ecules containing adjacent atoms with lone pairs, turn out to give some reasonably accurate predictions.

Acknowledgment. The authors are grateful to the National Science Foundation and the National Institutes of Health for partial financial support of this research and to Robert W. Strozier and Alex Nicolson for modifications of the computer programs used in this work.

References and Notes

(1) (a) NATO Fellow, 1975; on leave from the University of Pavia, Italy; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.
(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).
(3) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).
(4) K. N. Houk, *J. Am. Chem. Soc.*, **94**, 8953 (1972); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973).
(5) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973).
(6) J. Bastide and O. Henri-Rousseau, *Bull. Soc. Chim. Fr.*, 2294 (1973); J. Bastide, N. El Ghandour, and O. Henri-Rousseau, *ibid.*, 2290 (1973).
(7) A. Komornicki and J. W. McIver, Jr., OPTMO, Quantum Chemistry Program Exchange, No. 217; J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).
(8) N. Bodor, M. J. S. Dewar, E. Haselbach, and A. Harget, *J. Am. Chem. Soc.*, **92**, 3854 (1970).
(9) M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and P. K. Bischof, MINDO/3, Quantum Chemistry Program Exchange, No. 279; R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).
(10) See, for example, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1973; L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
(11) A. Imamura and T. Hirano, *J. Am. Chem. Soc.*, **97**, 4192 (1975).
(12) Calculations were carried out by setting matrix elements corresponding to $2p_z$-$2p_z$ interactions equal to 0: H. L. Hase and A. Schweig, *Tetrahedron*, **29**, 1759 (1973).
(13) P. Caramella and K. N. Houk, *J. Am. Chem. Soc.*, **98**, 6397 (1976).
(14) E. F. Hayes and A. K. Q. Siu, *J. Am. Chem. Soc.*, **93**, 2090 (1971).
(15) A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, **98**, 5021 (1976).
(16) K. N. Houk, P. Caramella, L. L. Munchausen, Y.-M. Chang, A. Battaglia, J. Sims, and D. C. Kaufman, *J. Electron Spectrosc. Relat. Phenom.*, in press.
(17) This type of reasoning was proposed for AH_3 molecules by C. C. Levin, *J. Am. Chem. Soc.*, **97**, 5649 (1975).
(18) NOTE ADDED IN PROOF. Optimizations by 4-31G give the following HCN angles for nitrilium betaines: ylide, 123°; imine, 180°; oxide, 180°.
(19) A planar geometry with a COC angle of 129° has been found from an STO-3G optimization: G. Leroy, M.-T. Nguyen, and M. Sana, *Tetrahedron*, **32**, 1529 (1976).

Thermal Sigmatropic [1,*j*] Shifts in Cyclic Systems. A Perturbation Approach and INDO Calculations

Jan R. de Dobbelaere,* Jan M. F. van Dijk, Jan W. de Haan, and Henk M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, The Netherlands. *Received April 27, 1976*

Abstract: Some fundamental aspects of sigmatropic shifts are discussed with the help of INDO calculations and perturbation theory. In cyclic systems the degeneracy of the highest occupied molecular orbital is lifted in the transition state. A suprafacial H shift is determined by a combination of the 1s orbital of the migrating hydrogen with the symmetric MO's of the system and an antarafacial shift by a combination with the antisymmetric MO's. The used perturbation model offers the possibility to reconcile somewhat the concepts of "allowed" and "forbidden". Formally forbidden reactions which, however, have been found experimentally can be explained with this model. Many "forbidden" reactions are in fact "allowed", but they proceed with a higher activation enthalpy. Some transition state geometries have been calculated and the occurring charge transfer is explained in terms of aromaticity.

In 1965 Woodward and Hoffmann postulated their concept of orbital symmetry rules governing pericyclic reactions.[1] In the particular case of sigmatropic reactions, the transition state is thought to be determined by the migrating group and the HOMO or LUMO of the radical-like species left behind, after splitting off the migrating group in thermal and photochemical rearrangements, respectively. In principle, the symmetry properties of the HOMO or LUMO were considered for acyclic polyenes. The major part of the experimental work reported in the last ten years is in agreement with the predictions.

Curiously enough, this applied also to a host of cyclic systems. Whereas the description of acyclic systems is relatively straightforward, cyclic systems have, so far, defied a truly general explanation. The major problem has been the fact that in these systems all but the lowest molecular orbitals are doubly degenerate in the transition state. In 1968 Anastassiou tried to work out the degeneracy problem in C_nH_{n+1} monocycles.[2] It was postulated that the presence of the migrating group will disturb the symmetry of the radical, thereby lifting the degeneracy. It was then concluded that the migrating group will combine with the "genuine" HOMO again.

