

MODERN ELECTRONIC STRUCTURE THEORY AND APPLICATIONS IN ORGANIC CHEMISTRY

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**MODERN ELECTRONIC
STRUCTURE THEORY
AND APPLICATIONS IN
ORGANIC CHEMISTRY**

PREFACE

This volume on *Modern Electronic Structure Theory and Application in Organic Chemistry* focusses on the use of quantum theory to understand and explain experiments in organic chemistry. High level *ab initio* calculations, when properly performed, are useful in making quantitative distinctions between various possible interpretations of structures, reactions and spectra. Chemical reasoning based on simpler quantum models is, however, essential to enumerating the likely possibilities. The simpler models also often suggest the type of wave function likely to be involved in ground and excited states at various points along reaction paths. This preliminary understanding is needed in order to select the appropriate higher level approach since most higher level models are designed to describe improvements to some reasonable zeroth order wave function.

In the first chapter in this volume, Zimmerman discusses a wide variety of thermal and photochemical reactions of organic molecules. Quantum theory is used mostly as a qualitative tool to explain facts taken from experiments. The next two chapters focus in greater depth on two particular classes of reactions. Gronert discusses the use of *ab initio* calculations and experimental facts in deciphering the mechanism of β -elimination reactions in the gas phase. He gives a detailed review of the experimental facts, the important questions they raise, and the answers obtained from high level calculations. Bettinger *et al.* focus on carbene structures and reactions with comparison of the triplet and singlet states. This chapter also contrasts the results found by many of the standard *ab initio* methods with the large body of experiments on carbenes. Next, Hrovat and Borden discuss more general molecules with competitive triplet and singlet contenders for the ground state structure. Again, the focus is on experimental facts, qualitative reasoning and quantitative calculations with the most appropriate *ab initio* methods.

None of the preceding chapters describe the theoretical methods in detail. All of the methods used have already been treated in a more elaborate fashion in the book, *Modern Electronic Structure Theory*, edited by David R. Yarkony. These chapters illustrate the use of these standard *ab initio* methods, coupled with reasoning based on simple quantum models, to treat problems in organic chemistry.

The final three chapters are somewhat different in nature. Treatment of the large variety of possible wave functions for excited states is not a routine problem. Reliable "black-box" methods do not yet exist. Cave explains the difficulties and considerations involved with many of the methods and illustrates the difficulties by comparing with the UV spectra of short polyenes.

Jordan *et al.* discuss long-range electron transfer using model compounds and model Hamiltonians. For compounds of this size, *ab initio* calculations are still not feasible for studying the mechanism of electron transfer. Hence, the approach follows the long tradition of semi-empirical theory applied to organic molecules.

Finally, Hiberty discusses the breathing orbital valence bond model as a different approach to introducing the crucial $\sigma\pi$ correlation that is known to be important in organic reactions (see, e.g. W.T. Borden and E.R. Davidson, *Acc. Chem. Res.* **29**, 67 (1996)). This concept is illustrated by looking at the bond energies of very small inorganic and organic molecules.

Ernest R. Davidson

CONTENTS

Preface	v
1. Some Theoretical Applications to Organic Chemistry <i>Howard E. Zimmerman</i>	1
2. <i>Ab Initio</i> Studies of Elimination Reaction Mechanisms <i>Scott Gronert</i>	33
3. Computational Analyses of Prototype Carbene Structures and Reactions <i>Holger F. Bettinger, Paul v.R. Schleyer, Peter R. Schreiner and Henry F. Schaefer III</i>	89
4. Violations of Hund's Rule in Organic Diradicals — Where to Look for Violations and How to Identify Them <i>David A. Hrovat and Weston Thatcher Borden</i>	171
5. <i>Ab Initio</i> Methods for the Description of Electronically Excited States: Survey of Methods and Selected Results <i>Robert J. Cave</i>	197
6. Long-Range Intramolecular Interactions: Implications for Electron Transfer <i>Kenneth D. Jordan, Dana Nachtigallova and Michael N. Paddon-Row</i>	257
7. The Breathing Orbital Valence Bond Method <i>P. C. Hiberty</i>	289
Index	369

