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Effect of Ring Size and Migratory Groups on [1,*n*] Suprafacial Shift Reactions. Confirmation of Aromatic and Antiaromatic Transition-State Character by Ring-Current Analysis

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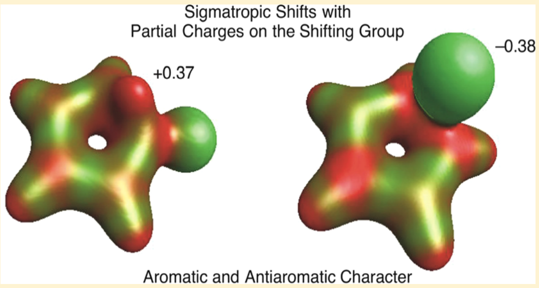
Ⓢ *Supporting Information*

ABSTRACT: Suprafacial sigmatropic shift reactions of 5-substituted cyclopentadienes, 3-substituted cyclopropenes, and 7-substituted cycloheptatrienes have been studied computationally at the MP2/6-31+G* level for structures and energetics and with the ipsocentric method at the CHF/6-31G** level to calculate current−density maps. The hydrogen shifts in cyclopentadienes have a diatropic ring current indicating aromatic, cyclopentadienide anion character. This result stands in contrast to the fluorine shift in 5-fluorocyclopentadiene which requires much more energy and has a paratropic ring current in the TS pointing to antiaromatic, cyclopentadienyl cation character. [1,3] hydrogen shifts in cyclopropenes are very difficult, passing through transition states that have an extended C−C bond. For 3-fluorocyclopropene, the [1,3] fluorine shift is much easier than the hydrogen shift. For 7-fluorocycloheptatriene, the [1,7] hydrogen shift is predicted but requires very high energy and has a paratropic ring current and antiaromatic character. The [1,7] suprafacial fluorine shift is relatively easy, having a TS with cycloheptatrienyl cation character. Patterns of currents, and the reversal for H and F migration, are rationalized by orbital analysis based on the ipsocentric method. Calculated charges and structural features for reactants and transition states support these conclusions.



INTRODUCTION

Sigmatropic rearrangements are well-studied processes. They have found utility in synthetic chemistry and display intriguing mechanistic pathways and constraints. They are discussed not only in advanced texts but also in first-year organic textbooks.[1] In this class of reactions, [1,*n*] hydrogen shifts have attracted attention from both experimental and computational chemists. Suprafacial migrations are allowed by Woodward−Hoffmann orbital symmetry considerations[2] for conjugated pentadienes ([1,5] shifts) but not for propenes ([1,3] shifts) or conjugated heptatrienes ([1,7] shifts), although the latter have an allowed antarafacial pathway theoretically available to them. Again, these and other pericyclic processes have been discussed in great detail in organic texts[3] and the extensive secondary literature.[4]

A particularly useful computational paper by Alabugin and co-workers deals with [1,5] shifts and contains extensive references to the primary literature.[5] One of several issues discussed there is the presence of aromatic character in the transition states (TSs) of [1,5] hydrogen shifts, a factor that increases kinetic reactivity. The authors report a NICS(1) value of −9.6 for the 5-membered ring in the TS for the [1,5] hydrogen shift in cyclopentadiene, which is taken to indicate that this TS has aromatic cyclopentadienide anion character, consistent with a lower activation barrier and a more facile shift compared with acyclic analogues. Attribution of a degree of aromatic character to the TS for this and similar reactions features (implicitly or explicitly) in much previous work.[6]

In this paper, we report calculations at the MP2/6-31+G* level of TS structures, activation enthalpies, and NPA (natural population analysis) charge distributions for [1,5] shift reactions of cyclopentadiene and 5-substituted cyclopentadienes, [1,3] shifts of cyclopropene and 3-fluorocyclopropene, and [1,7] shifts of cycloheptatriene and 7-fluorocycloheptatriene. In order to explore the question of aromaticity, calculations of current−density maps were also carried out for the transition states for these shift reactions at the CHF/6-31G** level using the ipsocentric approach. The effect of ring size and the influence of highly electronegative fluorine substituents are emphasized throughout.[7]

RESULTS AND DISCUSSION

i. Structure and Energies. *Cyclopentadienes.* Among the simplest and fastest of [1,5] suprafacial shifts are those of 5-substituted cyclopentadienes. The reaction of the parent

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compound, cyclopentadiene itself, has been well studied both experimentally and computationally.[5]

The activation enthalpy for the [1,5] hydrogen shift, an identity reaction, has been reported as 24.3 kcal/mol.[8] Computations by a number of workers using different methods have given similar values.[5,6b,d,e,k] Using data from MP2/6-31+G* calculations, we obtain a somewhat higher activation enthalpy, $\Delta H^{\ddagger}$, of 25.8 kcal/mol; see Table 1.[9]

Table 1. Energies of Activation for [1,5] Sigmatropic Shifts in Substituted Cyclopentadienes, [1,3] Shifts in Substituted Cyclopropenes, and [1,7] Shifts in Cycloheptatrienes[a]

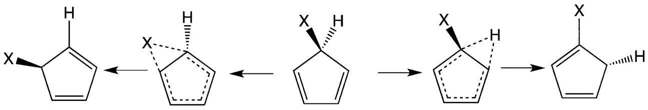
reaction	$\Delta H^{\ddagger}$ (kcal/mol)
Cyclopentadienes	
cyclopentadiene, 5,1-hydrogen shift	25.8[b]
5-trimethylsilylcyclopentadiene, 5,1-TMS shift	13.5[b]
5-methylcyclopentadiene, 5,1-hydrogen shift	24.0[c]
5-methylcyclopentadiene, 5,1-methyl shift	42.6
5-allylcyclopentadiene, 5,1-hydrogen shift	24.3
5-allylcyclopentadiene, [3,3] allyl shift[d]	29.5
5-(3-cyclopropenyl)cyclopentadiene 5,1-cyclopropenyl shift	31.1
5-fluorocyclopentadiene, 5,1-hydrogen shift	28.6
5-fluorocyclopentadiene, 5,1-fluorine shift	48.0[e]
1-fluorocyclopentadiene, 5,4-hydrogen shift[f]	27.9
2-fluorocyclopentadiene, 5,4-hydrogen shift[f]	26.6
1,2,3,4-tetrafluorocyclopentadiene, hydrogen shift	35.9
5-dimethylborylcyclopentadiene, 5,1-boryl shift	0.3
3- and 7-Membered Rings	
cyclopropene, 3,1-hydrogen shift	65.5
3-fluorocyclopropene, 3,1-hydrogen shift	63.5
3-fluorocyclopropene, 3,1-fluorine shift	42.3
1-fluorocyclopropene, 3,2 hydrogen shift	63.3
cycloheptatriene, 5,1-hydrogen shift	29.4
7-fluorocycloheptatriene, 7,1-hydrogen shift	83.7
7-fluorocycloheptatriene, 7,1-fluorine shift	28.3