In our opinion, however, the real perturbation is formed by a hydrogen nucleus *in the transition state* in contrast with Anastassiou's approach in which the perturbation was applied to the reactant. This leads to an entirely different result (see also next section).

There are no compelling reasons to confine the discussion to the HOMO, as already suggested by Berson[3] and, in a more elaborate way, by Anh[4] and Fukui,[5] who worked out the application of perturbation theory to pericyclic rearrangements. The implications of this method have, so far, not been discussed in detail for sigmatropic rearrangements. In general, the nomenclature and selection rules derived for acyclic systems are used without modifications for cyclic polyenes as well.

Here we wish to present evidence that simple perturbation theory allows one to predict several aspects of [1,*j*] rearrangements in simple systems in a relatively simple fashion. The results are substantiated by INDO calculations. Before specific examples are discussed, it should be realized that a migrating hydrogen, involved in a suprafacial shift, will have to interact with symmetric molecular orbitals. On the other hand, in antarafacial rearrangements the interaction necessarily originates from combination with asymmetric orbitals.

These statements apply to both cyclic and acyclic systems. However, antarafacial shifts in small cyclic systems are only feasible when the hydrogen shifts are along the edge of the ring, i.e., from one carbon atom to a neighboring carbon atom, such as the antara [1,3] and [1,5] shifts in cyclopropene and cyclopentadiene, respectively. In the transition state of these shifts the migrating hydrogen resides in the plane of the ring, a situation in which no interaction with the π system will exist. The only remaining interaction is with the σ framework. In larger rings Möbius arrangements of the polyene fragment are possible, enabling formal antarafacial shifts to occur relatively easy. Möbius-type transition states presumably are also responsible for antarafacial rearrangements in acyclic systems.

For suprafacial rearrangements, the migrating group will interact with a linear combination of molecular orbitals which have a suitable symmetry. For edge-type rearrangements the position of the migrating group may be derived from a simple inspection of the Hückel orbitals. However, in face-type shifts (across the ring) the proper position can only be found by taking recourse to MO calculations. Furthermore, it will be shown that even for shifts in acyclic polyenes molecular orbitals of a cyclic transition state have to be considered. It will also be discussed why some Woodward/Hoffmann "forbidden" reactions occur.

Finally, the limitations of the present approach will be outlined.

Perturbation Treatment

The parameter determining whether or not a particular H shift will occur is the activation enthalpy. We will derive that the activation enthalpy is predominantly determined by the orbital symmetry at migration origin and terminus. We postulate that the following restrictions can be made when considering the transition state: (a) The discussion is confined to the π electrons plus the two electrons of the σ-H bond that is shifting. These electrons participate in the overall conjugation of the system. (b) The π MO's are approximated by the perturbed π MO's of the initial system, the perturbation being the hydrogen nucleus. (c) For the unperturbed π MO's we take the Hückel MO's.

The perturbation treatment consists of two parts: the perturbation of the energy levels and the perturbation of the MO's.

Rayleigh-Schrödinger perturbation theory gives for energy and wave functions:

$$E_n = E_n{}^0 + \langle n^0|V|n^0\rangle + \sum_m{}' \frac{|\langle m^0|V|n^0\rangle|^2}{E_m{}^0 - E_n{}^0} \quad (1)$$

$$|n\rangle = |n^0\rangle - \sum_m{}' |m^0\rangle \frac{\langle m^0|V|n^0\rangle}{E_m{}^0 - E_n{}^0} \quad (2)$$

The prime indicates the skipping of $m = n$. We take as zero-order functions the π MO's of the intermediate state and the 1s orbital of the hydrogen atom. The perturbation is constituted by the interaction between the π MO's and the 1s orbital. This interaction will be appreciable if the orbitals overlap. The first-order correction to the energy $\langle n^0|V|n^0\rangle$ will be about the same for the different π MO's (and in the same direction), because it arises through the electrostatic effect of the presence of the hydrogen nucleus, without any mixing of orbitals.

The second-order correction to the energy depends on both the interaction element $\langle n^0|V|m^0\rangle$ and the energy difference $E_m{}^0 - E_n{}^0$ of the interacting orbitals. The numerator is always positive with the effect that the energy will be lowered/raised depending on whether the perturbing level is higher/lower than the level being perturbed.

