Configuration Interaction and the Woodward–Hoffmann Rules. 1. Electrocyclic Reactions[†]

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Abstract: The effect of configuration interaction on the orbital symmetry control of electrocyclic reactions is investigated using the Hueckel–Hubbard Hamiltonian with full CI. For thermal reactions and the reactions of triplets, CI does not strongly affect the qualitative predictions obtained from Hueckel configuration energies. For excited singlets the effect of CI is, in general, more complex, suggesting that the observed stereospecificity of these reactions may be due to factors other than orbital symmetry.

I. Introduction

A well-known failing of the Woodward–Hoffmann,[1] Longuet-Higgins–Abrahamson,[2] and related formalisms[3] is that these approaches do not explicitly take into account electron repulsion. As a result, selection rules for the pericyclic reactions of states of different spin multiplicity arising from the same MO configuration are found to be identical. Further, the neglect of electron repulsion implies that configuration interaction cannot be properly included and thus excited state orderings sensitive to electron correlation are not adequately treated.

In this paper we obtain singlet and triplet reaction paths for the electrocyclic reactions of the even electron systems C_3 through C_8 using the Hueckel–Hubbard Hamiltonian with full configuration interaction at the π-electronic level.[6] The Hueckel–Hubbard approach is the simplest way of invoking configuration interaction while retaining the conceptual simplicity of the Hueckel approach. For example, the multiplicity of the ground state of planar cyclobutadiene is correctly predicted to be singlet,[7] in apparent agreement with experiment,[8-9] and with ab initio extended basis calculations which include sufficient CI[10] and in disagreement with the MINDO/3 predictions.[11] This model also gives a good estimate of the singlet–triplet splitting in trimethylenemethane[12] and correctly predicts the presence of a low-lying $^1E_{2g}$ state in benzene[13] and low-lying ^1A_g states in linear polyenes.[14] The last result is obviously important in photochemical electrocyclic reactions. Further, the Hubbard interaction is the simplest one which correctly correlates MO and valence bond states.[15]

For computational convenience, the calculations are carried out in the spin-free unitary group formulation of the many-electron problem.[16] Where possible, the results are compared to more elaborate calculations.

II. The Reaction Hamiltonian

We write the Hueckel–Hubbard Hamiltonian for an electrocyclic reaction of a ρ carbon atom system as

$$\mathbf{H}_h{}^{\mp}(x) = \mathbf{H}_h{}^{\mp}(x) + \mathbf{H}_I \tag{2.1}$$

The first term of eq 2.1 is the N-electron Hueckel Hamiltonian for the reaction and may be partitioned into three parts:

$$\mathbf{H}_h{}^{\mp}(x) \equiv (1 - x)\mathbf{H}_\sigma{}^{\mp} + x\mathbf{H}_\pi + \mathbf{H}_{\pi'} \tag{2.2}$$

Here $\mathbf{H}_\sigma{}^{\mp}$ corresponds to the σ bond which is formed or broken during the isomerization and the $-(+)$ sign refers to the disrotatory (conrotatory) path. $\mathbf{H}_\pi$ corresponds to the π bonds broken or formed by the twisting of the terminal methylene groups. Thus $x = 0$ corresponds to the cyclic isomer and $x = 1$ corresponds to the linear polyene. The remaining π bonds are assumed to remain constant along the reaction coordinate x and are contained in the term $\mathbf{H}_{\pi'}$. In terms of the infinitesimal generators of the unitary group $U(\rho)$, these three terms are

$$\mathbf{H}_\sigma{}^{\mp} = \mp sT(\mathbf{E}_{1\rho} + \mathbf{E}_{\rho 1}) \tag{2.3}$$

$$\mathbf{H}_\pi = -T(\mathbf{E}_{12} + \mathbf{E}_{21} + \mathbf{E}_{\rho-1,\rho} + \mathbf{E}_{\rho\rho-1}) \tag{2.4}$$

$$\mathbf{H}_{\pi'} = -T\sum_{r=2}^{\rho-2} (\mathbf{E}_{rr+1} + \mathbf{E}_{r+1r}) \tag{2.5}$$

The parameter s is introduced to allow for weakened σ bonds in small rings. For C_3 we take $s = 1.25$ and for C_4, $s = 1.5$; otherwise, $s = 2.0$. T is the negative of the Hueckel β.