[a] Calculated at the MP2/6-31+G* level using scaled HF/6-31+G* ZPVEs. See: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. [b] Activation enthalpies for the hydrogen shift in cyclopentadiene and for the silyl shift in 5-trimethylsilylcyclopentadiene, at the M06/6-311++G** level, are 23.4 and 13.6 kcal/mol, respectively. [c] An E_a value of 20.4 ± 0.3 kcal/mol has been measured: McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329. [d] This value is for a [3,3] sigmatropic Cope rearrangement. [e] A calculation at the CCSD(T)/6-311+G**//MP2/6-31+G* level gives a barrier of 51.1 kcal/mol. We also considered the process in the triplet state and located a TS at the MP2 level. The barrier is very high: the difference in MP2 electronic energies is 95.9 kcal/mol (the TS was not located at the HF level and no frequencies were available to provide an enthalpy difference). [f] The numbering system for the 1-fluoro- and 2-fluorocyclopentadiene H-shift transition states retains that of their respective substrates.

We have also varied the migratory group at C5, examining the migratory abilities of trimethylsilyl, methyl, 3-cyclopropenyl, fluorine, and dimethylboryl, all with hydrogen at C5; see Scheme 1. Additionally, we have calculated activation enthalpies for the [1,5] hydrogen shift with ring substituents: 5-methyl, 5-allyl, 5-fluoro, 1-fluoro, 2-fluoro, and 1,2,3,4-tetrafluoro.

We note here that our attempted calculation of the [1,5] allyl shift in 5-allylcyclopentadiene gave not the [1,5] shift but the [3,3] suprafacial degenerate Cope rearrangement. Activation enthalpies for all these reactions are also found in Table 1.

Scheme 1. Generalized [1,5] Shifts of 5-Substituted Cyclopentadienes



X = H, Me, F, Me_3Si, c-C_3H_3, and Me_2B

These results may be compared with the [1,5] hydrogen shift in the acyclic molecule, 1,3-pentadiene, for which activation energies on the order of 36 kcal/mol have been reported experimentally[8] and computationally.[5,6e,7c,d] Unusual spin coupling and resonance effects have also been identified with (*Z*)-1,3-pentadiene.[6g] Additionally, the hydrogen shift rearrangement of (*E*)-2-methyl-1,3-pentadiene has a reported experimental E_a value of 32.8 kcal/mol.[10] The greater reactivity of the cyclic substrate may be explained as a combination of the conformational rigidity of the five-membered ring which enforces proximity of the reaction termini and the amplified, aromatic, cyclopentadienide anion character in the TS (described in section ii).

From the results listed in Table 1, several trends are apparent. The electropositive migratory groups, trimethylsilyl and especially dimethylboryl, greatly reduce the activation barrier for the [1,5] group shift.[11] In the boryl case, this barrier is extremely small. Another trend is that hydrogen shifts are faster than alkyl shifts, and among the latter, 3-cyclopropenyl is faster than methyl transfer. There is significant charge separation in the TSs for these reactions: The silyl, boryl, hydrogen, and alkyl moieties are all partially positive in the TSs for these rearrangements, significantly more than in the reactant states for the hydrogen and alkyl cases but not for the others. The rings are therefore partially negative, giving rise to enhanced cyclopentadienide anion character in the TSs (which is confirmed by the ring-current calculations to be described more fully in section ii). See Table 2 for a list of pertinent calculated NPA charges.

The greater reactivity for the cyclopropenyl shift over the methyl shift is perhaps also explained by this result: the two groups have essentially the same NPA charge in the reactant state, but the cyclopropenyl group is more positive in the TS, indicating a measure of cyclopropenyl cation character in the migratory group. It is interesting that the examples with the lowest barriers, the silyl and boryl transfers, have the *least* charge *difference* on the migratory group between reactant and transition states; in fact, the boryl group is *less* positive in the TS than in the reactant. The boron atom in the reactant is formally coordinatively unsaturated, and its bond to C5 is elongated (1.631 Å). Moreover, this bond leans closer to the reaction terminus than in the other reactants: the C1−B−C5 angle is only 45°. The boron is symmetrically bound to both carbons in the TS, becoming four-coordinate with C−B bond distances of 1.776 Å (see Table S3 of the Supporting Information for selected geometric features of reactant and transition states calculated in this study). Two entries occur where two migrating groups are possible, as in the fluoro compounds as identified in the footnotes. In the migratory groups column, a second value is that for hydrogen as the migrating entity and, therefore, has the opposite sign compared to that in the ring column.

The effects of fluorine substituents on the reaction are very interesting. The hydrogen shift in 5-fluorocyclopentadiene has

Table 2. NPA Charges on the Ring and Migratory Group for 5-XCyclopentadienes and Their [1,5] X Shift Transition States[a] and Charges on the Ring and the Migratory Atom or Group for 3-X Cyclopropenes, 7-X Cycloheptatrienes, and Their [1,*n*] Shift Transition States

compound	NPA charge on ring[b]	charge on migratory group
Cyclopentadienes		
cyclopentadiene	0.0	0.277
cyclopentadiene, H shift TS	−0.387	0.387
5-TMScyclopentadiene	−0.509	0.509
5-TMScyclopentadiene, TMS shift TS	−0.504	0.504
5-methylcyclopentadiene	−0.057	0.057
5-methylcyclopentadiene, H shift TS	−0.388	0.388
5-methylcyclopentadiene, methyl shift TS	−0.170	0.170
5-allylcyclopentadiene	−0.035,[c] −0.278[d]	0.035, 0.278
5-allylcyclopentadiene, H shift TS	−0.387	0.387
5-allylcyclopentadiene, allyl shift TS	−0.099[c]	0.099
5-(3-cyclopropenyl)cyclopentadiene	−0.055	0.055
5-(3-cyclopropenyl)cyclopentadiene, C shift TS	−0.202	0.202
5-fluorocyclopentadiene	+0.383,[c] −0.237[e]	−0.383, 0.237
5-fluorocyclopentadiene, H shift TS	−0.369	0.369
5-fluorocyclopentadiene, F shift TS	+0.379	−0.379
5-fluorocyclopentadiene, F shift, triplet TS	NA	NA
1-fluorocyclopentadiene	+0.343,[c] −0.284[e]	0.284
1-fluorocyclopentadiene, H shift TS	−0.388	0.388
2-fluorocyclopentadiene	0.344,[c] −0.279[e]	0.279
2-fluorocyclopentadiene, H shift TS	−0.379	0.379
1,2,3,4-tetrafluorocyclopentadiene	−0.294	0.294
1,2,3,4-tetrafluorocyclopentadiene, H shift TS	−0.359	0.359
5-dimethylborylcyclopentadiene	−0.274	0.274
5-dimethylborylcyclopentadiene, B shift TS	−0.203	0.203
3- and 7-Membered Rings		
cyclopropene	−0.214	0.214
cyclopropene, H shift TS	−0.301	0.301
3-fluorocyclopropene	+0.419,[f] −0.212[g]	−0.419, 0.212
3-fluorocyclopropene, H shift TS	−0.283	0.283
3-fluorocyclopropene, F shift TS	+0.704	−0.704
1-fluorocyclopropene	−0.219	0.219
1-fluorocyclopropene, H shift TS	−0.330	0.330
cycloheptatriene	−0.257	0.257
cycloheptatriene, 5,1-H shift TS	−0.341	0.341
7-fluorocycloheptatriene	+0.392,[h] −0.234[i]	−0.392, 0.234
7-fluorocycloheptatriene, H shift TS	−0.341	0.341
7-fluorocycloheptatriene, F shift TS	+0.636	−0.636

