is diametrically opposite to the predictions of Hueckel theory, which says that an "aromatic" complex of an odd number of bonds has much lower energy than the bonds at infinite distance apart. Our argument is illustrated by reference to A_6 in Figure 1.

We can now use these ideas to spell out a recipe for concerted multicenter reactions. We illustrate our approach by reference to the Diels–Alder reaction of the olefin A=A and 1,3-butadiene shown in Scheme I. A one-step reaction is expected to lead to stereospecific 4 + 2 adduct (cyclohexene derivative) while a two-step reaction is expected to produce both a 4 + 2 and a 2 + 2 adduct (vinylcyclobutane derivative), each nonstereospecifically to the extent dictated by the ratio of the rate constants for rotation about a single bond and ring closure of the diradical intermediate. In each molecule, each reacting π-bond is being "observed" by a corresponding underlying σ-bond. The condition for a one-step reaction is that there is strong charge alternation at the pericyclic complex. To promote such charge alternation, we require that the observer σ-system is polarizable so that it can respond to charge separation in the overlying π-system. An observer σ-bond is said to be polarizable if two conditions are met: (a) the two atoms defining the bond have similar electronegativities and (b) the two atoms are weak overlap binders and the bond weak in an overlap sense. If these conditions are met, resonance stabilization of the type shown below becomes significant. Note how charge transfer in the π-system in, e.g., I, is annihilated by reverse charge transfer in the σ-system in III, which, however, demands the destruction of the σ-bond formed via spin-pairing. As a result, the energy separation of I and III decreases, and the stabilization due to their interaction increases as the A–A σ-bond becomes weaker. In short, to stabilize a π-zwitterion, we must have a weak observer σ-bond. Needless to say, the rigorous σ–π distinction within each reactant is lost as they proceed to the transition state, but this does not affect the tendency of each reaction center to attain a neutral, "carbenic" (see III and IV) configuration.



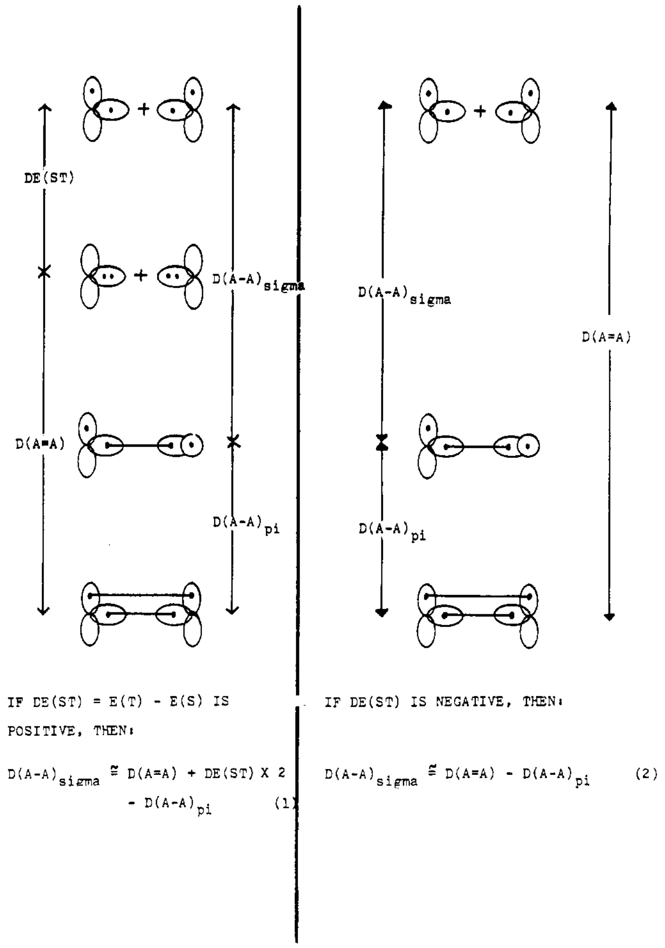


Figure 2. Definitions of the various thermochemical quantities that enter in the approximate determination of the strength of the σ-bond of A=A. Note that the way of computing $D(A–A)_\sigma$ depends on whether DE(ST) is positive or negative.