The first-order correction to the wave function depends on both the interaction and the energy difference. In fact the only relevant interaction element is:

$$V_{mn} = \langle m^0|V|n^0\rangle = \int \phi_{\mathrm{H}_{1s}}(\mathbf{r}) \cdot |\mathbf{r}_\mathrm{H} - \mathbf{r}|^{-1} \cdot \phi_\mathrm{n}(\mathbf{r})\, \mathrm{d}\mathbf{r} \quad (3)$$

where $\mathbf{r}$ is the electron position vector, $\mathbf{r}_\mathrm{H}$ is the position vector of the hydrogen nucleus, $\phi_{\mathrm{H}_{1s}}$ is the 1s orbital of hydrogen, and ϕ_n is the π MO of the system. $\phi_{\mathrm{H}_{1s}}$ will be zero everywhere, except in the neighborhood of the H nucleus. So the p_z orbitals, where the contribution of the H_{1s} orbital is dominant, are the p_z orbitals of the C atoms in migration origin and terminus (for the possible effect of the other p_z orbitals, see next section).

V_{mn} then becomes:

$$V_{mn} \simeq \{c_n(\mathrm{C_0}) \times |\mathbf{r}_\mathrm{H} - \mathbf{r}_{\mathrm{C_0}}|^{-1} + c_\mathrm{n}(\mathrm{C_t}) \times |\mathbf{r}_\mathrm{H} - \mathbf{r}_{\mathrm{C_t}}|^{-1}\} \quad (4)$$

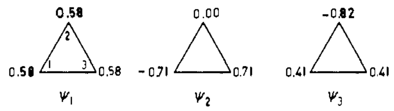
where $\mathrm{C_0}$ is the carbon atom at the migration origin, $\mathrm{C_t}$ is the carbon atom at the migration terminus, $c_\mathrm{n}(\mathrm{C_0})$ is the coefficient of p_z on atom $\mathrm{C_0}$ in MO n, and $c_\mathrm{n}(\mathrm{C_t})$ is the coefficient of p_z on atom $\mathrm{C_t}$ in MO n.

In the transition state it follows that $|\mathbf{r}_\mathrm{H} - \mathbf{r}_{\mathrm{C_0}}| = |\mathbf{r}_\mathrm{H} - \mathbf{r}_{\mathrm{C_t}}|$ (symmetrical transition state). Thus V_{mn} will be maximal when both $c_\mathrm{n}(\mathrm{C_t})$ and $c_\mathrm{n}(\mathrm{C_0})$ are maximal and of the same sign. Coefficients of equal magnitude but different sign will cause V_{mn} to be zero. In the transition state the migrating hydrogen will be most involved in the MO which is able to cause the greatest $V_{mn}/(E_m{}^0 - E_n{}^0)$. Qualitative examples will be given in the next section. Quantitative evidence is given by our INDO calculations.

Results

In this section we will present the implications of the use of perturbation theory to some specific examples.

(1) The Cyclopropene System. The Hückel MO's are as depicted below:

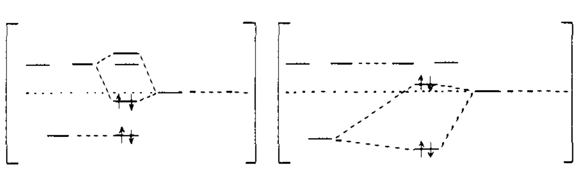


The suprafacial [1,3] H shift from C_1 to C_3 is described by the function in which ϕ_{1s} and the symmetrical MO's ψ_1 and ψ_3 are involved.

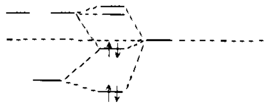
$$\chi_\mathrm{supra} = a\phi_{1s} + b\psi_1 + c\psi_3$$

where ϕ_{1s} is the 1s hydrogen orbital.

The perturbed energy levels are thus determined by two contributions:[15]



Thus, the real situation will be as follows:



Perturbation theory predicts the hydrogen to shift along the edge C_1-C_3 of the ring, because of the "wrong" coefficient on C_2 in ψ_3. The relative energy differences predict the combination with ψ_3 to prevail.

These predictions are in agreement with the INDO results. The calculated geometry of the transition state is given in Table I and Figure 1. In the transition state a partial charge transfer occurs from the ring system to the migrating hydrogen. The electron density on the migrating hydrogen $\rho_\mathrm{H} = 1.18$. This is in excellent agreement with the aromaticity rules: the tran-

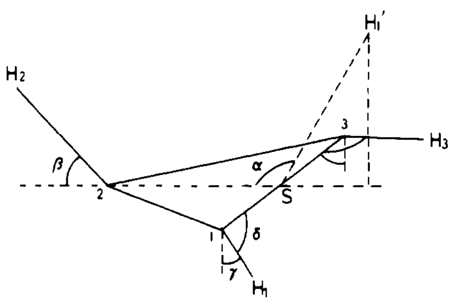


Figure 1. The transition state of the cyclopropene system.

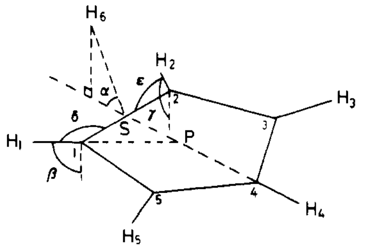


Figure 2. The transition state of the cyclopentadiene system.