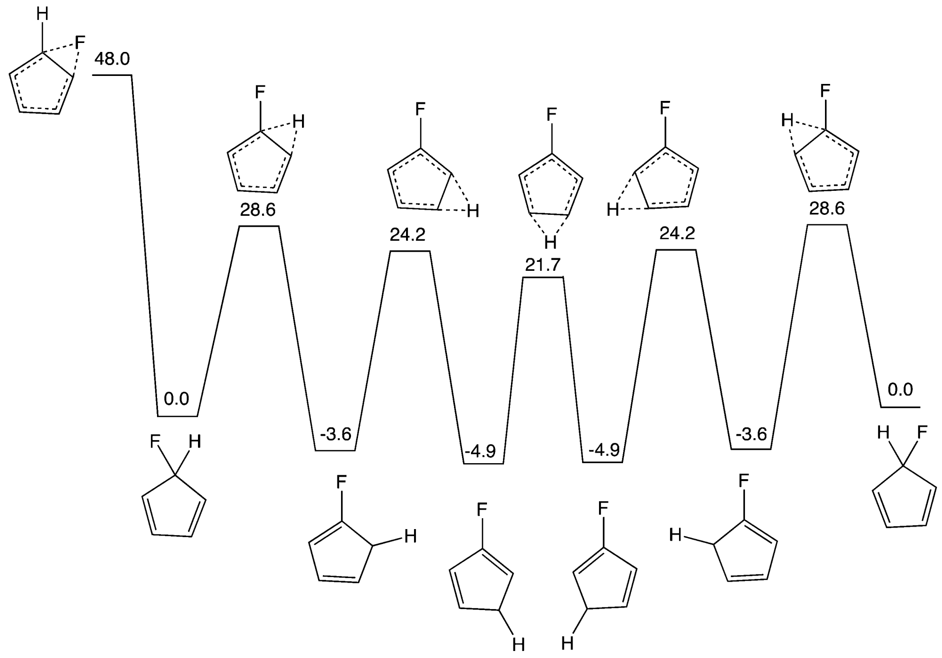
[a] Calculated at MP2/6-31+G*. [b] Charge on the molecule (0.0) less the charge on the migrating group. Charges on hydrogens are summed onto the attached heavy atom. [c] Charge on the C_5H_5 ring. The allyl shift reaction is a [3,3] sigmatropic Cope rearrangement. [d] Charge on the allyl-C_5H_4 ring [e] Charge on the C_5H_4F ring. [f] Charge on the C_3H_3 ring. [g] Charge on the C_3H_2F ring. [h] Charge on the C_7H_7 ring. [i] Charge on the C_7H_6F ring.

$\Delta H^{\ddagger}$ = 28.2 kcal/mol, which is a few kcal/mol greater than the shift in cyclopentadiene itself. Sequential hydrogen shifts starting with the 5-fluoro isomer give the results shown in Scheme 2 for a complete tour of the ring by hydrogen. In this tour, the hydrogen shift barriers are all slightly higher than the hydrogen shift in the unsubstituted system. However, when the ring is substituted with fluorines at all carbons except C5, the H-shift barrier rises to 35.9 kcal/mol. This surprised us since we expected the accumulated fluorines to stabilize the cyclopentadienide anion moiety in the TS (see also the ring current calculations in section ii). This result might instead reflect stabilization of the reactant by the double-bond stabilizing effect of fluorine, suggested by Hine to be 3.3 kcal/mol.[12]

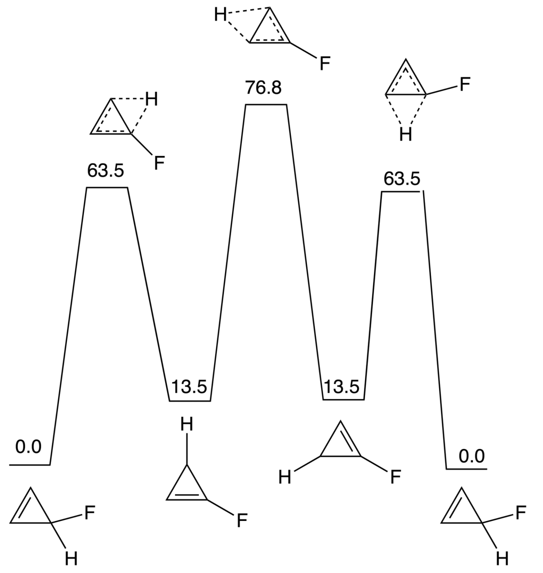
5-Fluorocyclopentadiene also undergoes a [1,5] fluorine shift, but its activation enthalpy is much higher, at 48.0 kcal/mol. The TS for this shift does not have a diatropic ring current; in fact, it has a paratropic current. In this TS, as well as in the reactant, the fluorine has a partial negative charge. The ring therefore has a partial positive charge, giving it some of the character of the antiaromatic cyclopentadienyl cation, hence the paratropic ring current and destabilization of the TS. A more explicit account of the origin of the paratropic current can be based on π orbital nodal character, as discussed in detail in section ii.