SOME THEORETICAL APPLICATIONS TO ORGANIC CHEMISTRY

HOWARD E. ZIMMERMAN

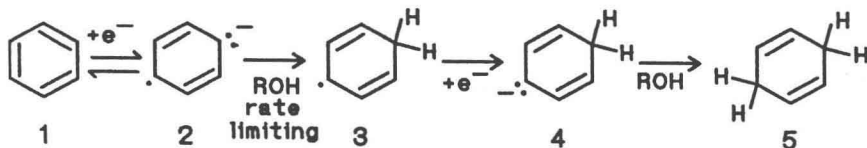
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The material in this chapter is a survey of some theoretical concepts, ideas and methods introduced in our research. Most of the theory has been in conjunction with experimental results. Thus, theory has proven especially useful in understanding ground state chemistry and much more essential in interpreting excited state behavior.

1 Ground State Examples

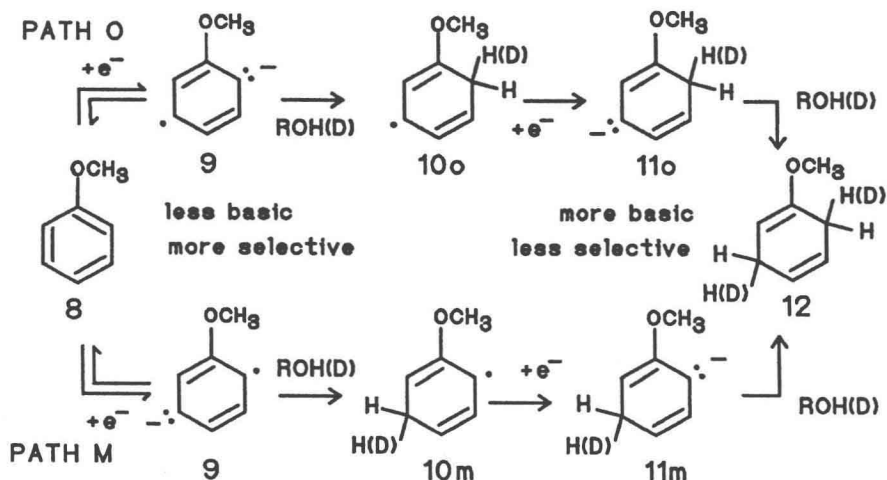
1.1 *The Birch Reduction*

The basic mechanism of the Birch Reduction,¹ as postulated by Birch, involved a one-electron reduction to give the radical-anion, followed by subsequent protonation of this species by an alcohol, introduction of a second electron, and finally a second protonation step. The kinetics reported by Krapcho and Bothner-by² established that the rate-limiting step is the protonation of the radical-anion **2**. However, what was controversial was the regioselectivity of that initial protonation step. The original Birch



mechanism suggested, on a qualitative basis, that the site of greatest negative charge and thus the initial protonation was at the meta position in alkoxyated and alkylated benzenes (e.g. anisole, compound **8** in Scheme I). However, in our very early studies,³ simple Hückel calculations were the best available and these were used to probe the electron densities for a variety of alkoxyated aromatics. It was found that it was invariably the ortho position which was the site of highest density in the radical-anion. This became a controversial topic, and the views on the two mechanisms shown in Scheme I oscillated over the years. Finally, in more recent research⁴ we obtained experimental evidence indicating that ortho protonation was preferred seven to one. Since more modern computational methodology was available, Gaussian90^{5a} and Gamess^{5b} (ROHF/3-21G) were used with the result that the electron density at the ortho position was found to be 1.302 versus 1.259 at the meta one. Interestingly, the frontier MO coefficients (i.e. the singly occupied antibonding MO) did not correlate with

experiment. Additionally, the energy of the ortho-protonated species proved to be lower than that of the meta-protonated counterpart. Similar results were obtained with alkyl substitution.



Scheme I: Possible mechanisms for the Birch reduction of anisole.

With regard to the second protonation step in the Birch reduction, wherein the central site of a cyclohexadienyl carbanion is protonated at the central carbon giving the unconjugated Birch product, we note that this is a general phenomenon. The highest electron density is obtained at the central carbon. This has precedent in the case of the dienolates obtained from enones⁶ where kinetic protonation of the dienolate affords the thermodynamically less stable β,γ -enone.