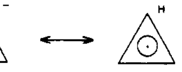
Table I. The Transition State Geometry of the Cyclopropene System

C_1-C_2 = 1.44 Å	α = 122°
C_1-C_3 = 1.38 Å	β = 47°
C_1-H_1 = 1.10 Å	γ = 85°
C_2-H_2 = 1.12 Å	δ = 151°
S-H_1' = 1.16 Å	

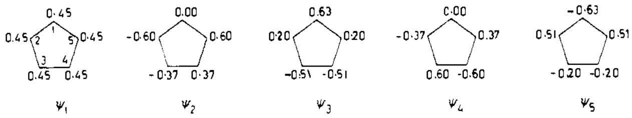
Table II. The Transition State Geometry of the Cyclopentadiene System

C_1-C_2, Å	1.471	δ, deg	125.9
S-H_6, Å	1.058	ϵ, deg	125.3
α, deg	76.0	$C_1C_2C_3$, deg	107.0
β, deg	81.2	ΔE, kcal/mol	17.2
γ, deg	84.2	ρH_6	0.86

sition state contains a 2π-electron contribution. The transition state can be described as a hybrid of two configurations, the former of which is aromatic; the latter, too, has an appreciable resonance energy:



(2) The Cyclopentadiene System. The Hückel MO's are:



Any suprafacial shift can be described by the function:

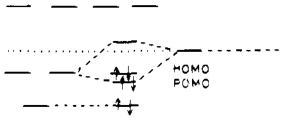
$$\chi_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3 + d\psi_5$$

The contribution of ψ_3 will be most important, because $|E_{\psi_3} - E_{\phi_{1s}}|$ is relatively small.

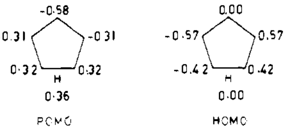
In principle, two suprafacial shifts should be considered in this system: (a) a [1,5] shift from C_3 to C_4; (b) a [1,3] shift from C_2 to C_5. The former shift will be of the edge type, avoiding overlap with C_2 and C_5 ("wrong" coefficients in ψ_3 and ψ_5). The latter shift is of the face type. Perturbation theory predicts the C_3-C_4 part of the molecule to bend away in the transition state to avoid overlap. This situation corresponds more or less to the transition state that has been calculated by Ustynyuk.[6] However, considering the magnitude of the C_3-C_4 coefficients and the relatively small interaction with "wrong sign" carbon atoms, the edge-type rearrangement will be favored. The calculated activation enthalpy for the edge-type shift indeed is smaller than for the face-type shift (difference: 51 kcal/mol).[12]

In cyclic polyenes with an even number of double bonds ($C_{4n+1}H_{4n+2}$) an interesting phenomenon occurs. Whereas the ϕ_{1s} function of the migrating hydrogen combines with the highest occupied *symmetric* molecular orbital (s-HOMO) of the cyclopolyene, the newly formed orbital in the transition state is no longer "the HOMO" in an absolute sense. The term POMO (penultimate occupied molecular orbital) is more appropriate. It should be emphasized, however, that in transition states derived from cyclopolyenes with an odd number of double bonds ($C_{4n-1}H_{4n}$), the HOMO of the cyclopolyene fragment remains the absolute HOMO in the transition state.

For cyclopentadiene this is illustrated in the next diagram:

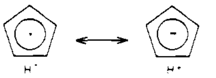


The coefficients of the POMO and HOMO were calculated by means of the INDO method and are shown in the following figure:



The calculated geometry of the transition state is depicted in Figure 2 and compiled in Table II.[7]

The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.



(3) The Cycloheptatriene System. A consequent and straightforward extension of the perturbational treatment would involve the consideration of a planar C_7H_7 radical in the transition state. In this situation, the migrating hydrogen in a [1,5] shift cannot sufficiently overlap with both the migration origin and terminus (distance, 3.1 Å). A suprafacial [1,7] shift would not suffer from this difficulty as the optimum distance between the migrating hydrogen and the edge of the ring can always be obtained. The use of (4) in order to predict the relative rates of different sigmatropic rearrangements shows that simple additions of the coefficients of the Hückel MO's are no longer adequate, because of the different distances entering via the $|\mathbf{r}_H - \mathbf{r}_C|^{-1}$ term. Starting from the well-known nonplanarity of cycloheptatriene in the ground state, a more convenient way to approach the transition state would imply the use of open pentadienyl radical molecular orbitals. These orbitals are as follows:

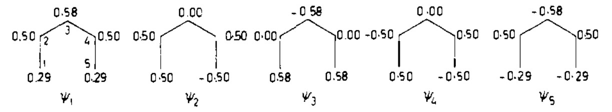


Table III. The Transition State Geometry of the Cycloheptatriene System

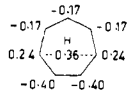
	Distance, Å		Angle, deg
C_1-C_2	1.38	($C_1C_2C_3$)	116.0
C_3-C_4	1.41	($C_2C_3C_4$)	121.0
C_4-C_5	1.46	($C_3C_4C_5$)	124.0
C_5-C_6	1.34	($C_4C_5C_6$)	109.4
C_1-C_3	2.33	($H_1C_1C_2$)	118.5
C_4-C_7	2.31	($H_1C_1C_7$)	120.0
		($H_2C_2C_1$)	121.9
C_1-H_1	1.12	($H_4C_4C_3$)	111.6
C_2-H_2	1.12	($H_4C_4C_5$)	111.9
C_4-H_4	1.14	($H_5C_5C_4$)	122.2
C_5-H_5	1.12	($H_5C_5C_6$)	128.4
$H_{7'}$-S	0.67		

$\alpha = 106.0°$ $\beta = 50.3°$ $\gamma = 0.2°$

The interaction element between ϕ_{1s} and ψ_3 will be most important. The most favorable shift will be the [1,5] shift from C_1 to C_5:

$$\chi_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3 + d\psi_5$$

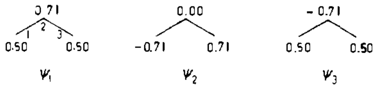
The comparable fully optimized transition state as calculated by means of INDO yields the coefficients as depicted below for the highest molecular orbital, containing the ϕ_{1s} function of the migrating hydrogen atom.



The geometry of the nonplanar transition state as calculated by the INDO method is given in Figure 3 and Table III.[8] The charge transfer in this system is calculated to be approximately zero: 0.99 electron density on the migrating hydrogen, a result to be expected for an open pentadienyl system. In this case, however, the pentadienyl system is perturbed by an ethene moiety, which results in the particular MO as depicted. Further evidence for this situation is yielded by the π bond order between the atoms C_6 and C_7 (or C_4 and C_5), which is approximately zero.

In the course of this study we also calculated by INDO the transition state energies of the suprafacial [1,5] and [1,7] hydrogen shifts assuming a planar C_7H_7 moiety. As expected, the activation energy of the latter type of rearrangement winds up at a lower value than the former. Both numbers are, however, prohibitively large compared with the value of the "normal" [1,5] shift, assuming a nonplanar C_7H_7 system. Important information from a theoretical viewpoint is yielded by the charge transfer in the transition state of the [1,7] shift: the migrating hydrogen is calculated to carry 1.08 electrons. This result, together with that obtained from the cyclopropenyl system, lends additional support to the concept of aromaticity in the transition state.

(4) The Propene System. The Hückel MO's are:



A suprafacial [1,3] shift can be described by the function:

$$\chi_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3$$

In any case the coefficients a and c will be small because of the relatively large energy differences between ϕ_{1s} and ψ_1 and ψ_3. The contribution of ψ_1 will prevail because of the "right" coefficient on C_2, which is very important in small systems. The activation enthalpy of the suprafacial [1,3] H shift in propene (49 kcal/mol) has been calculated by Bingham and Dewar, using the MINDO/CI method.[9]

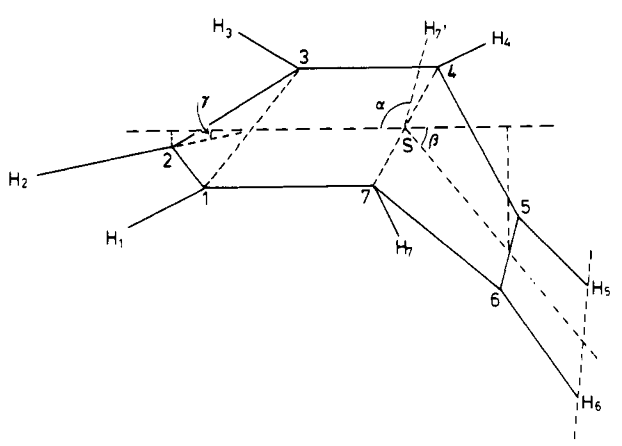


Figure 3. The transition state of the cycloheptatriene system.