Cyclopropene, 1-Fluorocyclopropene and 3-Fluorocyclopropene. The degenerate [1,3] hydrogen shift in cyclopropene, the degenerate [3,2] hydrogen shift in 1-fluorocyclopropene, and the rearrangement of 3-fluorocyclopropene to 1-fluorocyclopropene by a [1,3] hydrogen shift were also investigated (see Scheme 3). These reactions have similar, and large, activation barriers, about 65 kcal/mol, as given in Table 1. The size of the barrier for the 3-fluoro- to 1-

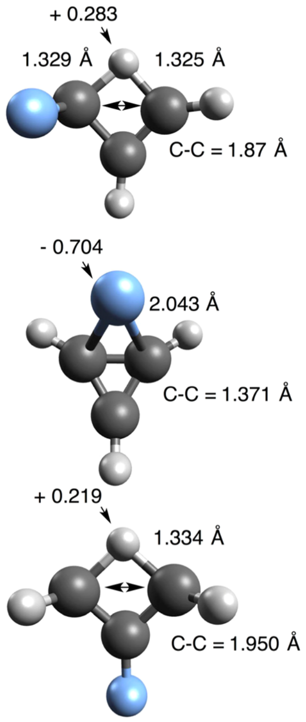
Scheme 2. Sequential [1,5] Hydrogen Shifts in the Fluorocyclopentadiene System (Energies in kcal/mol)



Scheme 3. Sequential [1,3] Hydrogen Shifts for 3-Fluorocyclopropene (Energies in kcal/mol)



Scheme 4. Transition-State Structures for the [1,3] Hydrogen and Fluorine Shifts for 3-Fluorocyclopropene and 1-Fluorocyclopropene[a]



[a] Selected bond lengths are given, and the NPA charge on the transferring atom is shown.

fluorocyclopropene isomerization is in part due to the endothermicity of the reaction: ΔH_{ISOM} = 13.5 kcal/mol.

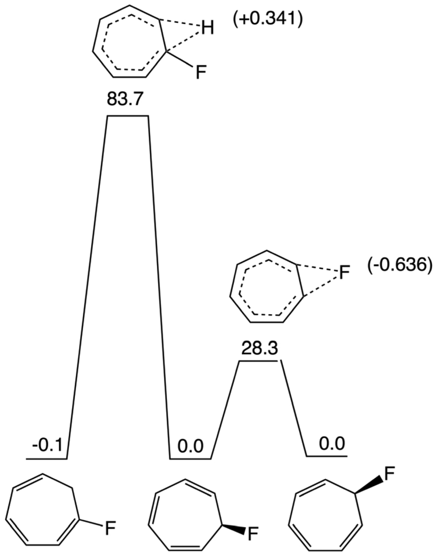
As usual for hydrogen shifts, the migrating hydrogen has a higher positive charge in the TS relative to the reactant, and the remainder of the molecule is consequently more negative. However, the most striking feature of the TSs for these three reactions is that the C1−C3 bond is very long, about 1.9 Å; see Scheme 4. That is, the cyclopropene ring is partially opened and the TS does not resemble a conventional 1,3-sigmatropic shift. In fact, the TSs for these hydrogen shifts resemble intramolecular proton-transfer transition states in which a proton is being transferred between the negatively charged end groups of bent, three-carbon moieties having both carbanion and carbene character.

In stark contrast, the ring is intact in the TS for the degenerate fluorine shift reaction in 3-fluorocyclopropene (the C1−C3 distance is normal at 1.37 Å), and the activation enthalpy is reduced to 42.3 kcal/mol. The negativity of the fluorine is greatly enhanced in this TS; thus, the ring is positive, suggesting some aromatic, cyclopropenyl cation character.

However, calculations in this case were inconclusive (see section ii). An additional stationary point was also found.[13]

1,3,5-Cycloheptatriene and 7-Fluoro-1,3,5-cycloheptatriene. Results for these 7-membered rings give interesting similarities and reversals compared with those in the 5-membered rings. We were not able to find a TS structure for the orbital-symmetry disallowed, suprafacial [1,7] hydrogen-shift reaction of cycloheptatriene. Instead, we found the allowed, degenerate, intramolecular [1,5] shift, a relatively facile and well-known reaction with $\Delta H^\ddagger$ = 29.4 kcal/mol.[14] Okajima and Imafuku did find the suprafacial [1,7] hydrogen shift and reported large activation energies, $\Delta E^\ddagger$, of about 69 kcal/mol, the exact figure depending on the DFT method used. Their $\Delta E^\ddagger$ value is a calculated electronic energy of activation, not an Arrhenius-like activation energy. They found very little charge separation between the migrating hydrogen and the ring in the TS in this reaction.[6d] For 7-fluorocycloheptatriene, we did find a suprafacial [1,7] hydrogen shift TS leading to 1-fluorocycloheptatriene and calculated a very large enthalpy of activation of 83.7 kcal/mol for this reaction. On the other hand, the degenerate suprafacial [1,7] fluorine shift has a dramatically smaller calculated $\Delta H^\ddagger$ of 28.3 kcal/mol. In this reaction, as for the fluorine shift of 3-fluorocyclopropene, the fluorine carries more negative charge in the TS, and thus, the 7-membered ring is positive and can be considered to have cycloheptatrienyl cation character. Indeed ring-current calculations support the implied diatropicity of the 7-membered ring in the TS in this case (see section ii). Scheme 5 shows the suprafacial [1,7] hydrogen and fluorine-shift reactions for 7-fluorocycloheptatriene.

Scheme 5. Suprafacial [1,7] Hydrogen and Fluorine Shifts for 7-Fluorocycloheptatriene (Energies in kcal/mol)[a]



[a]NPA charges are shown for the migrating atoms.

Okajima and Imafuku[6d] studied the degenerate [1,7] chlorine shift in 1,7,7-trichlorocycloheptatriene and found a value of $\Delta E^\ddagger$ of only 12 kcal/mol, substantially lower than the 16.5 kcal/mol barrier calculated for the [1,5] chlorine shift in the same substrate. The rapid [1,7] chlorine shift is in agreement with their observation that in the proton NMR spectrum of this substrate at room temperature only three signals are found. Okajima and Imafuku ascribe the rapidity of the [1,7] chlorine shift to an attractive Coulombic interaction between chlorine and the ring in the TS. It is clear from their language that the aromatic nature of the 7-membered ring in the TS is implied.

An additional important observation is made by these workers. Their [1,7] hydrogen shift TS in cycloheptatriene also has an almost planar ring structure strongly resembling that of cycloheptatrienyl cation but has very little charge separation between the migrating group and the ring.[6d]

Geometry can be a poor indicator of aromaticity. Aromaticity as defined by the presence of a diatropic ring current can survive considerable deviations from ideal geometries. For example, the chair-shaped TS for the [1,5] hydrogen shift in acyclic 1,3-pentadiene is thought to have aromatic character; the reported NICS(1) value is −8. 8,[5] and according to our calculations, the TS exhibits a diatropic ring current (see Scheme S3). The TS for the relatively rapid [1,5] hydrogen shift reaction of cycloheptatriene is decidedly nonplanar yet has a ring current that suggests the presence of aromaticity. Benzene itself can be profoundly distorted, both in terms of C−C bond length alternation and buckling of the ring, without gaining very much energy. The effects of the distortions on the current depend on how the distortions are achieved. Bond length alternations induced by "clamping" with saturated groups hardly affects the current, whereas similar alteration induced by unsaturated groups may quench the current entirely. The crucial factor is whether the nodal characteristics of the HOMO and LUMO are changed in the distorted molecule.[15] Antiaromaticity, as diagnosed by a paratropic current, is similarly insensitive to distortions produced by saturated clamping groups.[16] Paratropic current also survives a modest amount of out-of-plane distortion, for example, en route from the planar TS to the tub-shaped equilibrium structure of COT, 1,3,5,7-cyclooctatetraene.[17] In Appendix A of the Supporting Information we list the results of MP2/6-311+G** calculations addressing both types of geometric distortion for benzene.

