Symmetry Selection Rules for Sigmatropic Migrations in C_nH_{n+1} Monocycles

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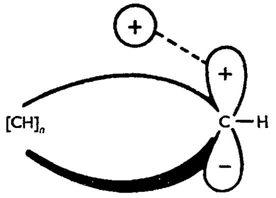
ONE of the many sets of orbital symmetry rules recently advanced by Woodward and Hoffmann deals with the subject of concerted allylic shifts, termed sigmatropic rearrangements.[1] The selection rules in this case were derived strictly on the basis of acyclic models, but were shown to account correctly for observed migrations within acyclic as well as cyclic systems. The success of the rules in describing migrations in cyclic systems[2] is puzzling, since the acyclic models employed in the derivation of these rules are incapable of allowing for the necessary cyclic π-interaction introduced by the developing p-orbital at the migration origin of a cyclic system. For example, an appropriate representation of the transition state leading to migration of hydrogen within a reactant containing $n\pi$ electrons is shown in (I).



Molecular orbital theory[3] requires that any odd-membered monocyclic C_nH_n π-system in a regular polygonal arrangement, has all its molecular orbitals (MO's), except that of lowest energy, paired in doubly degenerate sets. Such systems are therefore not amenable to frontier-orbital symmetry criteria since the frontier orbitals always occur in pairs and the members of each pair invariably differ in their symmetry properties. However, theory also predicts that C_nH_n odd-membered monocycles containing $n\pi$ electrons (radicals) will be subject to energetically beneficial skeletal distortions, so that their lowest energy arrangement will not possess regular polygonal symmetry.[4] The net result of such distortions will be to lift the degeneracies of the various MO's so that distorted $n\pi$ electron odd-membered monocycles become amenable to frontier-orbital symmetry criteria. With this in mind, and also because the presence of the migrating group would quite likely prevent the ring from assuming regular polygonal symmetry in the transition state leading to a sigmatropic shift, we examined the symmetry requirements for such migrations by employing polygons, slightly distorted in the direction of the reactants, as models.† In each case the frontier orbital of interest was chosen on the basis of first order perturbation theory[4] which requires that splitting of a pair of degenerate MO's upon partial bond fixation (distortion) occur in such a way as to increase the energy of the MO with the largest number of nodes crossing formal double bonds and to decrease the energy of the alternate MO. The results obtained in this fashion are collected in the Figure and the Table.

All frontier orbitals shown in the Table except ψ_4 of C_5H_5 were obtained on the basis of the nodal properties of the MO's shown in the Figure. The excited configuration of C_5H_5 could not be determined by simple inspection of ψ_4 and ψ_5 since both of these MO's possess the same number of nodes across double bonds. The choice in favour of ψ_4 was arrived at from an explicit MO computation employing appropriate parameters.‡

The symmetry restrictions tabulated are in perfect agreement with all available experimental observations§ and thus correspond quite closely to those derived on the basis of the less complete acyclic models. The two models do, however, lead to conflicting predictions concerning photochemical migrations within the cycloheptatriene system. Thus, use of an acyclic model[1] leads to the conclusion that only [1,3] and [1,7] shifts are allowed whereas on the basis of a cyclic model *all* shifts are permitted since the migration origin coincides with a node (ψ_5). Unfortunately, experiment does not provide a choice between the two predictions, as photochemical migrations in cycloheptatrienes occur specifically in a 1,7-fashion[1,2] which is allowed by both models.¶

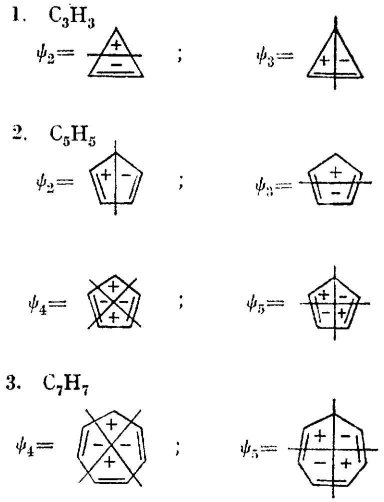


FIGURE. *Symmetry properties of pertinent MO's of cyclopropenyl, cyclopentadienyl, and cycloheptatrienyl radicals.*