An antara [1,3] H shift can be described by the function:

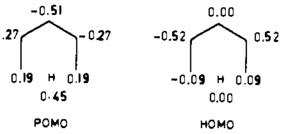
$$\chi_{\text{antara}} = a\phi_{1s} + b\psi_2$$

However, it will be difficult to obtain the Möbius transition state in which the C-C bonds must be twisted, if H migration is considered. It can be reached easier in the case of alkyl migration with inversion of the migrating group. The excellent experimental data of Berson show both the alkyl shifts with retention and inversion of configuration.[3]

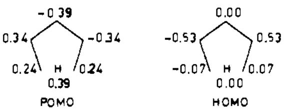
(5) The 1,3-Pentadiene System and the 1,3-Cyclohexadiene System. The Hückel MO's have been given already in the section "cycloheptatriene". Again the [1,5] H shift should be described with the function:

$$\chi_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3 + d\psi_5$$

Somewhat to our surprise, INDO calculations on this system yield a picture which deviates in certain aspects from the above mentioned completely open pentadienyl fragment. The symmetries of the various MO's comply with a (homo)cyclopentadienyl rather than an open pentadienyl moiety. In addition, the π bond orders between C_1 and C_5 are appreciable.[14] The calculations further show that the migrating hydrogen is involved mainly in the POMO, the coefficient for the H 1s function being zero in the HOMO. The electron density on the migrating hydrogen is calculated to be 0.81.



There is no reason to assume that this phenomenon will be restricted to the 1,3-pentadienyl system. In fact, every open 1,3-dienyl system will probably follow this pattern. This conclusion is corroborated quite elegantly by the results obtained for the 1,3-cyclohexadiene system. Even in this case the shift also proceeds via a homocyclopentadienyl transition state as depicted in Figure 4 and Table IV. Electron density on the migrating hydrogen: 0.95.



A similar procedure can be envisaged for larger cycloalka-1,3-dienes. Qualitative predictions regarding relative activation energies are also possible.[8]

In open systems [1,5] antarafacial shifts are to be considered

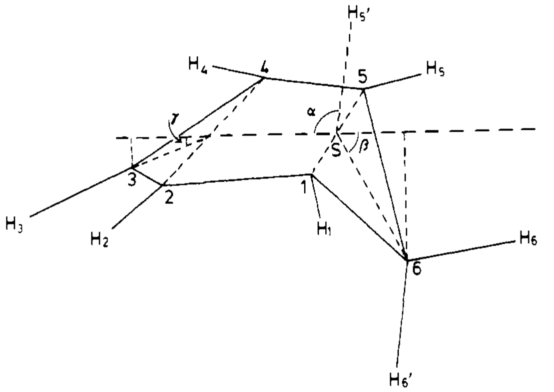


Figure 4. The transition state of the cyclohexadiene system.

Table IV. The Transition State Geometry of the Cyclohexadiene System

Distance, Å		Angle, deg	
C_1-C_2	1.43	($C_1C_2C_3$)	111.2
C_2-C_3	1.39	($C_2C_3C_4$)	114.5
C_5-C_6	1.48	($C_2C_1C_6$)	116.8
C_1-C_5	1.77	($C_1C_6C_5$)	73.3
C_2-C_4	2.33	($H_1C_1C_2$)	119.8
		($H_1C_1C_6$)	114.5
C_1-H_1	1.13	($H_2C_2C_1$)	123.7
C_2-H_2	1.12	($H_2C_2C_3$)	123.4
C_3-H_3	1.12	($H_3C_3C_2$)	122.4
C_6-H_6	1.13	($H_6C_6H_{6'}$)	108.7
C_6-$H_{6'}$	1.12	($H_6C_6C_1$)	118.2
$H_{5'}$-S	0.95	($H_{6'}C_6C_1$)	117.5

$\alpha = 100.6°$ $\beta = 65.5°$ $\gamma = 5.0°$

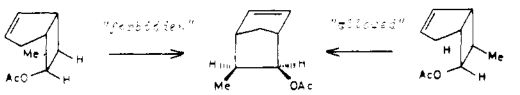
as well (vide supra). In 1,3-pentadiene this is described by the function:

$$\chi_{\text{antara}} = a\phi_{1s} + b\psi_2 + c\psi_4$$

In order to enable this shift, the pentadiene fragment will be forced into a Möbius arrangement. As a consequence, positive overlap is only possible with asymmetric subjacent molecular orbitals. This, in turn, will decrease the interaction elements because of the increased energy difference between the polyene molecular orbitals and the hydrogen 1s function, as compared with the suprafacial case. The result is that the activation enthalpy of the antarafacial shift is considerably higher than for the suprafacial shift. Both activation enthalpies have been calculated by Bingham and Dewar: 28.3 kcal/mol for the suprafacial [1,5] H shift in 1,3-pentadiene, and 37.0 kcal/mol for the antarafacial [1,5] H shift in the same system.[9]