Some chemical consequences are discussed by Bernasconi and co-workers who find, computationally, that aromaticity persists in transition states of bimolecular identity proton transfer reactions even though the pertinent ring system in the TS undergoes significant bond length distortion from the aromatic reactant state. Similarly, a reaction leading to an aromatic product develops aromatic character early in the proton-transfer event, even though bond lengths are not yet close to the values of the fully aromatic product.[18a,b] However, sufficient bond-length distortion can affect the chemistry of a cyclic six-π-electron system. Vollhardt and co-workers have synthesized triangular [4]phenylene in which the central six-membered ring has alternating bond lengths of 1.335 and 1.494 Å; in other words, it is a cyclohexatriene moiety. This is consistent with the observation from calculations that ring currents are suppressed in the central ring through changes in the frontier orbitals in the π-clamped system.[15] The Vollhardt phenylene compound undergoes palladium-catalyzed hydrogenation of the central ring at atmospheric pressure.[18a,b] Presumably the stability of the central ring has been sufficiently compromised that addition is allowed exclusively. Other double-bond reagents have also been shown to add to the central ring.[18e]

Effect of ring size. With respect to the hydrogen shifts, the patterns in reaction barriers with the three-, five-, and seven-membered rings fit the predictions for symmetry-allowed suprafacial sigmatropic shifts of the [1,3], [1,5], and [1,7] variety, respectively. The results for the fluorine shifts in the three- and seven-membered rings indicate that the usual Woodward–Hoffmann expectations for [1,3] and [1,7] suprafacial shifts do not apply because more favorable paths via a stabilized TS are available. In these cases, there are strong contributions from charge-separated resonance forms that are stabilized by aromatic character in the ring. This leads to transition states with ion-pair character that are freed from the constraints of the Woodward–Hoffmann guidelines.

ii. Ring-Current Calculations.[19] The comparative activation enthalpies listed in Table 1 and the increase in charge separation found for the transition states of the orbital-symmetry allowed reactions reported in Table 2 both imply aromatic character in the cyclic moieties at the TS. As discussed in the previous section, the calculated geometric features given in Table S3 would be compatible with aromaticity for those TSs but do not give conclusive evidence.

Evidence for aromaticity can be inferred through the magnetic criterion, which states that aromatic and antiaromatic systems will possess a ring current induced by an external magnetic field. The presence of ring currents, or lack thereof, is detected directly using the ipsocentric approach[19b] with the SYSMO98 computational package.[20] This method takes the origin for calculation of current-density at any point as the point itself, as first proposed by Keith and Bader,[21] and implemented an analytical derivative formulation by Lazzeretti et al.[22] As a consequence, the first-order response of the wave function can be partitioned into diatropic and paratropic current contributions that obey frontier-orbital selection rules based on translational and rotational symmetries.[19] An advantage of using this method is that the total magnetic response can be partitioned into canonical (CMO)[23] or localized (LMO)[24] contributions from occupied molecular orbitals, which do not remix in the presence of the field and which are well converged in even modest basis sets. Calculations are performed here in the 6-31G** basis (at the CHF level of theory) which is already sufficient to give the sense and strength of the current.[25]

Calculations of response properties such as magnetic susceptibility using higher level methods such as CASSCF have been reported.[26] Integrated properties themselves require interpretation as they do not produce the detail of the current map. Calculations beyond the CHF level have, in general, shown little effect in the predictions for diatropic systems[27] but do indicate some variability between methods for magnitudes of paratropic currents,[28] but these are not sufficient to reverse their predicted sense. Other quantities have been proposed as indicators of (magnetic) aromaticity, such as ACID, NICS, and NICS scans, reviewed in detail in several special issues.[29] The advantages of current–density mapping for direct visualization of this property, modeling all of the magnetic response properties, have been documented elsewhere.[30]

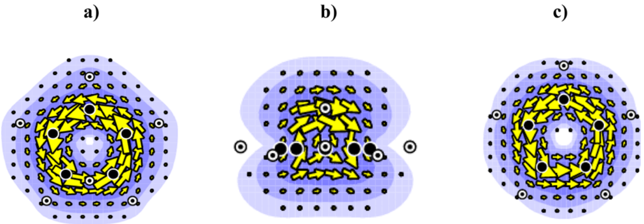
A quantitative indicator of aromaticity is the value j_{max}, representing the maximum modulus of current–density in the plotting plane. In favorable cases, this quantity allows for comparisons of aromaticity between systems and identification of the dominant orbital contributions.

We discuss the TSs treated in the previous section on a case-by-case basis, reporting current maps and, in key examples, giving an orbital breakdown that explains the observed current. Aromatic (antiaromatic) systems are associated with diatropic (paratropic), anticlockwise (clockwise) currents induced by an external magnetic field perpendicular to the plane of the ring. Atomic positions are projected into the plotting plane. All current maps are generated using the geometries (Table S3) used in the calculation of activation energies, and j_{max} is typically reported for a height of 1 a_0 (0.529 Å) from the face of the molecule opposite to the migratory unit. All maps are generated from the contributions of those orbitals that exhibit π-like character in the ring, which are identified by inspection of individual orbital response (CMO or LMO) or of standard orbital plots (Gaussian09).

In discussing aromaticity effects on barriers, it is useful to compare ring–current characteristics of TSs with reactants. Current–density maps for reactants are shown in (Scheme S4). In the cases considered here, the reactant is typically weakly aromatic or nonaromatic, and the ring-current is an emergent property of the transition state. However, the comparison is revealing in some cases, as will be discussed later.

Cyclopentadiene. First, we consider the parent compound cyclopentadiene. The π current–density map at the TS for the [1,5] hydrogen shift, shown in Scheme 6a, shows a typical diatropic ring current for the face opposite the migratory group, as expected for an aromatic transition state. The j_{max} value on this face of 0.086 au (as a reference the j_{max} for benzene is 0.078 au at the same level) indicates that the shift proceeds via a TS that is at least as aromatic as benzene. In detail, the current distribution on the same face as the migrating group shows a change in shape, as it is diverted via a CHC bridge, as shown in the transverse view (Scheme 6b). A coherent ring current is present in the reactant (Scheme S4a) but is weaker than the TS current by a factor or more than 2.