The last term of (2.1) is the Hubbard interaction. In terms of the $U(\rho)$ generators we have

$$\mathbf{H}_I = \frac{I}{2}\sum_{r=1}^{\rho} (\mathbf{E}_{rr}{}^2 - \mathbf{E}_{rr}) \tag{2.6}$$

where I is an empirical parameter. The parameter choice $2T = I = 6.0$ eV is used in these calculations since this value correctly fits the unpaired electron density of allyl radical[17] and the spectrum of benzene.[13]

For $I = 0$, eq 2.1 reduces to the usual treatment. For $I \neq 0$, the reaction paths are computed by diagonalizing eq 2.1 in the full spin-free configuration spaces of the desired multiplicity for several values of x. For $\rho \leq 6$, this may be done quite easily by direct diagonalization. However, since the full configuration spaces for $\rho = 7$, $N = 6$ have dimensions 490 (singlet) and 588 (triplet) and for $\rho = N = 8$, 1764 (singlet) and 2352 (triplet), Davidson's method[18] for obtaining extreme eigenvalues was employed. The matrix elements of the infinitesimal generators were obtained using the closed-form expressions of Louck[19] and of Paldus.[20]

The eigenvalues of eq 2.1 exhibit a striking particle-hole symmetry of which the pairing symmetry of alternant hydrocarbons is a special case.[21,22] The origin of this symmetry within the unitary-group formulation has been discussed elsewhere.[23] The results are as follows: If $E_N{}^{\mp}(x)$ is an N-particle eigenvalue ($N \leq \rho$) of $H^{\mp}(x)$ on the full configuration space then there will exist a $(2\rho - N)$-particle eigenvalue $E^{\mp}{}_{2\rho-N}(x)$ such that

$$E^{\mp}{}_{2\rho-N}(x) = \begin{cases} E_N{}^{\mp}(x) + I(\rho - N), & \rho \text{ odd} \\ E_N{}^{\mp}(x) + I(\rho - N), & \rho \text{ even} \end{cases} \tag{2.7}$$

It follows that when ρ is odd, the disrotatory surface for the cation, for example, is identical with the conrotatory surface of the anion. Also, reactions of neutral radicals are predicted to be nonstereospecific, as has been previously exemplified for $\rho = 3$.[5] When ρ is even, the anionic and cationic surfaces are identical and exhibit the same stereochemical preferences. This

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Table I. Difference in Computer Barrier Heights for $I = 2$ and $I = 0$. Here $\Delta E_a \equiv E_a(\text{dis}) - E_a(\text{con})$ and $\Delta(\Delta E_a) \equiv |\Delta E_a(I = 0)| - |\Delta E_a(I = 2)|$

	S_0			T_1		
ρ	$\Delta E_a(I = 2)$	$\Delta E_a(I = 0)$	$\Delta(\Delta E_a)$	$\Delta E_a(I = 2)$	$\Delta E_a(I = 0)$	$\Delta(\Delta E_a)$
3	−0.75	−0.92	0.17	0.50	0.50	0.00
4	0.53	1.00	0.47	−0.22	−0.53	0.31
5	0.73	0.82	0.09	−0.51	−0.60	0.09
6	−0.39	−0.84	0.45	0.29	0.68	0.39
7	−0.61	−0.72	0.11	0.45	0.53	0.08
8	0.29	0.66	0.37	−0.22	−0.54	0.32
	S_1 (ring closure)			S_1 (ring opening)		
3	1.00	0.59	−0.41	1.00	0.47	−0.53
4	−0.59	−0.90	0.31	0.21	−0.53	*a*
5	−0.67	−0.60	−0.07	−0.85	−0.60	−0.25
6	0.21	0.70	0.49	0.00	0.68	0.68
7	0.53	0.53	0.00	0.53	0.53	0.00
8	−0.05	−0.54	0.49	−0.05	−0.54	0.49

[a] Prediction reversed.