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† It was correctly pointed out by a referee that the magnitude of the Jahn–Teller splitting of degenerate MO's in C_nH_n odd-membered monocycles is quite small($\simeq$1 kcal./mole) and as such cannot allow for a firm choice of frontier molecular orbitals. It should be noted however that the distortion of the ring and consequently the energy difference between initially degenerate MO's will undoubtedly be further increased by the presence of the migrating group, since this, is quite likely, not equally bound to all the ring carbons in the transition state leading to its migration. Thus, for a sigmatropic shift in which the migrating group is strongly associated with the migration origin (early transition state) the magnitude of the splitting may be reasonably approximated by the appreciable energy difference between the corresponding MO's of an appropriate $C_{n-1}H_{n+1}$ acyclic olefin, which correlate well with the MO's of the C_nH_n cyclic system. Compare for example the symmetry properties of ψ_3 and ψ_4 of hexatriene with those of ψ_4 and ψ_5 of C_7H_7.

Unfortunately, the general lack of symmetry in the transition states describing sigmatropic shifts precludes the use of the more rigorous correlation procedure recently advanced by H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2045 and R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

‡ The resonance integrals employed in the calculation were: $H_{12} = H_{15} = 0\cdot6\beta$, $H_{23} = H_{45} = \beta$ and $H_{34} = 0\cdot8\beta$. The MO energies thus obtained were $\epsilon(\psi_4) = \alpha - 1\cdot14\beta$ and $\epsilon(\psi_5) = \alpha - 1\cdot49\beta$.

§ For an exhaustive list of experimental results see reference 1.

¶ The prediction that photochemical shifts within the cycloheptatriene system are not subject to any symmetry restrictions, may be generalized to include all C_nH_{n+1} π-monocycles containing $2k + 3$ carbons ($k = 0,2,4\ldots$) since in such systems, the lowest energy unoccupied MO invariably possesses a node across C(1).

TABLE

Symmetry restrictions for suprafacial, sigmatropic migrations of hydrogen (H) within C_nH_{n+1}, *monocycles*

	Thermal		Photochemical	
n	Confign.	Allowed shifts	Confign.	Allowed shifts
3	$\psi_1^2\psi_2^1$	none	$\psi_1^2\psi_3^1$	all (1,3)
5	$\psi_1^2\psi_2^2\psi_3^1$	1,5	$\psi_1^2\psi_2^2\psi_4^1$	1,3
7	$\psi_1^2\psi_2^2\psi_3^2\psi_4^1$	1,5	$\psi_1^2\psi_2^2\psi_1^2\psi_5^1$	all (1,3; 1,5; 1,7)

Finally it should be noted that the approach employed here in order to describe homolytic shifts of hydrogen in three ring systems may be readily applied to larger rings[5] and extended to include heterolytic shifts of hydrogen (H^+, H^-),** and possibly of other groups, as well.[6]

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** Care should be exercised in employing the present procedure to describe cases in which the ring is associated with $4m + 2\pi$ electrons in the course of the migration, since such rings, when free, are known to possess regular polygonal arrangements. Thus, the method may not be employed to predict the course of hydride shifts in cyclopropenes and cycloheptatrienes or of proton shifts in cyclopentadienes and cyclononatetraenes.

[1] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.

[2] For two recent, arbitrary applications of the rules to group shifts in substitute cycloheptatrienes, see: L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, 1967, **89**, 1880 and G. W. Borden, O. L. Chapman, R. Swindel, and T. Tezuka, *J. Amer. Chem. Soc.*, 1967, **89**, 2979.

[3] See, for example, A. Streitwieser, jun., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1961, ch. 10.

[4] For a lucid account see, L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, 1966, ch. 8.

[5] The MO's of a large number of monocyclic π systems are available: Heilbronner and Straub "Hückel Molecular Orbitals," Springer Verlag, New York, 1966.

[6] No firm predictions concerning homolytic or heterolytic migrations of groups other than hydrogen can be made, since any group having ready access to *p*-orbitals can, in principle, migrate in one of two distinct ways (references 1 and A. G. Anastassiou and R. P. Cellura, *Chem. Comm.*, 1967, 762).