Scheme 6. π Current–Density Maps for the [1,5] Hydrogen Shift in Cyclopentadiene Compared with Cyclopentadiene Anion[a]



[a]Key: (a) current on the face opposite to the migration (j_{max} = 0.086 au); (b) transverse section of the current in a plane showing the diversion of one streamer of current through the CHC bridge; (c) current in the cyclopentadiene anion (j_{max} = 0.069 au).

For comparison, the π current–density map of cyclopentadiene anion, isoelectronic with the [1,5] H-shift transition state, is shown in Scheme 6c, indicating that the TS for the [1,5] hydrogen shift is more aromatic than cyclopentadiene anion. The orbital explanation of the current and its similarity to benzene and cyclopentadiene ring currents will be discussed below.

5-Fluorocyclopentadiene. There are four different transition states in 5-fluorocyclopentadiene. Three correspond to the cascade of hydrogen migrations shown in Scheme 2 and one to a [1,5] fluorine shift. First, considering the hydrogen shifts, our calculations show that all proceed via an aromatic TS, as diagnosed by the π current–density maps shown in Scheme 7. Current maps for the reactants 5-fluoro-, 1-fluoro-, and 2-fluorocyclopentadiene are given in Scheme S4b–d. For 1-fluoro- and 2-fluorocyclopentadiene there is a weak diatropic π-

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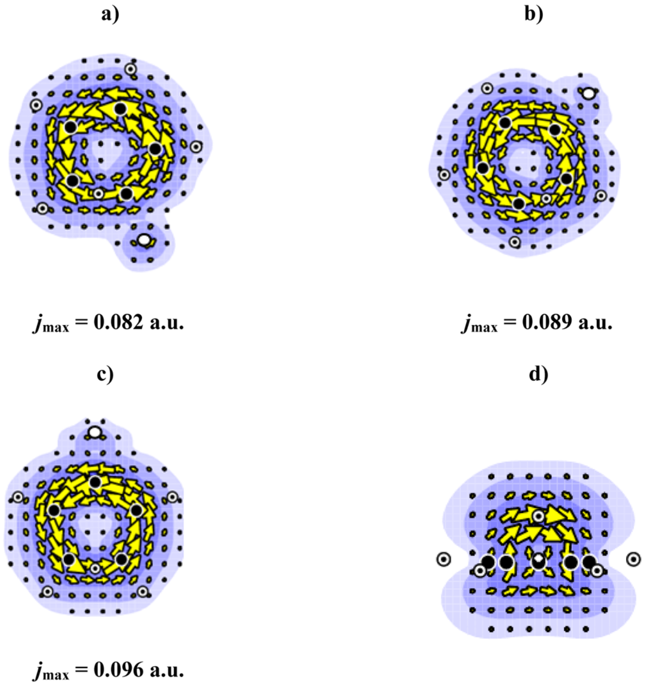
Scheme 7. π Current−Density Maps for the Three Hydrogen Migrations in 5-Fluorocyclopentadiene[a]



[a] Key: (a) the [1,5]; (b) the [1,2]; (c) the [2,3] hydrogen shifts with current viewed from above the ring. (d) [2,3] hydrogen shift with current viewed from the side, confirming that the current near the migratory atom has spatial π character flowing on both faces of the ring.

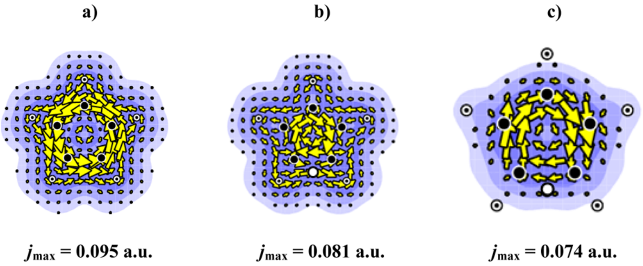
current in the reactant. For 5-fluorocyclopentadiene the current is mixed, showing a weak paratropic circulation associated with the four unsaturated carbon centers and some diatropic current at the CHF bridge.

The currents in the three TSs are of similar strength and spatial distribution to each other and to that calculated for the TS of the [1,5] hydrogen shift in cyclopentadiene with a similar implication of aromatic character.

In the TSs for the hydrogen shifts, the ring of carbon centers is close to planar and π/σ analysis of the orbitals is natural. However, in the TS for the fluorine shift, distortions from planarity are more significant and the π/σ distinction starts to break down, but a ring current is still discernible in our plots. Scheme 8 shows the total (all-electron, "$\pi + \sigma$") current−density map viewed from above the median plane of the carbon centers and compares it to the equivalent map for the cyclopentadiene anion. The diatropic circulation over carbon centers in cyclopentadiene anion is replaced by a *paratropic* current over the center of the molecule. Some of the central paratropic current can be ascribed to summation of σ bond currents, which give a localized paratropic vortex in molecules such as benzene itself.[25] However, the final map in Scheme 8 shows the distinct contribution from the HOMO of the TS, and this has the classic π-antiaromatic signature of a two-orbital, two-electron paratropic circulation.[19a] Our conclusion is that this TS, in contrast to those for the H shifts, is antiaromatic.

The fact that the "π" systems of the H-shift TS and the F-shift TS support ring currents that are in opposite senses can be rationalized very simply in terms of virtual excitations from occupied-to-unoccupied orbitals. Scheme 9 shows the frontier orbitals calculated for both H-shift and F-shift transition states.

Scheme 8. π Current−Density Analysis for the F Migration in 5-Fluorocyclopentadiene[a]



[a] Key: (a) total current map (π and σ contributions) for cyclopentadiene anion; (b) TS of the [1,5] fluorine shift in 5-fluorocyclopentadiene; (c) contribution from the occupied orbital 22 (see Scheme 9.

In the ipsocentric model, induced currents are generated by selection rules based on nodal character.[19a] The number of angular nodes in π orbitals, associated with the ring, is determined by the angular momentum parentage (Λ = 0, 1··· etc., where Λ is the component of angular momentum along the magnetic field direction, treated in full rotational symmetry). Excitations where the occupied-to-unoccupied transition would increase the number of angular nodal lines by one ($\Delta\Lambda$= +1) lead to diatropic currents; excitations that preserve the number of nodes on the ring ($\Delta\Lambda$= 0) lead to paratropic currents. The frontier orbitals of the TSs in Scheme 9 can be understood qualitatively using a C_s pseudosymmetry to clarify the interactions of orbitals on the migratory atom with the π/π^* manifold of the ring. We can quantify this qualitative interpretation of orbital contributions as arising from sets of virtual transitions. This is done via spectral decomposition of the first-order wave function.[31] With this analysis, we can pick out the most significant contributing transitions, and these are the transitions marked with arrows in Schemes 9 and 14.