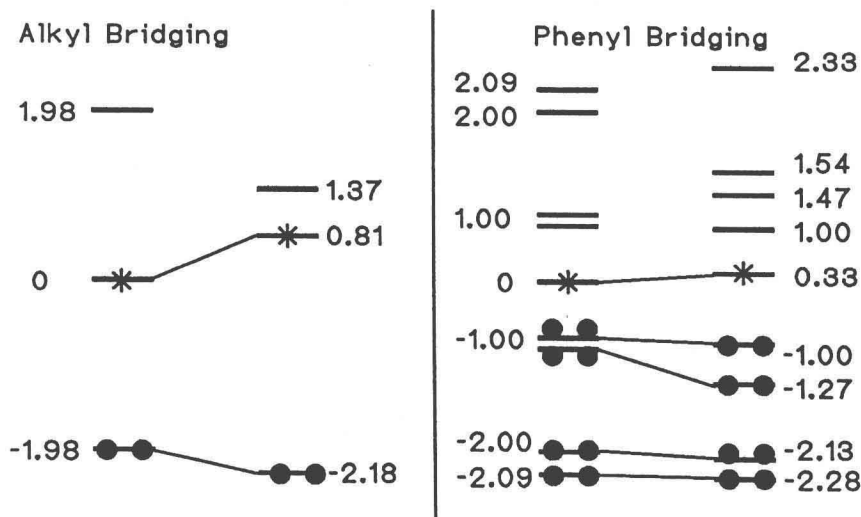
Several points should be noted. First, use of frontier MO reasoning runs a risk of giving incorrect predictions. Secondly, Hückel computations are generally of real value. Hückel theory is synonymous with graphic theory and reflects topology. While more sophisticated computations are needed, in many cases Hückel results give insight to the electronics of molecular systems.

1.2 1,2-Carbanion Rearrangements

While 1,2 carbon to carbon shifts of alkyl and aryl groups are common for carbocations, the corresponding odd-electron and carbanions case are more rare. The electronic

rationale for this behavior was noted by the present author in 1961.⁷ Interestingly, this paper presented the first correlation diagram for an organic reaction; note Scheme II. A group was considered to migrate from carbon-1 to carbon-2, and the computations used a truncated basis set. This set was comprised of two p-orbitals and an sp^2 hybrid for the alkyl migration and a total of nine localized basis orbitals for the phenyl migration where there were six p-orbitals in the aromatic ring. One in-plane sp^2 -hybrid at the ring carbon originally bonded to carbon-1 and one localized orbital was taken at each of C-1 and C-2 as shown in Figure 1. The correlation diagram considered the starting MO's and those of the half-migrated species, either with an alkyl group (e.g. methyl) half-migrated from C-1 to C-2 or with the phenonium intermediate being formed. The solid dots indicate electron occupation in the MO's and the asterisk represents zero electrons for the carbocation case, one electron for the free radical situation, or two electrons for a carbanion rearrangement.

It is seen that for a carbanion, the two non-bonding electrons taken as at an energy defined as zero, become badly anti-bonding where an alkyl group as methyl is migrating. However, for the phenyl migration, the rise in energy is much smaller. This was shown to be a general situation with further variation in substitution [also see Ref 8 for more details].



Scheme II: Correlation diagrams for alkyl and phenyl migration; reactant and half-migrated species given.

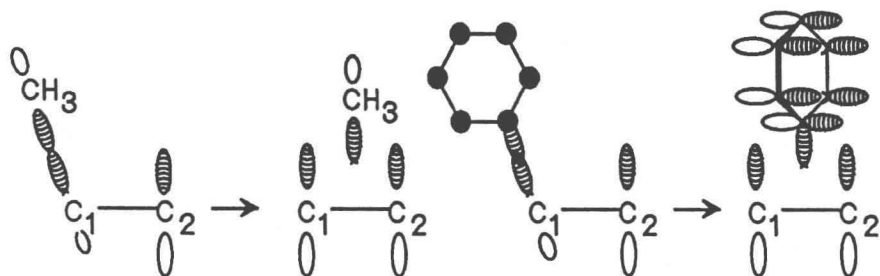


Figure 1: Basis Set Orbitals for Methyl and Phenyl 1,2-Migrations.

