

# Configuration Interaction and the Woodward-Hoffmann Rules. 2. Sigmatropic Shifts

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**Abstract:** The Hückel-Hubbard theory is applied to thermal and photochemical [1,3], [1,4], [1,5], and [1,6] sigmatropic shifts. Inclusion of electron correlation is explicit in this treatment and gives considerably more detailed information than the usual molecular orbital theories. Qualitative differences in low-lying excited state surfaces of differing spin symmetry are found. These differences appear to be important in the observed photochemistry of 1,5-dienes.

## I. Introduction

Sigmatropic rearrangements are uncatalyzed intramolecular reactions involving the migration of a  $\sigma$  bond, adjacent to a  $\pi$ -electron system, to a new position in the molecule. Such reactions occur thermally in some systems, whereas in others they only occur photochemically. In the specific case of the [1, $j$ ] shift involving migration of an asymmetric carbon, the reaction occurs with either retention or inversion of configuration at that center. Theoretical considerations based on orbital theory, such as those of Zimmerman<sup>1</sup> and Woodward-Hoffmann,<sup>2</sup> are found to be quite successful in interpreting this behavior and are widely used. However, in some cases the observed photochemistry is different for states of different multiplicity which arise from the same MO configuration. Since reaction surfaces based on MO considerations are identical for such states, electron repulsion must be explicitly treated in order to account for the observed chemistry. This can be most simply accomplished by Hückel-Hubbard theory.<sup>3,4</sup> In this paper we obtain reaction paths for low-lying states for the [1, $j$ ] sigmatropic shifts ( $j = 3, 4, 5$ , and 6) using the Hückel-Hubbard approach with full configuration interaction among the  $\pi$  electrons.

## II. Development of the Reaction Hamiltonian

In this section we will develop the Hückel-Hubbard reaction Hamiltonian for the suprafacial [1, $j$ ] shift of an asymmetric carbon atom. Figure 1 depicts a [1,3] shift in a Hückel MO framework. We employ Zimmerman's concept of a Möbius transition state (right-hand side of the figure) which corresponds to a shift with inversion of configuration. (Note sign change in MO matrix.) The left-hand side of the figure represents the alternate path, namely, that which retains configuration and is given a usual Hückel representation. If one assumes a transition state lying midway between reactant and product, then  $\beta' = \frac{1}{2}\beta$ . Analysis of these reaction paths for both ground and excited MO configurations, using Woodward-Hoffmann or Longuet-Higgins and Abrahamson methods,<sup>5</sup> predicts that the thermal rearrangement occurs with inversion and that the photochemical process occurs with retention of configuration.

As we shall note in the next section, intramolecular photochemical rearrangements sometimes depend on the spin symmetry of the reactant undergoing rearrangement. Since the low-lying excited states involved are degenerate in the MO picture above, we include electron repulsion explicitly by considering the corresponding Hückel-Hubbard model.

The Hückel-Hubbard Hamiltonian for a [1, $j$ ] shift involving  $j + 1$  carbon atoms is written

$$H^\mp(x) = H_h^\mp(x) + H_I \quad (2.1)$$

where  $x$  is a reaction coordinate,  $H_h^\mp(x)$  is the  $n$ -electron

Hückel Hamiltonian (Figure 1 is the one-electron Hückel-Hamiltonian matrix),  $H_I$  is the Hubbard electron repulsion interaction, and the  $-(+)$  sign refers to the Möbius (normal Hückel) path. We partition  $H_h^\mp(x)$  as follows:

$$H_h^\mp(x) = (1-x)(H_\sigma + H_\pi) + x(\mp H_{\sigma'} + H_{\pi'}) + H_{\pi''} \quad (2.2)$$

Here  $H_\sigma(H_\pi)$  refers to the  $\sigma(\pi)$  bonds being broken,  $H_{\sigma'}(H_{\pi'})$  refers to the ones being formed, and  $H_{\pi''}$  contains  $\pi$  bonds which are assumed constant along the reaction path,  $0 < x < 1$ . In terms of the infinitesimal generators of the unitary group  $U(\rho)$ ,

$$\begin{aligned} H_\sigma &= -2T(\mathbf{E}_{12} + \mathbf{E}_{21}) \\ H_{\sigma'} &= -2T(\mathbf{E}_{1,j+1} + \mathbf{E}_{j+1,1}) \\ H_\pi &= -T(\mathbf{E}_{j,j+1} + \mathbf{E}_{j+1,j}) \\ H_{\pi'} &= -T(\mathbf{E}_{23} + \mathbf{E}_{32}) \\ H_{\pi''} &= -T \sum_{r=3}^{j-1} (\mathbf{E}_{r,r+1} + \mathbf{E}_{r+1,r}) \end{aligned} \quad (2.3)$$

Here  $T$  is the negative of the Hückel parameter  $\beta$ , and we note that  $H_{\pi''} = 0$  for the [1,3] shift.