For H migration, there is an s-orbital on H interacting with the π orbitals with angular momentum parentage Λ = 0, 1 and 2, giving a 4 × 4 problem for the symmetric and a 2 × 2 problem for the antisymmetric orbitals. The symmetric block yields two bonding orbitals (derived for Λ = 0 and Λ = 1) and two antibonding orbitals of Λ = 2 parentage, one of which becomes the LUMO, orbital 23. The antisymmetric block has a bonding Λ = 1 orbital, which becomes the HOMO (orbital 22) and an intrinsically antibonding Λ = 2 orbital which appears as the LUMO+1 (orbital 24). Hence, the π-like orbitals of the TS for the [1,5] H shift form a closed angular momentum shell with $\Delta\Lambda$= +1 for the HOMO−LUMO transition. This leads overall to a four-electron diatropic ring current, for the same reasons, as in benzene and cyclopentadiene anion.[19a]

In the case of the F shift, the relevant orbitals on the migrating atom can be considered as a symmetric p-like pointing at the ring, a 4 × 4 problem, and an antisymmetric p-orbital tangential to the ring, a 3 × 3 problem. The 4 × 4 interaction block leads to two symmetric bonding combinations of Λ = 0 and Λ = 1 parentage, identified as orbitals 18 (the lowest lying π-orbital, not shown in Scheme 9) and 21, and two antibonding combinations of Λ = 1 and Λ = 2 parentage (orbitals 23 and 25). The 3 × 3 block leads to two bonding combinations with Λ = 1 parentage and an antibonding Λ = 2. The result of the extra tangential F-orbital, not present in the case of the H shift, is that the HOMO and LUMO both have Λ = 1 parentage leading to a two-electron paratropic HOMO−

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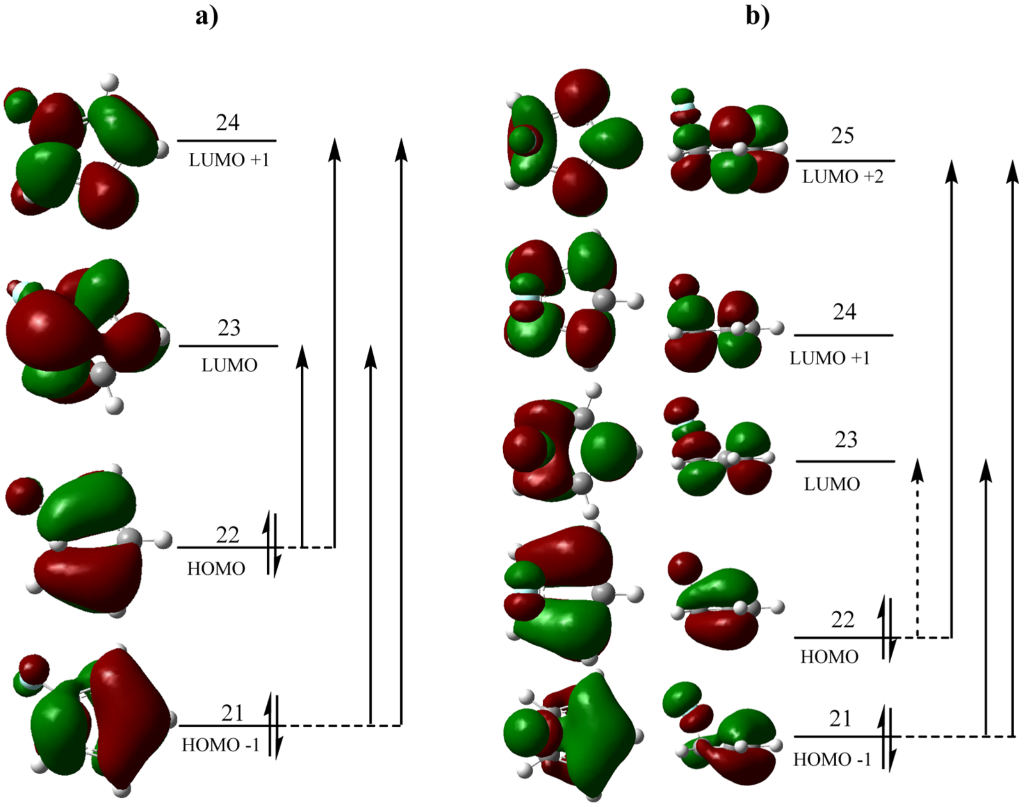
Scheme 9. Orbital Breakdown for the Excitations That Yield the Diatropic Current for (a) the [1,5] Hydrogen Shift and (b) the Paratropic Current for [1,5] Fluorine Shift in 5-Fluorocyclopentadiene[a]



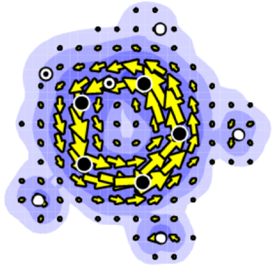
[a] Dashed arrows indicate excitations that preserve the number of angular nodes in the MO (rotational symmetry, i.e., paratropic current), and full arrows indicate excitations where the angular node is changed (translational symmetry, i.e., diatropic current).

LUMO current, partially cancelled by diatropic contributions of orbitals below the HOMO. This is in close analogy to the paratropic current in the antiaromatic planar form of 1,3,5,7-cyclooctatetraene.[19a]

This simple orbital picture accounts for the reversal of the ring-current between the two TSs and gives support to the rationalization of $\Delta H^{\ddagger}$ values given earlier. As an aside, the orbital picture carries the presumption that a change of 2 in electron count would reverse each ring current leading to paratropicity for the first TS and diatropicity for the second. Explicit calculations of current maps for dianions with frozen geometry confirm this hypothesis.

1,2,3,4-Tetrafluorocyclopentadiene. It has been noted in the previous section that fluorination at all other centers increases the predicted activation barrier for the [1,5] H shift from the CH_2 center. However, current−density maps show this chemical change is not accompanied by any loss of diatropicity in the 5-membered ring. Scheme 10 shows the π current on the face where migration takes place. It has j_{max} = 0.087 au and so is of similar strength to that in TSs for H shifts in the monofluoro species. The ring current of the reactant is again sensibly weaker than in the TS (Scheme S4e).

Scheme 10. π Current−Density Map for the [1,5] Hydrogen Shift in 1,2,3,4-Tetrafluorocyclopentadiene (j_{max} = 0.087 au)[a]



[a] To avoid local currents on the F centers, the map is plotted 1 a_0 above the ring in the same face as the migrating hydrogen.