Table I. Thermochemical Data for A=A (in kcal/mol)

	$H_2C=CH_2$	$F_2C=CF_2$	$H_2Si=SiH_2$
$D(A=A)^a$	172	69	51
$D(A–A)_\pi{}^b$	59	52	22
$DE(ST)^c$	-10	+51	+18
$D(A–A)_\sigma$	113	119	65

[a] $D(A=A)$ data from Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115 (A = CH_2, CF_2) and by combining the data reported in: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246, and in Olbrich, G.; Potzinger, P.; Reimann, B.; Walsh, R. *Organometallics* **1984**, *3*, 1267 (A = SiH_2). [b] $D(A–A)_\pi$ data from Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502 (A = CH_2). Wu, E.-C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112 (A = CF_2). Olbrich, G., et al. in *a* above (A = SiH_2). [c] DE(ST) data from Borden, W. T.; Davidson, E. R. *Ann. Rev. Phys. Chem.* **1979**, *30*, 125 (A = CH_2). Feller, D.; Borden, W. T.; Davidson, E. R. *Chem. Phys. Lett.* **1980**, *71*, 22 (A = CF_2). Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537 (A = SiH_2).

We can determine approximately the σ-bond dissociation energy of A=A, $D(A–A)_\sigma$, by using available thermochemical data as indicated in Figure 2. By using eq 1 or 2 of Figure 2, depending on whether A is ground state singlet or triplet, we have determined the σ-bond dissociation energies of the three olefins of Table I. We have deliberately chosen A to be CF_2, CH_2, and SiH_2 so as to have a wide spectrum of $D(A–A)_\sigma$ values. If our analysis is correct, we expect that going from ethylene (ET) to tetrafluoroethylene (TFE) will tend to cause the Diels–Alder reaction to become a two-step reaction while going from ET to disilene (DSI) will increase the likelihood of a concerted reaction. Indeed, it was well known[8a] even

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(8) (a) Coffman, D. D.; Barrick, P. L.; Cramer, R. D.; Raasch, M. S. *J. Am. Chem. Soc.* **1949**, *71*, 7. (b) Montgomery, L. K.; Schueller, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1964**, *86*, 622. (c) Bartlett, P. D.; Montgomery, L. K. *J. Am. Chem. Soc.* **1964**, *86*, 628. (d) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1970**, *24*, 473. (e) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; pp 179–189.

before the classic work of Bartlett[8b–d] that fluoroalkenes display aberrant behavior as dienophiles, giving rise to mixtures of cyclohexene and vinylcyclobutane whereas ET yields nearly 100% cyclohexene. The observation of mixtures of 2 + 2 and 4 + 2 adducts is indicative of a stepwise mechanism via a diradical intermediate. On the other hand, it has been recently found that derivatives of DSI give only 4 + 2 adducts.[9] The significance of this last observation is the following: It has been assumed that intervention of a diradical is reasonable when substituents that stabilize a radical center are present. The diradical resulting from both TFE and DSI addition to butadiene will have one pyramidalized radical center because it is well known that CF_3 and SiH_3 are pyramidal.[10] If one were to view this pyramidalization as a manifestation of some σ radical stabilization mechanism, he could conclude that both TFE and DSI will add to butadiene in a stepwise fashion. But, this is not so. Furthermore, if what really promoted the stepwise mechanism were *radical-site stabilization*, then one could expect tetracyanoethylene (TCNE) to have a much greater chance of favoring a stepwise mechanism than TFE simply because cyano is known to be a far more efficient radical stabilizer than fluoro.[11] In fact, it is questionable whether π-donors such as F and OR confer any stability to a radical center through the action of their lone pairs.[12]

Let us next focus our attention on the ET–TFE comparison. The stronger C–C σ-bond of the latter compared to the former molecule is due to rehybridization caused by replacement of H by the more electronegative F, and this is exclusively a σ-effect. The bond diagrammatic representation (see Appendix) of $X_2C{=}CX_2$ (viewed as "C_2 plus X_4" and assuming X to be a univalent ligand devoid of any lone pairs) is shown in Figure 3. As the electronegativity of X increases, the contribution of the Θ_1 bond diagram increases, the carbon orbital used to make the C–C σ-bond becomes richer in C2s while the carbon orbital used to make a C–X bond becomes richer in C2p character. As a result, the C–C bond gets stronger and the XCX bond angle decreases. Experimentally, it is found that the C=C bond distance in TFE is shorter than the same one in ET[13] *despite the fact that the π-bond is weaker in the former*[14] and the XCX angle is much smaller when X = F than when X = H,[13] according to our expectations. The MOVB explanation of the effect of ligand electronegativity on geometry in $X_2C{=}CX_2$ is identical with the one given for other molecules, like H_2O, HC≡CH, etc.[6f]