Discussion, Scope, and Limitations

The literature on sigmatropic shifts reveals several examples of nominally "forbidden" rearrangements which nevertheless occur.[10] On the other hand, some "allowed" shifts have never been observed. The present perturbation treatment sheds more light on these phenomena. An "allowed" transition state can be hampered by the absence of a suitable (from a symmetry viewpoint) molecular orbital within a reasonable energy distance from the orbital of the migrating group. Further, interaction of the migrating group with subjacent orbitals of the π moiety might assist a migrating group in following a "forbidden" pathway, as already pointed out by Berson:[3]

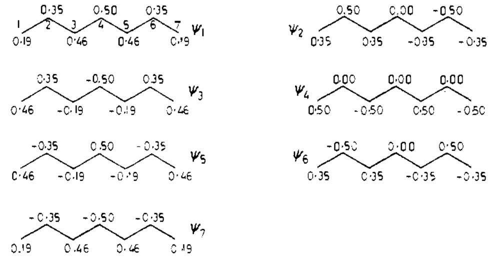


In a similar way "forbidden" antarafacial shifts are possible in a Möbius arrangement via asymmetric orbitals (the symmetric orbitals have a negative overlap in this Möbius arrangement), for example, the antarafacial [1,5] H shift in 1,3-pentadiene.

The present treatment shows that even in formally allowed transitions subjacent molecular orbitals are involved in the determining MO of the transition state.

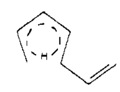
Another interesting aspect of the method is the possibility of predicting molecular conformations in the transition state from simple inspection of the Hückel MO's. Molecular parts with "wrong" signs of the coefficients will tend to avoid overlap with the migrating group. This was demonstrated in cyclohexadiene and cycloheptatriene where our calculations show that those parts of the framework bend away from the migrating group.

Quite obviously, the complexity of the molecular orbitals and the accompanying possibilities of combination grow rapidly with polyenes of increasing chain length. An example is formed by the 1,3,5-heptatriene system. The Hückel MO's are:



In principle, several shifts are possible in this system. Considering symmetry and coefficients, for example, shifts are possible via ψ_3 and ψ_5 from C_1 to C_7 or via ψ_4 from C_1 to C_5.

Meaningful predictions are difficult to make. In cases like this the more sensible approach will be to take recourse to INDO calculations right from the start. The perturbation theory combined with the Hückel orbitals will now serve mainly to indicate logical starting points. For example, a [1,5] H shift in 1,3,5-heptatriene will require a transition state as follows, in which interaction with the lone double bond might occur.



On the other hand, a [1,7] shift will require a homocycloheptatrienyl system. In order to determine which shift will be favored, the respective transition states of different pathways will have to be compared by way of INDO calculations. The suprafacial [1,7] H shift will be a hydride-like shift, comparable with the suprafacial [1,3] H shift in cyclopropene. The difference in absolute magnitude of the charge transfer calculated for the cyclopropenyl and cycloheptatrienyl systems seems relevant and is to be ascribed to the difference in ionization potentials. This way of comparing charge transfers is similar to the use of differences in electron affinities between the cyclopentadienyl, homocyclopentadienyl, and open pentadienyl systems.[8]

Another very obvious extension of the present approach is the treatment of homogenous catalysis of rearrangements by transition metals. Two possibilities are to be distinguished: acceleration of allowed transitions and transformation of forbidden rearrangements into allowed ones. By interaction of the migration framework with the metal, the orbitals of both will be affected. As a result, also the interaction terms with potential migrating groups will be altered.

Recently, a similar theory of catalytic activity has been worked out.[11]

References and Notes

(1) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) *ibid.*, **87**, 2046 (1965); (c) *ibid.*, **87**, 2511 (1965).

(2) A. G. Anastassiou, *Chem. Commun.*, 15 (1968).

(3) (a) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **92**, 1096 (1970); (b) J. A. Berson and L. Salem, *ibid.*, **94**, 8917 (1972).

(4) O. Eistenstein, J.-M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971).

(5) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971).

(6) G. A. Shchembelov and Yu. Ustynyuk, *Theor. Chim. Acta*, **24**, 389 (1972).

(7) J. R. de Dobbelaere, J. W. de Haan, H. M. Buck, and G. J. Visser, *Theor. Chim. Acta*, **31**, 95 (1973).

(8) J. R. de Dobbelaere, E. L. van Zeeventer, J. W. de Haan, and H. M. Buck, *Theor. Chim. Acta*, **38**, 241 (1975).

(9) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).

(10) (a) G. R. Krow and J. Reilly, *J. Am. Chem. Soc.*, **97**, 3837 (1975); (b) see R. K. Lustgarten and H. G. Richey, Jr., *ibid.*, **96**, 6393 (1974), and ref 54-56.

(11) A. Imamura and T. Hirano, *J. Am. Chem. Soc.*, **97**, 4192 (1975).