1.3 The Möbius-Hückel Concept

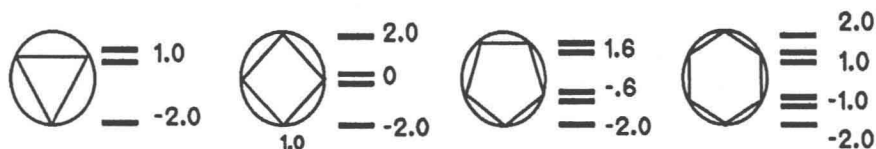
The idea of allowedness vs. forbiddenness, or aromaticity vs anti-aromaticity, of pericyclic reactions was advanced by Woodward and Hoffmann⁹ and Longuet-Higgins and Abrahamson.¹⁰ Edgar Heilbronner¹¹ had published a paper noting that a twisted, Möbius cyclic annulene would have a set of MO's which differed from that cyclic Hückel systems; and a counterpart algebraic formula for these twisted annulenes was given. Unlike the Hückel systems, the twisted annulenes preferred having $4N$ electrons for a closed shell. However, as a consequence of the twisting, the energies were never lower than that of the corresponding Hückel counterpart.

With this as background, the present author¹² suggested that for reaction transition states where alternative geometries, Hückel and Möbius, had equal twisting and equal diminution of overlap between adjacent basis set orbitals, one would find Möbius systems to be preferred as transition states when $4N$ electrons were delocalized while Hückel systems would be preferred, as expected, when there were $6N$ electrons.

For Möbius a circle mnemonic was presented¹² which was the counterpart of the well-known Frost-Musulin¹³ device for Hückel systems. These mnemonics are shown in Figure 2 for the case of a four orbital system. The Möbius mnemonic differs from the Frost-Musulin one in requiring a polygon 'side' down rather than a vertex at the bottom of the circle as for Hückel systems. Note Figure 2.

To identify Möbius and Hückel systems, given a cyclic array of basis set orbitals, in an actual molecule or in a transition state, one needs to count the number of sign inversions between pairs of basis set orbitals. With zero or an even number of such inversions, the system is of the Hückel variety. With an odd number (e.g. 1), the system is a Möbius one.

HÜCKEL SYSTEMS:



MÖBIUS SYSTEMS:

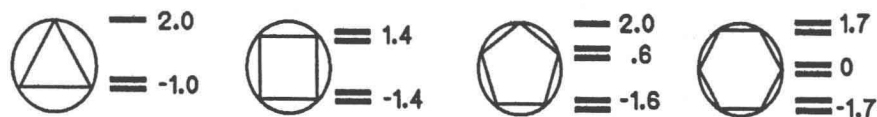


Figure 2: The Möbius - Hückel circle mnemonics.

For consideration of allowedness versus forbiddenness, one can write the cyclic array for a given pair of pericyclic reaction transition states, populate the MO's, and then compare energies of the Hückel and the Möbius counterparts. The lower energy one is the allowed reaction pathway. More interestingly, one can develop the correlation diagram for the reactions without the use of symmetry. This is done by recognizing that for each degenerate pair in the transition state, there is a crossing of a set of MO's as one proceeds from reactant to product.

Figures 3 and 4 give one example. This shows that the opening of cyclobutene to give butadiene in the ground state will prefer a conrotatory pathway as opposed to a disrotatory one (Note Figure 4), in which a Möbius transition state is employed. The correlation diagram for both conrotatory and disrotatory reactions is readily drawn by obtaining the transition state degeneracies from the circle mnemonics and recognition that each degeneracy gives rise to crossing of two MO's. The conrotatory mechanism leaves all of the bonding MO's as bonding while the disrotatory mechanism converts a bonding MO to an antibonding one. Thus if one were to picture the first-order situation of an adiabatic reaction (i.e. before any configuration interaction), a ground state reactant proceeding in a disrotatory fashion would afford a very high energy doubly excited state of product.