The analysis presented above suggests that there exist experimental quantities that are direct indices of the ability of $X_2C{=}CX_2$ to react with some other polyene in a concerted "allowed" fashion. These are as follows: (a) The C=C bond length, $r_{C=C}$. (b) The vertical excitation energy for arriving at the $\pi\pi^*$ triplet state, E(T). This is so because the energy of this state depends on the C=C bond length. (c) The energy separation of the purely covalent $\pi\pi^*$ triplet and the purely zwitterionic $\pi\pi^*$ singlet, DE(ST). This is so because the underlying σ C–C bond can appreciably stabilize the overlying π-system only if the latter has zwitterionic character. Our prediction is that, *as $r_{C=C}$ increases and E(T) and DE(ST) decrease, the molecule $X_2C{=}CX_2$ will be increasingly capable of supporting charge alternation at the pericyclic transition state of a multicenter reaction with another polyene.* As a result, the concerted will become increasingly favorable relative to the stepwise path.

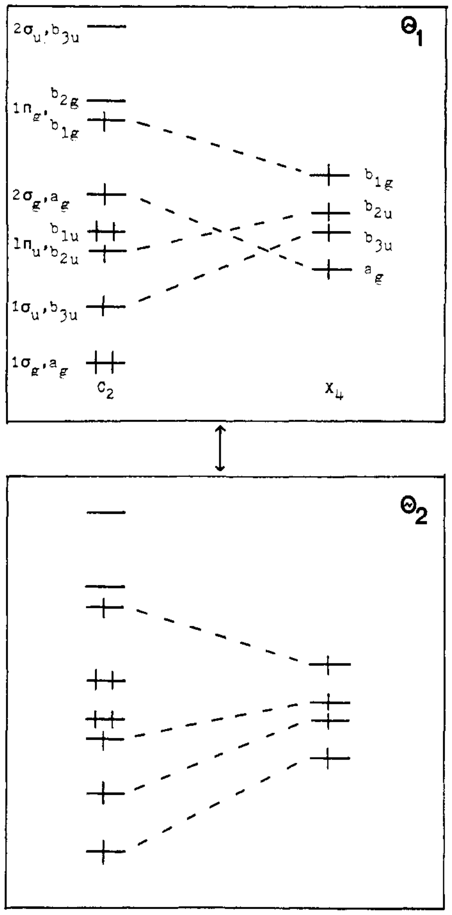

Figure 3. Bond diagrammatic representation of $X_2C{=}CX_2$ viewed as "C_2 plus X_4". The C_2 orbitals are classified according to D_h symmetry of the isolated diatomic (for reference) and according to the molecule D_{2h} symmetry. One key aspect is that the $1\sigma_g$ MO has principal C2s AO character while the $2\sigma_g$ MO has dominant 2p (σ) AO character.

The role of the observer σ-bonds in stabilizing a pericyclic transition state complex may well be illustrated by the results of Piers and Maxwell[15] who discovered that the rearrangement of the vinylcyclopropane derivative shown below is directed by X in the following way: When X = OMe, the generation of a reactive AO over the σ C–O bond is avoided while when X = $SiMe_3$, the rearrangement occurs over an underlying C–Si bond. We suggest that this preference may very well be the consequence of the greater polarizability of the observer C–Si compared to the C–O bond.

Is there any evidence that charge alternation at the transition state is important in multicenter reactions? It has been known for a long time that unsymmetrical dienophiles, such as $H_2C{=}C(CN)_2$, react much faster than isomeric symmetrical dienophiles, such as (NC)HC=CH(CN),[16] with dienes even though the latter are better π-acceptors than the former. In fact, recent work at

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[9] (a) Sakurai, H.; Nakadaira, Y.; Kobayashi, T. *J. Am. Chem. Soc.* **1979**, *101*, 487. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[10] For pertinent data and MO interpretation, see: Cherry, W.; Epiotis, N. D.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167.

[11] Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469.

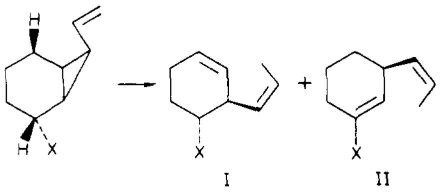
[12] Beckwith, A.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893.

[13] Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. In Landolt-Börnstein Numerical Data and Function Relationships in Science and Technology, Vol. 7, New Series, *Structure Data on Free Polyatomic Molecules*; Hellwege, K. H., Ed.; Springer-Verlag: West Berlin, 1976.

[14] Wu, E.-C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112.

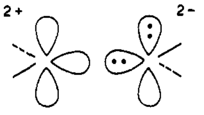
[15] Piers, E.; Maxwell, A. R. *Can. J. Chem.* **1984**, *62*, 2392.

[16] Huisgen, R.; Grashey, R.; Sauer, J. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: New York, 1964.



if X = MeO, I is exclusive.
if X = Me_3Si, II is major.