The last term in the expression 2.1 is

$$H_I = \frac{I}{2} \sum_{r=1}^{j+1} (\mathbf{E}_{rr}^2 - \mathbf{E}_{rr}) \quad (2.4)$$

where  $I$  is an empirical parameter. We chose  $I = 2T = 6.0$  eV since this value correctly predicts both the unpaired electron density of the allyl radical<sup>6</sup> and the observed spectrum of benzene.<sup>7</sup>

The eigenvalues of eq 2.1 have a particle-hole symmetry which has been discussed in detail elsewhere.<sup>8</sup> For our purposes the results are as follows: If  $E_N^\mp(x)$  is a  $N$ -particle eigenvalue ( $N \leq j + 1$ ) of  $H^\mp(x)$ , then there exists a  $(2j + 2 - N)$  particle eigenvalue  $E_{(2j+2-N)}^\mp(x)$  such that

$$E_{(2j+2-N)}^\mp(x) = \begin{cases} E_N^\pm(x) + (j + 1 - N)I, & j \text{ even} \\ E_N^\mp(x) + (j + 1 - N)I, & j \text{ odd} \end{cases} \quad (2.5)$$

It follows that when  $j$  is even (e.g., [1,4] shift), the surface for inversion of the cation, for example, is identical with the retention surface for the anion. Also, for even  $j$ , the reactions of neutrals are predicted to be nonstereospecific. When  $j$  is odd (e.g., [1,3] shift), cationic and anionic surfaces are identical. When  $N = j + 1$  (even), there are no restrictions on the reaction paths (e.g., [1,3] shift of the neutral:  $N = 4$ ). These symmetries are exact for this treatment and are approximate even in more elaborate calculations.

For sigmatropic shifts, there is also a symmetry between supra- and antarafacial rearrangements. For antarafacial shifts, the Möbius path corresponds to retention. Thus, for

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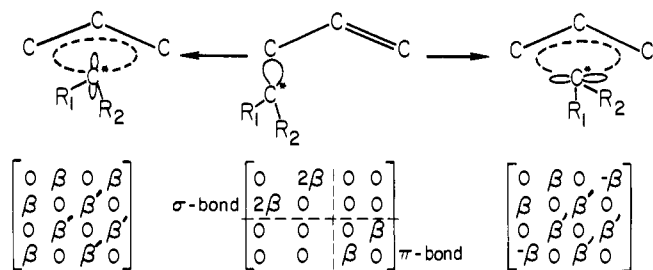
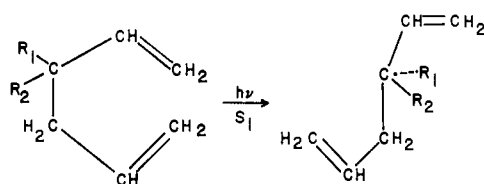


Figure 1. Molecular orbital picture of the [1,3] sigmatropic shift. Right-hand side indicates the Möbius path (inversion). Left side shows the path which retains configuration. The Hückel matrices are given for each path.

(A) Singlet  $S_1$  Reaction; [1,3] Shift



(B) Triplet  $T_1$ ; 1,5 : 2,6 cross addition

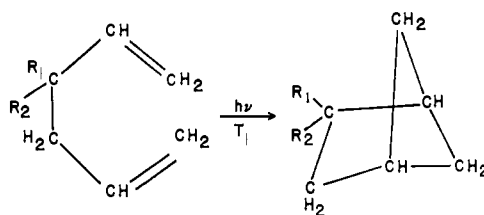


Figure 2. Photochemistry of 1,5-dienes.

larger shifts for which the antarafacial process is possible, the surface for antarafacial rearrangement with retention, for example, corresponds to the suprafacial shift with inversion computed here.