The Möbius-Hückel concept applies to more than the transition states discussed above. There are many Möbius molecules already known. One is barrelene. This molecule has three ethylene bridges. One may start with the bonding MO's of ethylene

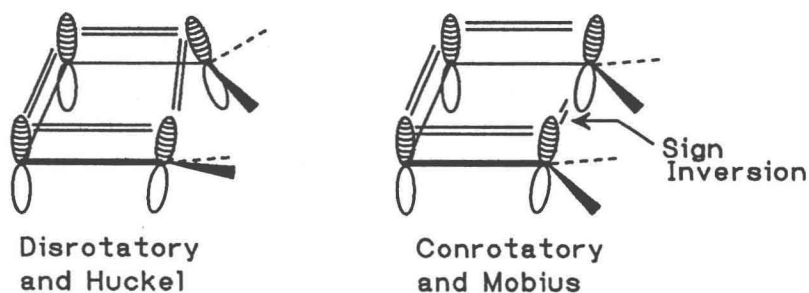


Figure 3: Basis set orbitals and twisting of Möbius and Hückel transition states for cyclobutene opening.

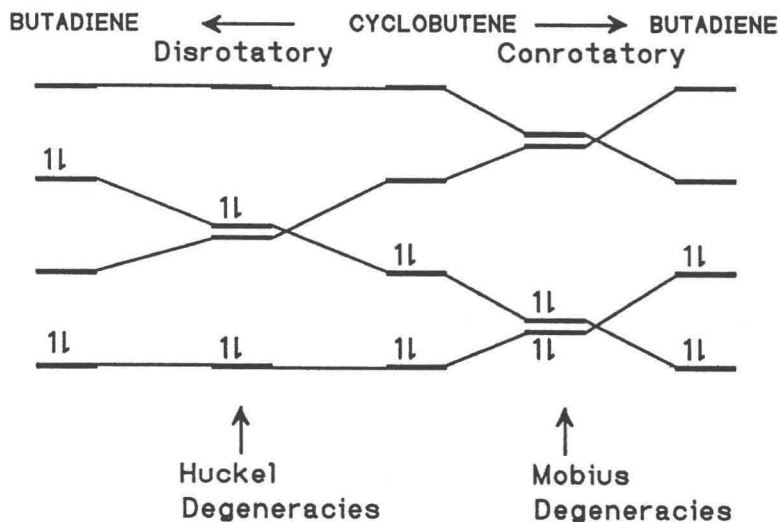


Figure 4: Correlation diagram interconverting cyclobutene and butadiene by conrotatory and disrotatory twisting.

on each bridge and note that these interact in a Möbius fashion. At a simple Hückel level, the bonding MO of ethylene is at -1 , the energy scale using units of the absolute value of β . The transannular overlap is less by a factor (ϵ) than that for two adjacent p-orbitals. The Möbius splitting of the three bonding MO's thus results in a degenerate pair of MO's at $-1 - \epsilon$ and a single MO at $-1 + 2\epsilon$. This is illustrated in Figure 5. Similar consideration of the antibonding ethylenic orbitals as a basis set, leads to a similar splitting about the antibonding ethylenic MO at $+1$. Note Figure 5.

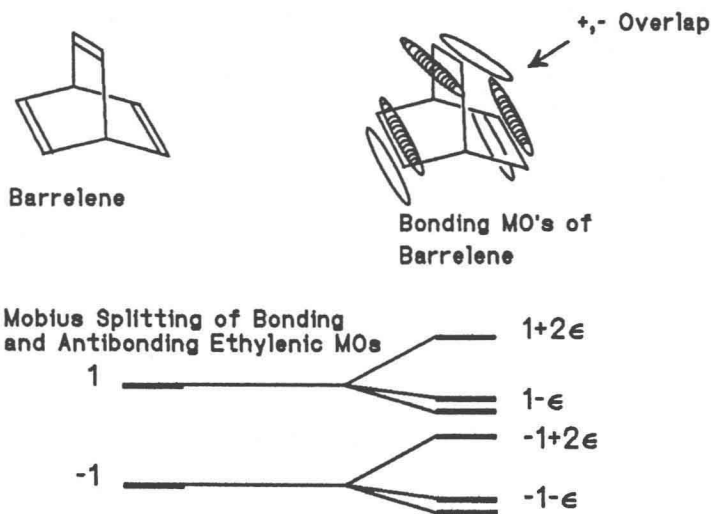


Figure 5: Admixture of three ethylene bridges of barrelene.