(12) The experimental and theoretical activation enthalpies are in good agreement. See ref 8.

(13) The geometry of the cyclopentadiene transition state has been optimized with respect to eight variables (see Table II). A fully optimized transition state as calculated by Ustynyuk et al. shows no essential difference.[6] Our optimization resulted in an approximately symmetric structure as can be derived from Table II, which shows β approximately equal to γ and $\delta = \epsilon$. Consequently for all other cyclic systems the symmetry plane was assumed, while optimizing all other variables. In all systems it was assumed that the transition state has only one negative force constant.

(14) The reason for the cyclic symmetry properties in the present case is probably to be ascribed to the enhanced flexibility of the system. This enables a closer approach between migration origin and terminus in the transition state as compared to cycloheptatriene. In the acyclic pentadienyl system therefore the p_z orbitals of migration origin and terminus overlap in order to form a partial π bond. In the cycloheptatriene system, the two carbon atoms involved are held apart by the rather rigid ethylene moiety.

(15) NOTE ADDED IN PROOF. In reality the H_{1s} level lies about 1β ($\beta = -2.4$ eV) below the zero level, but this does not affect any of the conclusions.

Global Topology of Triatomic Potential Surfaces

Ernest R. Davidson

Contribution from the Chemistry Department, University of Washington, Seattle, Washington 98195.

Received July 26, 1976

Abstract: A new coordinate system for describing triatomic molecules is introduced. Within this coordinate system various topological features of importance are discussed. Particular emphasis is placed on the Jahn-Teller theorem and the resulting branch-cuts on the potential surface.

Potential surfaces are of importance in chemistry for explaining geometry, spectra, and chemical reactions. Triatomic potential surfaces (especially for excited states) have recently become of even greater interest because of work in plasmas, lasers, and atmospheric pollution associated with various aspects of the energy crisis. Unlike diatomic molecules which are fairly well characterized, polyatomic potential surfaces are only vaguely understood. While the general features expected for a diatomic molecule potential curve over the whole range of possible molecular conformations are well known, such a global topology for triatomic molecules is not usually discussed.

General Considerations

A potential surface, for the purpose of the present discussion, will be a function $U(X_1, \ldots, X_K)$ generated as one of the solutions to an electronic (Born-Oppenheimer) Schrödinger equation

$$H\psi(r_1 \ldots r_N; X_1 \ldots X_K) = U(X_1 \ldots X_K)\psi(r_1 \ldots r_N; X_1 \ldots X_K) \qquad (1)$$

where the r_i are electronic coordinates and the X_i are coordinates for describing the conformation of the nuclei in the molecule. The operator H in the simplest approximation is just the usual electronic hamiltonian involving electronic kinetic energy and coulomb interactions,

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - e^2 \sum_i \sum_A Z_A r_{iA}^{-1} + e^2 \sum_{A \neq B} Z_A Z_B r_{AB}^{-1} + e^2 \sum_{i \neq j} r_{ij}^{-1} \qquad (2)$$

For discussing a potential surface U it is sufficient to pick the complete set of coordinates X_i which affect the shape or size of the molecule but not its position or orientation in space. Hence for three or more atoms K is $3N_A - 6$ where N_A is the number of atoms (for a global discussion of U the question of whether the molecule is "linear" or not does not enter).

The Schrödinger equation for a molecule actually defines an infinite family of potential surfaces, of course. Because of the possibility of intersections, great care must be exercised in identifying a surface. In general, there are certain elements of symmetry such as electron spin which are global in nature (i.e., commute with H for all values of the X_i). Diatomic molecules are always linear and triatomics are always planar, while larger polyatomics have no global geometric symmetry. In any case, the electronic wave functions and associated potential surfaces can be labeled with whatever global symmetry is present. Beyond that, at each set of nuclear coordinates X_i the potential surfaces of the same global symmetry are simply numbered in order of increasing energy. With this convention the kth potential energy surface of symmetry Γ, $U_k(\Gamma)$, will be a continuous function of the X_i. For diatomic molecules this convention is known to lead to smooth (differentiable) functions U_k (except for the $2s\sigma_g$ and $3d\sigma_g$ curves[1] for H_2^+) which do not intersect other curves of the same symmetry[2] in the open interval $0 < R < \infty$.

By global topology is meant the study of the shape and structure of the potential energy surface over the entire range of the nuclear position coordinates. Certain kinds of structural features are well-known. For example, wherever two nuclei coincide the potential surface has a coulomb singularity. This singularity is easily removed by subtracting the nuclear–nuclear repulsion from U to get the "electronic energy" U_e

$$U_e = U - e^2 \sum_{A \neq B} Z_A Z_B r_{AB}^{-1} \qquad (3)$$