Professor Sauer's laboratories indicates that even a monosubstituted unsymmetrical dienophile like $XHC{=}CH_2$ can react faster than the superior π-donor $XHC{=}CHX$ ($X = \pi$ donor substituent) with a diene in a reverse electron demand Diels–Alder reaction.[17] Charge alternation is favored by unsymmetrical reactants. The faster reactions of unsymmetrical dienophiles with dienes are predicted to be one-step asynchronous (by symmetry) reactions. Is there any evidence that a σ C–C bond can stabilize an overlying zwitterionic π-system? The answer is to be found in ab initio calculations of the zwitterionic $\pi\pi^*$ excited state of ethylene carried out by Davidson and McMurchie.[18] They report that σ–π correlation, which effectively accentuates the I–III interaction at the expense of the interaction of I with the unfavorable resonance structure V, is critical for stabilizing this excited state of ethylene and enhancing its valence (as opposed to Rydberg) character.



V

Our final conclusions are as follows:

(a) Nature has decreed that overlap bonds connecting nonmetal atoms repel each other, i.e., there is a principle of minimum aggregation. Correlated electron transfer represents the best weapon for counteracting this intrinsic tendency. If this stabilization mechanism is in any way diminished, breakage of a bond (diradical formation) becomes superior to "allowed" bond aggregation, e.g., $A_2 + A_2 + A^\bullet + A^\bullet$ can attain lower energy than hexagonal A_6.

(b) If reactive π-systems are placed over weak underlying observer σ-bonds, these systems will tend to undergo one-step, "allowed" multicenter reactions essentially because of σ–π correlated electron motion. Strong observer bonds will favor a stepwise path.

(c) Making a transition from Hueckel to many-electron theory alters radically one's viewpoint of mechanistic organic chemistry: The focus is now on stepwise mechanisms with concerted mechanisms being regarded as a consequence of correlated electron motion. This reminds us that, most of the time, experiment is far ahead of qualitative theory in suggesting broad mechanistic concepts: The viability of stepwise mechanisms has been emphasized in the pioneer works of Bartlett and Doering[8,19] and the more recent important contributions of Berson,[20] Roth,[21] Klaerner,[22] Gajewski,[23] Dolbier,[24] Dervan,[25] and others.

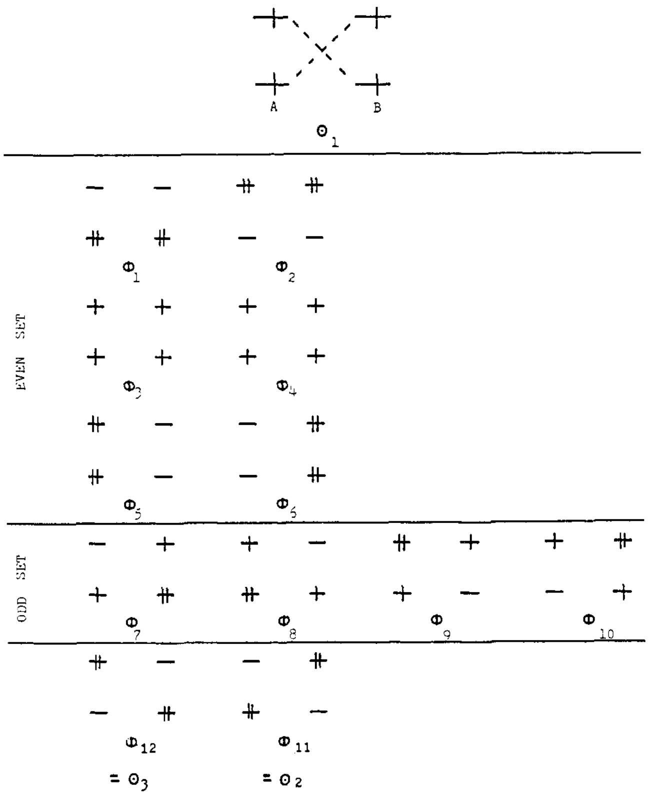


Figure 4. The configurations which are "contained" within the Θ_1, Θ_2, and Θ_3 bond diagrams.

Some of these mechanistic proposals were made when many workers, including this author, were partial to concerted mechanism simply because they were looking through the glass of one-electron (Hueckel-type) theory.