1.4 Prediction of Organic Reactions Using Group-Group Polarizability

In Hückel theory bond-bond, atom-bond, bond-atom, and atom-atom polarizabilities give the change in one part of the molecule as another is modified. For example, in bond-bond polarizability, one obtains the change in a bond order (e.g. r-s) as the resonance integral β is changed for another pair of atoms (e.g. t-u). In the case of atom-atom polarizability, one obtains the change in charge at one center as the Coulomb integral at another atom is modified. The atom-bond and bond-atom parameters are defined similarly.

While these polarizabilities¹⁴ are of intellectual interest, they have had severe limitations. (a) They have been limited to use with π -systems (e.g. aromatics), (b) the neglect of overlap approximation has assumed different p-orbitals do not overlap, (c) and the approximate nature of Hückel wavefunctions is generally a problem.

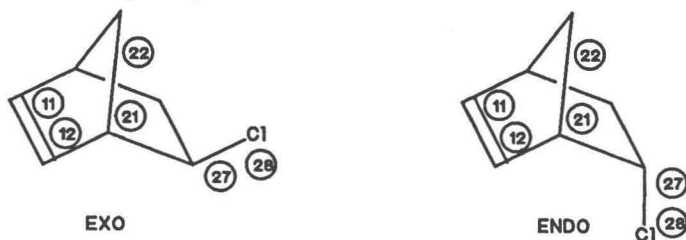
It was recognized by the author¹⁵ that the mutual-polarizability concept could be applied to organic molecules in general, including those having both sigma and pi bonds. Further, the most modern self-consistent field methods could be employed, not only the more approximate semi-empirical wavefunctions, but also ab initio ones. This was made possible by the realization that Weinhold "natural hybrid orbitals" (i.e. NHO's)¹⁶ comprise an orthogonal basis unlike a Hückel set. Additionally, the NHO basis orbitals are readily available from both semi-empirical computations (e.g. AM1)

and ab initio ones (e.g. 3-21G, 6-31G*, etc.). A minor addition is required wherein the ϵ_{rs} and ϵ_{tu} elements included are +1 or -1 depending on the basis set overlap and were obtained from the Fock matrix signs for off-diagonal elements. Thus the bond-bond polarizabilities are given in Equation 1.

$$P(r,s,t,u) = \epsilon_{rs} \epsilon_{tu} \sum_k^{occ} \sum_l^{vir} \frac{(C_{rk} C_{sl} + C_{rl} C_{sk}) (C_{lk} C_{ul} + C_{ll} C_{uk})}{(E_l - E_k)} \quad (1)$$

However, the application to chemical reactivity relies on recognizing in the molecule some group which is weakening or strengthening and hence initiating a reaction. Then group-group polarizability indicates the response of all other bonds and atoms in molecule. The result is a parallel to ordinary electron pushing; however, the method provides a quantitative prediction of molecular changes. For example, if there is a potentially departing tosylate moiety held by bond r-s, one can determine which other bonds will respond to tosylate loss by weakening and which bonding will be enhanced. Similarly, one can see what molecular sites become more electron deficient in such a case.

While a number of examples were given, one representative example is the solvolysis of exo- and endo-norbornyl chloride.¹⁷ It is well known that the exo stereoisomer solvolyses in polar media much more rapidly than the endo isomer. Also, there is evidence for participation of the π -bond.



Scheme III: The exo and endo norbornenyl systems with labeled orbitals.

We see interaction between the π -bond 11-12 and the C-Cl sigma bond with a positive polarizability (0.00575) in the case of the exo stereoisomer compared with essentially zero for the endo isomer. The positive value for the exo isomer indicates withdrawal of electron density and weakening of C=C π -bond 11-12 as the C-Cl sigma bond (27-28) is broken. The difference between the exo and endo isomers, again, correlates with the experimental behavior of the two compounds on solvolysis. One

Table 1: Exo and endo dehydronorbornyl bond-bond polarizabilities.