### III. Results and Discussion

In this section we will consider Hückel-Hubbard predictions concerning thermal and photochemical [1, $j$ ] shifts. Special attention will be given to two questions of chemical interest: (1) Does the shift occur with inversion or retention of configuration at the migrating carbon? (2) How do the excited state surfaces depend on spin symmetry? The first question has already received much attention using MO methods and there is good agreement with experiment. The second question is less widely studied. Its importance, though, is illustrated by the observed photochemistry of 1,5-dienes which undergo cross addition in the triplet state but undergo a [1,3] shift on the singlet surface (see Figure 2).<sup>9</sup>

The reaction paths for the [1,3] shift of the neutral system computed from eq 2.2 with  $j = 3$  and  $N = 4$  are given in Figure 3. In the ground state,  $S_0$ , the Möbius and Hückel paths exhibit maxima corresponding to activation energies of  $E_a(M) = 5.19$  eV and  $E_a(H) = 6.84$  eV, respectively. Accordingly, thermal [1,3] rearrangements are predicted to occur with inversion of configuration at the migrating carbon consistent with the Woodward-Hoffmann theory and with experiment.

The excited state surfaces both indicate a preference for the Hückel path, again consistent with MO theory. However, there are significant qualitative differences between the  $S_1$  and  $T_1$  reactions which occur as a consequence of the Hubbard in-

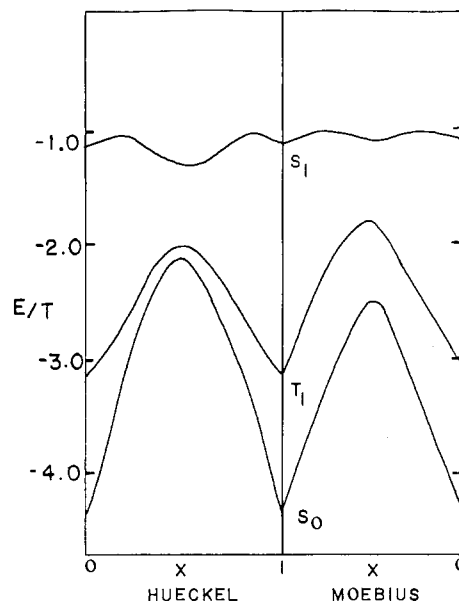


Figure 3. Hückel-Hubbard surfaces for the [1,3] shift.

Table I. Activation Energy for [1, $j$ ] Sigmatropic Shifts (Energies in Units of  $T = 3$  eV)

$j$	$N$	state	$I = 2T$		$I = 0$	
			$E_a(H)$	$E_a(M)$	$E_z(H)$	$E_z(M)$
3	3	$D_0$	1.63	1.35	1.77	1.46
		$D_1$	1.14	1.06	0.90	1.17
		$Q_1$	0.42	0.56		
3	4	$S_0$	2.28	1.73	2.70	1.75
		$T_1$	1.12	1.29	0.84	1.17
		$S_1$	0.33	0.38		
4	4	$S_0$	1.79	1.35	1.89	1.48
		$T_1$	1.20	1.59	1.11	1.48
		$S_1$	0.69	1.16		
4	5	$D_0$	1.68	1.68	1.68	1.68
		$D_1$	1.31	1.31	0.91	0.91
		$Q_1$	1.20	1.20		
5	5	$D_0$	1.54	1.77	1.60	1.85
		$D_1$	1.31	1.06	1.29	1.01
		$Q_1$	1.24	0.82		
5	6	$S_0$	1.73	2.07	1.72	2.38
		$T_1$	1.49	1.36	1.49	1.23
		$S_1$	1.21	1.01		
6	6	$S_0$	1.53	1.92	1.60	1.96
		$T_1$	1.62	1.38	1.62	1.34
		$S_1$	1.47	1.02		
6	7	$D_0$	1.74	1.74	1.78	1.78
		$D_1$	1.43	1.43	1.16	1.16
		$Q_1$	1.32	1.32		

teraction. The barrier is seen to be much higher along the triplet curve ( $\Delta E_a \equiv E_a(T_1) - E_a(S_1) = 2.37$ ) suggesting that the singlet rearrangement is more likely to occur. Also, the difference between barrier heights for the Hückel and Möbius singlet paths is only about 0.1 eV, suggesting that there may not be much stereospecificity in this reaction. The reactions of the 1,5-dienes depicted in Figure 2 are consistent with the predictions of a preference for reaction along the  $S_1$  path (note: in the thermal case 1,5-dienes undergo Cope rearrangement). The prediction concerning possible nonstereospecificity has not been verified.

While the choice of parameters  $T$  and  $I$  was made from comparisons to spectroscopic observations, our choice of reaction Hamiltonian has been somewhat arbitrary. Thus, while the general trends discussed remain valid for other possible

mechanisms (e.g., a cyclic intermediate), the absolute values of the barrier heights may vary considerably.

Table I gives the results for [1,3], [1,4], [1,5], and [1,6] suprafacial shifts. We discuss the results for thermal and photochemical reactions separately with an emphasis on even-electron systems.