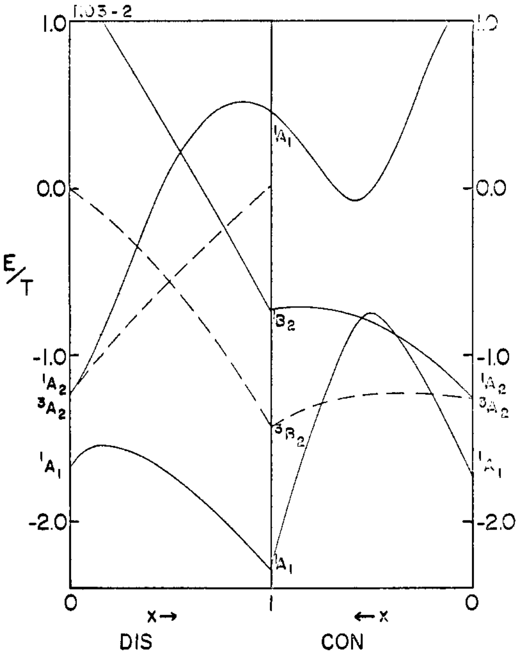

Figure 1. Hueckel-Hubbard reaction paths for $\rho = 3$, $N = 2$. — indicates singlets, - - - indicates triplets.

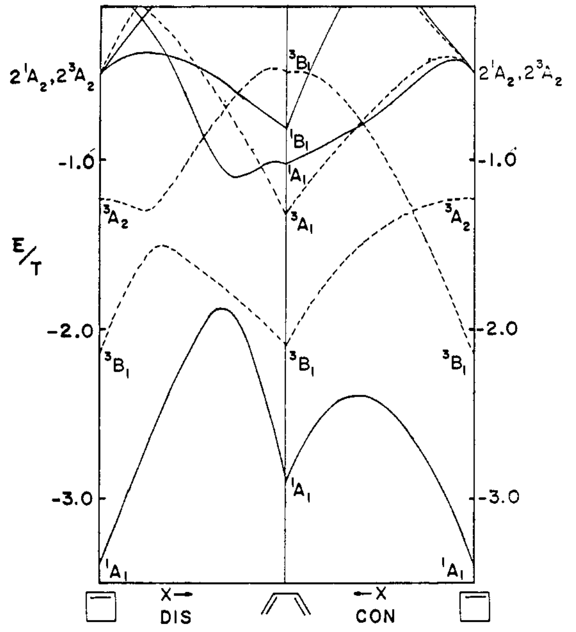

Figure 2. Hueckel-Hubbard reaction paths for $\rho = N = 4$. — indicates singlets, - - - indicates triplets.

particle-hole symmetry puts no restrictions on the reaction paths when $N = \rho$ (even).

These relationships are exact for the Hubbard and PPP Hamiltonians[23] for sigmatropic shifts[24] and cycloaddition reactions[25] as well as electrocyclic reactions. Furthermore, they are obeyed approximately in more elaborate calculations such as INDO,[26] MINDO/3,[27] and ab initio[28] calculations.

III. Results and Discussion

The computed reaction paths for $\rho = 3$ and 4 are given in Figures 1 and 2. The Hueckel-Hubbard barrier heights for the thermal and photochemical reactions have been computed graphically from plots similar to these for $3 \leq \rho \leq 8$. The results are summarized in Table I. We discuss the results for S_0, S_1, and T_1 separately.

A. Thermal Reactions. The stereospecificity of these reactions as determined by comparing the various barrier heights are in agreement with the Woodward-Hoffmann predictions. Further, there is semiquantitative agreement with more elaborate calculations. A comparison of the C_3 and C_4 results with various semiempirical and ab initio calculations is given in Table II.

An estimate of the effect of π configuration interaction on the difference in barrier heights for the two modes may be obtained by comparing the Hueckel-Hubbard barrier heights computed at $I = 2$ with those at $I = 0$ (no CI). The results of this comparison are given in Figure 3a. It is seen that the effect of CI is to reduce the difference in barrier heights for all ρ, but more so for ρ even than for ρ odd. This has in fact been observed in ab initio CI calculations on C_3 and C_4.[29,30] This effect is in fact expected in the Hueckel-Hubbard calculations since the electron repulsion in that model is proportional to the number of doubly occupied atomic orbitals in each component of the many-electron wave function. The fact that this effect is observed in the ab initio calculations is suggestive that the qualitative effect of CI may be strongly dependent on Hubbard-type interactions.

B. Singlet Photochemistry. Here, the barrier heights are determined by finding the point of highest energy along the reaction path between the reactants and the first local minimum in S_1, where we assume that conversion to S_0 is most efficient.[31-33]

Table II. Comparison of Various Estimates of ΔE_a for Thermal Electrocyclic Reactions. Units Are eV

ρ	Hueckel ($I = 0$)	Hueckel–Hubbard ($I = 2$)	MINDO/3[27]	Ab initio[29,30]	
				SCF	SCF–CI
3	−2.76	−2.25	−1.29	−3.52	−3.26
4	3.00	1.59	1.56[a]	2.17	0.61
5	2.46	2.19			
6	−2.92	−1.17			
7	−2.16	−1.83			
8	1.98	0.82			

[a] No symmetry retained in forbidden mode.