In conclusion, we suggest experimental and computational studies that probe the dependence of multicenter reaction mechanisms on the σ-bonds of the reacting polyenes. We predict that $X_2C{=}CX_2$ molecules with, e.g., $X = SiR_3$ and SR will react with dienes in a one-step fashion while, when X is a strong σ-withdrawer, the mechanism will switch to a stepwise process, involving diradical intermediates. The tacit assumption here is that replacement of, e.g., CH_3 by SiR_3 brings about a main effect due to replacing a C–C by a C–Si while other effects (e.g., steric effects) due to the remaining electrons of X remain relatively constant. We single out the prediction of our analysis that the ring opening of perfluorocyclobutene will occur by a stepwise mechanism, rather than concerted conrotation as in the case of the parent cyclobutene. We reemphasize that computational tests of these predictions can be carried out only at the MO–Cl, GVB–Cl, MCSCF, or other level of theory that properly accounts for electron correlation. This underscores the key feature of our approach: Rather than an approximate qualitative theory of chemical bonding, we now have at hand a conceptual scheme that operates at the same level as high-level theory to answer questions about trends.

Appendix

The basic MOVB theoretical recipe is the following: A molecule is cut into two fragments, one called the "core" and the other the "ligand" fragment, consistent with utilization of maximal local symmetry, and the canonical

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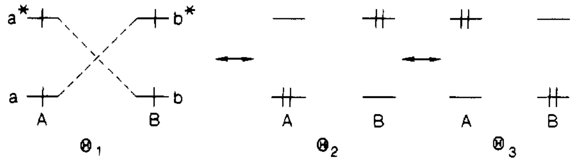
fragment orbitals are written. Next, nonorthogonal configurations are generated by allocating the valence electrons to the various orbitals in all possible ways. Then, the resulting configurations are grouped into packets, each packet is separately diagonalized to obtain packet substates, the ground state of each packet substate manifold is selected and denoted by Θ_{a0} (where a is the packet index and zero symbolizes the ground state of packet a), or, more conveniently, by Θ_i, where i is a numerical index, and the Θ_i are then diagonalized to produce the final eigenstates. The final ground state is a linear combination of substates, called bond diagrams, each one being a description of one possible, symmetry-allowed way of connecting the two fragments by bonds and/or antibonds. For example, the bond diagrammatic description of the ground state of A=B, where A and B each has two orbitals and two electrons and the upper orbital of A matches the symmetry of the lower orbital of B, and vice versa, is shown below. Θ_1 is a linear combination of 10 configurations generated by shifting electrons along the dashed lines starting with the parent configuration, Φ_3, and Θ_2 and Θ_3 are each made up of one configuration as shown in Figure 4. When the fragment orbitals are capable of strong overlap interaction with each other (i.e., when the AO resonance integrals are large), Θ_1 is the principal bond diagram. Bernardi and Robb and their co-workers have implemented computationally a version of this approach in their independent work.[26]



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Properties of Organic Diradicaloid Molecules Predicted by Semiempirical Molecular Orbital Theory. A Practical Procedure

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Semiempirical INDO and MNDO molecular orbital methods yield good results for both geometries and triplet–singlet (T–S) state ordering for a number of diradicals that have recently been examined experimentally. The putative pentamethylenepropane class of diradicals is computed to favor a triplet ground state, even though its members are formally disjoint. Diradicals **7**–**10** and bicyclic molecules **15**–**17**, formally related to tetramethyleneethane by heteroatom bridging, show a range of electronic nature from strongly diradicaloid for 3,4-dimethylenecyclopentadiene (**7**) to closed-shell zwitterionic for bicyclic **17**. Phenoxy radicals linked by ethylenic units as diradical models (**23**–**25**) for oligomeric superparamagnetic polyradicals are found to interact weakly (small T–S gaps), regardless of connectivity.

Introduction

π-Conjugated diradicals are of current interest as reactive intermediates and as tests of quantum theoretical calculations of the properties of an extraordinary form of matter.[1-6] Although ab initio theory is and must remain the method of choice for rigorous computational prediction of electronic properties of diradicals, it places constraints on the size of the molecules for which practical calculations can be done with presently available resources. Hence, semiempirical methods remain useful for qualitative and semiquantitative evaluation of trends among structurally analogous, moderately large molecules, including diradicals and related species.[7]

In this paper we apply semiempirical molecular orbital plus configuration interaction (MO-CI) methods in the study of the ground-state multiplicities and molecular structures of several diradicals under current investigation. We also explore two new kinds of species, one derived hypothetically by heteroatom substitution for the 3- and 7-CH units of pentalene, and the other belonging to the non-Kekulé series of stilbene dioxys. We find our results in good accord with other theoretical and experimental work (where available) for both molecular geometries and spin-state ordering, and we show the usefulness of the algorithm for examination of systems likely to be of particular interest to experimental chemists in the near future.

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