**A. Thermal Reactions.** The stereospecificity of the [1,3] and [1,5] neutral and the [1,4] cation reactions determined from the table are in agreement with much observed chemistry and with the Woodward–Hoffmann predictions. The barrier heights along the  $S_0$  path do not vary significantly with increasing  $j$ .

In order to study the effects of  $\pi$ -electron configuration interaction, Table I presents activation energies computed both with and without the Hubbard term. In most cases, the effect is to lower somewhat all barriers encountered. However, in even-electron systems, one can see a more pronounced lowering of the activation energy of the forbidden path for [1,3] and [1,5] neutral shifts while the energy along the allowed path is virtually unaffected. It is tempting to conclude from this that the electron correlation stabilizes the antiaromatic transition state compared to the Hückel treatment. However, consideration of the [1,4] and [1,6] cation rearrangements fails to confirm the preferential lowering of the antiaromatic transition state. In these cation reactions, however, there are more sites than electrons, which reduces the effects of electron repulsion by the increased electron delocalization. A similar behavior was noted previously in electrocyclic reactions<sup>9</sup> as well as in recent full CI calculations on cyclobutadiene which indicate a positive electron delocalization energy.<sup>10</sup>

The odd-electron systems agree quite closely with the MO picture both quantitatively and qualitatively.

**B. Photochemical Reactions.** Table I also shows the results for the first excited MO surface and the two low-lying HH excited surfaces (degenerate in MO). Again there is qualitative agreement between the methods, but in this case some new features emerge from the Hückel–Hubbard model. The most striking feature is difference in the barrier heights of the singlet

and triplet paths in the [1,3] neutral sigmatropic shift which was noted earlier. For even-electron systems, the MO barriers lie between those in the lowest excited HH states but have values closest to the  $T_1$  paths. For neutral radicals, the barriers are considerably higher with CI, but there is no stereospecificity in either treatment.

#### IV. Conclusion

As we found in the treatment of electrocyclic reactions, our results for [1, $j$ ] sigmatropic shifts are in general agreement with the stereochemical predictions of the Woodward–Hoffmann approach (particularly for  $S_0$  and  $T_1$ ). The introduction of electron repulsion, however, splits the  $S_1, T_1$  exchange degeneracy, yielding lower barriers along  $S_1$  paths. This prediction suggests that the photochemistry of these two states may differ as is indeed observed in the laboratory. In the [1,3] shift, the barrier is reduced so much that the  $S_1$  stereochemistry is open to question and may require more detailed study.

We have not discussed the odd-electron systems in detail because they are of lesser experimental interest. We note that these systems are in many respects similar to even-electron systems with regard to the effects of the introduction of the Hubbard electron repulsion term.

**Acknowledgment.** This work was supported in part by the Robert A. Welch Foundation, Houston, Texas.

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## Ab Initio Study of the Benzene Radical Anion

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**Abstract:** Ab initio molecular orbital calculations with the STO-3G and 4-31G basis sets have been carried out for the radical anions of benzene ( $Bz^-$ ) and fluorobenzene ( $FBz^-$ ). In accordance with the Jahn–Teller theorem,  $Bz^-$  is predicted to distort from regular hexagonal ( $D_{6h}$ ) symmetry. The best structures of  $Bz^-$  have  $D_{2h}$  symmetry. Two quite different  $D_{2h}$  structures are found, one with four longer and two shorter C–C bonds and the other with two longer and four shorter C–C bonds. Configuration interaction calculations suggest that these two structures have very similar energies. Interconversion of equivalent  $D_{2h}$  structures requires little activation energy, a result consistent with the experimental ESR spectrum. The ring skeletons of  $FBz^-$  and  $Bz^-$  are similar suggesting that the  $Bz^-$  structures might usefully serve as models in studies of radical anions of substituted benzenes.

The benzene radical anion ( $Bz^-$ ) is of interest in experimental organic chemistry as the species formed in the first stage of the Birch (metal/ammonia) reduction of benzene.<sup>2</sup> It is also of interest theoretically since it represents a Jahn–Teller situation<sup>3</sup> and in this capacity it has received considerable attention in the literature.<sup>4–14</sup> In this paper, and as part of a wider theoretical study of the Birch reduction, we present

the first application of ab initio molecular orbital theory to the problem. Our aim is to establish a model for  $Bz^-$  suitable for subsequent studies of the effect of substituents. To this end, we have carried out ab initio calculations on several possible structures of  $Bz^-$ . In addition, for reasons given below, we have also performed similar calculations on the radical anion of fluorobenzene.