The stereochemical predictions for the ring closure are in agreement with the Woodward–Hoffmann predictions. However, for ρ even the excited state which ultimately becomes involved in the allowed photochemical processes is the "nonspectroscopic" A state of the linear polyene. The Hueckel–Hubbard Hamiltonian is the simplest which correctly predicts this feature, first discussed by van der Lugt and Oosterhoff[31] and later supported by more accurate calculations.[34] In the ring-opening reaction, the stereospecificity tends to be greatly reduced. The $\rho = 4$ case even shows a reversal in the Woodward–Hoffmann prediction. Again, this behavior is due to the fact that for intermediate points along the reaction path the lowest lying singlet is a covalent-type state[15] rather than the spectroscopic singlet treated by the orbital symmetry approaches.[1,2] This general behavior has also been observed in more comprehensive calculations for $\rho = 4$.[31,32,34] For $\rho = 6$, this might allow the geometrical effects discussed by Bauld[26] et al. in thermal $C_6^{-}\cdot$ isomerizations to be of significance in C_6 photochemical ring openings.

The effect of CI on the various S_1 barrier heights is plotted in Figure 3c,d. The effect appears to fall off rapidly as ρ increases. We also note that, unlike the thermal case, the effect of CI is not always in the same direction.

C. Triplet Reactions. The selection rules for the triplet state are qualitatively similar to those for S_1 with the exception that in no case is there a local minimum between reactants and products. The results are summarized in Table I. As in the thermal reactions the effect of CI is greatest for the even systems (Figure 3b). We have assumed here that only T_1 is involved in triplet reactions. This has been verified in a number of cases[35,36] while in one exceptional case higher triplets have been implicated.[37]

IV. Conclusion

The use of the Hueckel–Hubbard Hamiltonian to generate reaction surfaces for electrocyclic reactions provides a simple extension of Hueckel theory and orbital selection rules. We have chosen the Hubbard interaction over the PPP interaction since the Hubbard interaction is geometry independent. That is, it allows all spatial symmetry properties to be determined at the orbital level, as Woodward and Hoffmann would have it. Further, the various parameterizations of the PPP Hamiltonian have been devised to fit the spectra of molecules and not excited state reaction paths. While this is also true for our Hubbard parameterization, the qualitative effects of the two interactions are quite similar and it is therefore doubtful whether inclusion of a PPP-type interaction would represent a significant refinement of the approach, considering the kind of conclusions we have made.

In taking this approach, we have isolated the effect of a single factor, π configuration interaction, on the Woodward–Hoffmann rules. The results, in general, substantiate the Woodward–Hoffmann approach, since in most cases (particularly for S_0 and T_1) the stereoselectivity does not change qualitatively. The stereochemistry of the S_1 reactions, however, is open to question and may involve factors other than simple π electronics.

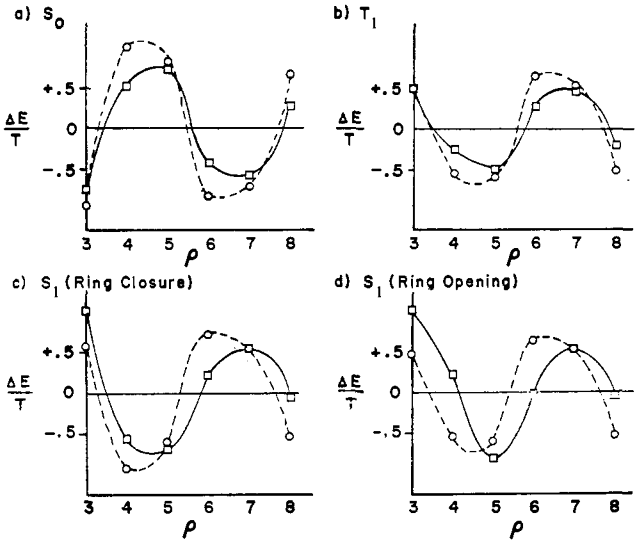

Figure 3. Differences in barrier heights for $I = 0$ (- - -) and $I = 2$ (—). $\Delta E \equiv E_a(\text{dis}) - E_a(\text{con})$.

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