Exo Norbornenyl Polarizabilities

r	s	t	u	Orb r	Orb s	Orb t	Orb u	Polarizability
27	28	11	12	C 5(Cl 8)	Cl 8(C 5)	C 2(C 3)	C 3(C 2)	0.005753
27	28	21	22	C 5(Cl 8)	Cl 8(C 5)	C 4(C 7)	C 7(C 4)	0.000723
28	28	11	12	Cl 8(C 5)	Cl 8(C 5)	C 2(C 3)	C 3(C 2)	-0.000429
28	28	22	22	Cl 8(C 5)	Cl 8(C 5)	C 4(C 7)	C 7(C 4)	-0.000547

Endo Norbornenyl Polarizabilities

r	s	t	u	Orb r	Orb s	Orb t	Orb u	Polarizability
27	28	11	12	C 5(Cl 8)	Cl 8(C 5)	C 2(C 3)	C 3(C 2)	-0.000092
27	28	21	22	C 5(Cl 8)	Cl 8(C 5)	C 4(C 7)	C 7(C 4)	0.011229
28	28	11	12	Cl 8(C 5)	Cl 8(C 5)	C 2(C 3)	C 3(C 2)	0.000158
28	28	22	22	Cl 8(C 5)	Cl 8(C 5)	C 4(C 7)	C 7(C 4)	-0.008572

interesting facet is the heavy electron withdrawal from the sigma bond 21-22 in the endo stereoisomer (i.e. the chlorine is endo, note 27-28:21-22). Additionally, the sigma bond anti-coplanar with the C-Cl bond of the exo-stereoisomer exhibits an appreciably large interaction with that bond.

While it is true that the polarizabilities computed are related to an "overlap path" of conjugating basis orbitals between interacting groups, the role of electron affinity and availability at the various centers plays a large role as well. But then these are the factors which control reactivity.

Further, polarizabilities represent a precise counterpart to electron pushing and something which has not been considered in predicting reactivity of sigma systems. Beyond this, polarizabilities represent just one case where one can extend the Hückel treatment to sigma systems as a consequence of the orthogonality of the basis orbitals (i.e. NHO's) used.

1.5 Electron Density and Central Protonation of Mesomeric Anions

In the Birch Reduction discussed above, the final step was protonation of a mesomeric carbanion. Since we know that conjugated dienes are lower in energy than the unconjugated ones, formation of the unconjugated reaction product cannot be controlled by relative thermodynamic stability of the product. While in some reactions, the final product energy is seen sufficiently in the transition state, that the more stable product is the one formed. Not so here. It is observed as a general phenomenon that kinetic protonation of anions of the type $C=C-C=C-\underline{C} \leftrightarrow C=C-\underline{C}-C=C \leftrightarrow \underline{C}-C=C-C=C$ occurs at the central carbon. The same is true of dienolates such as $C=C-C=C-O^-$.

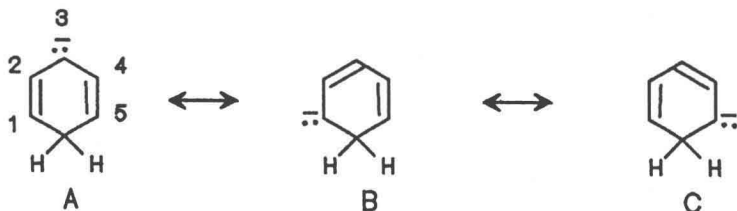


Figure 6: Three resonance structures for the cyclohexadienyl carbanion.

Simple Hückel calculations on the pentadienyl type anions predict an equal distribution of negative charge at atoms 1,3 and 5 (i.e. 0.333 e at each of the three centers) in agreement with the appearance of three resonance structures shown in Figure 6 for the example of the cyclohexadienyl carbanion. But in looking at the three resonance structures we note that two of the three structures have double bonds at C1-C2 and C4-C5 but single bonds at C2-C3 and C3-C4. Thus this qualitative resonance reasoning suggests that bond 1-2 and 4-5 should be shorter. In fact, if one adjusts the resonance integrals to reflect this, with the absolute value of the C1-C2 and C4-C5 values being larger, the electron density shifts towards C3. This is precisely what was done using the Mulliken-Wheland-Mann modification¹⁸ of Hückel theory in which the resonance integral β for bond r-s is given by Equation 2.

$$\beta_{rs} = \beta_0 [0.08(P_{rs}(\pi) + P_{rs}(\sigma)) + 0.115] / 0.276 \quad (2)$$

$P_{rs}(\sigma)$ was taken as unity while $P_{rs}(\pi)$ is obtained from one iteration and then used in Equation 2 for the next iteration. The constants were selected so that with a π -bond order of unity, β_{rs} becomes equal to the standard β_0 . Although not here, in other applications, the Coulomb integral was also varied. Interestingly, Equation 2 is