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Hetero-atom Effect on the Benzene-Prismane and Related Reactions Perturbation Density Matrix of Intramolecular Cycloadditions

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Synopsis. A formalism is presented for studying intramolecular cycloadditions in terms of their corresponding perturbation density matrices. The effect of hetero-atom on a particular *intra*molecular *cycloaddition* is discussed.

Although the conversion of benzene into prismance (I) might formally be considered as a $(\pi 2_s + \pi 2_a + \pi 2_a)$ intramolecular cycloaddition, and inspite of the fact that such a process is thermally "allowed," Reaction 1[1] and the related ones, Reaction 2 and 3, as well as the corresponding cycloreversions are not observed in the ground state.[2] On the other hand, derivatives of the oxa analogue (IV) of quadricyclene (III) are smoothly transformed into the corresponding oxepines when heated[3] (backward of Reaction 4 in Fig. 1). Conservations of orbital symmetry do not provide a clear explanation of such intramolecular cycloadditions. In this note a formalism is given in which such reactions are quantitatively described.

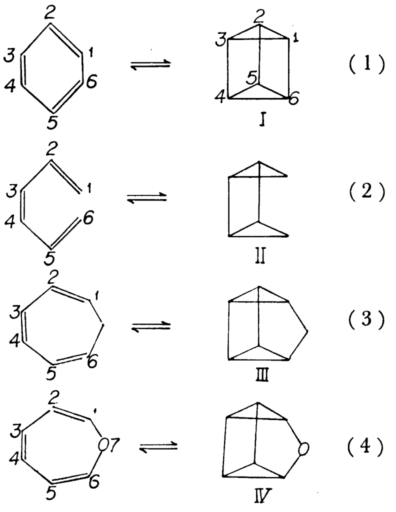

Fig. 1.

For a particular intramolecular cycloaddition reaction, calculations proceed as follows:

(1) An $n \times n$ perturbation matrix, P, is written to describe the particular intramolecular process, where n is the number of p-orbitals in conjugation in the starting polyene. The elements of such a matrix will vanish except those at positions where sigma resonance integrals change from a value of zero to some finite value as a result of overlap during the process.

(2) The initial perturbation ΔE which is a measure of the feasibility of a particular cycloaddition is given by

$$\Delta E = 1/2 \sum_{i=1}^{n/2} e_i \langle \phi_i | P | \phi_i \rangle = \sum_{r>s} \sum C_{ir} C_{is} \gamma_{rs}, \qquad (1)$$

where

$$\gamma_{rs} = \langle \chi_r | P | \chi_s \rangle = \begin{cases} -|\gamma| & \text{(r, s; interacting)} \\ 0 & \text{(otherwise)}. \end{cases}$$

In Eq. 1, e_i is the number of electrons in the ith MO. The eigenvectors $|\phi_i\rangle$ and $\langle\phi_i|$ are the SCF column and row vectors of the ith MO. The factor of 1/2 avoids counting a particular interaction twice. Matrix elements such as $\langle\phi_i|P|\phi_i\rangle$ form the main diagonal in the corresponding "perturbation density matrix."

Table 1. Initial perturbations[a)] ΔE for studied intramolecular cycloaddition reactions (Fig. 1)

Reaction	Contribution to ΔE from	ΔE_{total}	Exptl.
1	ϕ_1, $\Delta E_1 = -1.000$		
	ϕ_2, $\Delta E_2 = 1.000$		
	ϕ_3, $\Delta E_3 = 0.6667$	0.6667	Not observed
2, 3	ϕ_1, $\Delta E_1 = -3.6370$		
	ϕ_2, $\Delta E_2 = -0.7282$		
	ϕ_3, $\Delta E_3 = 4.3880$	0.0228	Not observed
4	ϕ_1, $\Delta E_1 = -0.1654$		
	ϕ_2, $\Delta E_2 = -2.0588$		
	ϕ_3, $\Delta E_3 = -0.6988$		
	ϕ_4, $\Delta E_4 = 2.7304$	-0.1926	Observed

a) All values are divided by $|\gamma|$. A negative ΔE implies stabilization of the system and *vice-versa*.

Table 1 outlines the results of calculations using a previously described version of the SCF-PPP method.[4] The following points are worth observing:

(1) While the dominating interactions are always contributed by HOMO, one should not draw a conclusion based upon such an interaction alone. Rather, all interactions must be considered. Reaction 4 is particularly illustrative of this point.

(2) Examination of Reactions 2 and 3 on one hand and Reaction 4, on the other, makes it clear that the HOMO provides the most destabilizing component to the cycloaddition process and that such destabilization is decreased upon introduction of the hetero-atom in the molecule. In simple terms one might say that the introduction of an oxygen atom in quadricyclene (III), "buffers" an "energy-raising" component into the transition state of its cycloreversion.

References

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