Remaining Transition States of Cyclopentadiene. Current−density maps were computed for a number of [1,5] shifts in substituted cyclopentadienes: H and Me shifts in 5-methylcyclopentadiene (Scheme 11a,b; H and allyl shifts in 5-allylcyclopentadiene (Scheme 11c,d; cyclopropene-shift in 5-(3-cyclopropenyl)-cyclopentadiene (Scheme 11e); TMS-shift in 5-trimethylsilylcyclopentadiene (Scheme 11f); the dimethylboryl-shift in 5-dimethylborylcyclopentadiene (Scheme 11g).

All TSs support a diatropic ring current of similar strength. The TS for migration of allyl is apparently stronger than the others but with a less continuous, patchy appearance. This can be attributed to mixing of the σ and π contributions in this nonideal geometry. All reactants show a ring current (Scheme S4f−j) which is weaker than the TS by a factor of 2 or more in all but two cases. The diatropic circulation in the TMS reactant has about three-quarters of the strength of the TS ring current, and in the boryl reactant the ring current is actually *stronger* by about 10% than in the TS. Interestingly these two cases correspond to the lowest calculated barriers (see Table 1). It

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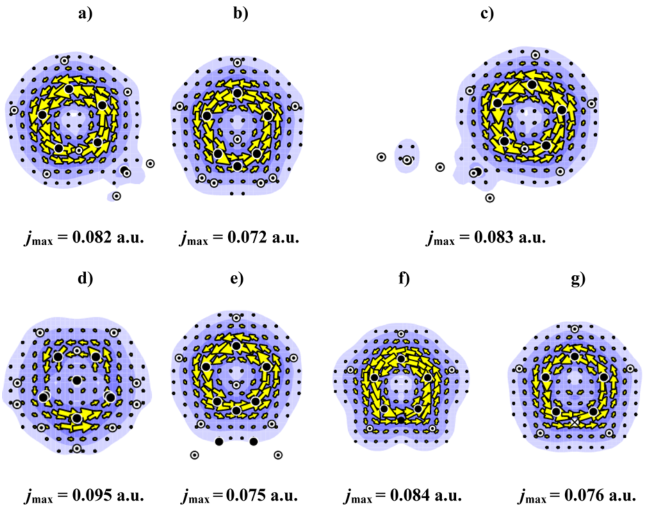
Scheme 11. π Current–Density Maps for a Series of [1,5] Shifts in Substituted Cyclopentadienes: (a) H shift and (b) Me Shift in 5-Methylcyclopentadiene; (c) H shift and (d) Allyl Shift in 5-Allylcyclopentadiene; (e) Cyclopropene Shift in 5-(3-Cyclopropenyl)cyclopentadiene; (f) TMS Shift in 5-(trimethylsilyl)cyclopentadiene; (g) Dimethylboryl Shift in 5-Dimethylborylcyclopentadiene[a]



[a] The projectionS of the methyl groups, boryl and TMS shifts, have been removed for clarity.

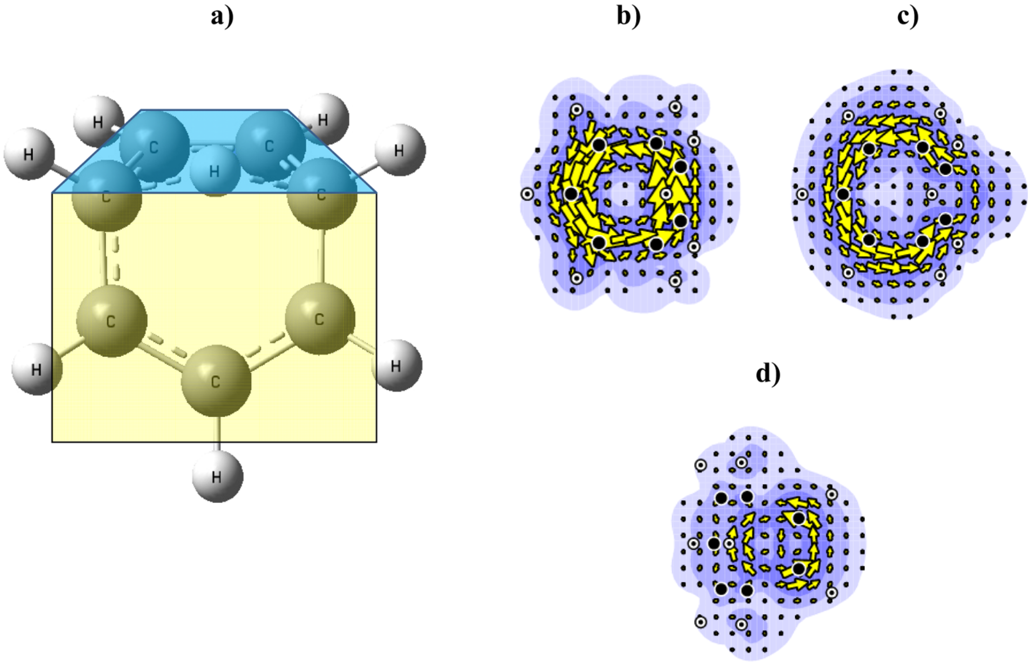
seems especially significant that the barrier of 0.26 kcal/mol for the 5,1-boryl shift should occur in a case where aromaticity, as judged from currents, is strong in both reactant and TS. As noted earlier, the change in geometry from reactant to TS is small for the 5,1-boryl shift; the currents indicate that rearrangement within the π-electronic structure is also minor. Cycloheptatriene: The TS for the [1,5] hydrogen shift in cycloheptatriene is far from planar and has the appearance of a tub in which the migratory hydrogen bridges the 1,5 gap; the 6,7 carbon pair corresponds to a double bond with bond length 1.35 Å. Detection of current distribution using our method of projection of current into the plotting plane is more difficult in this nonplanar system. Scheme 12 shows the current density maps plotted using the plane as the two sides of the "tub", rough indications of the locations of these planes are shown in Scheme 12a).

The maps reveal two components of the current–density. The first is a diatropic circulation of the C_6C_7 bond as illustrated in Scheme 12d. The second is a diatropic ring current on the cycle C_1 to C_5, as illustrated in Scheme 12b,c. This current is stronger on the upper face, map b, where is passes through the C_1··H··C_5 bridge of the TS. This has the effect of "pinching" down the two loops of a conventional π ring-current into one in the bridge region resulting in the apparent break in the "horseshoe" shaped current-density map, Scheme 12c), for the lower face. In spite of the unusual topology this ring current qualifies the TS as aromatic.

The geometry of cycloheptatriene reactant is also distinctly nonplanar, which blurs the distinction between σ and π orbitals and introduces sometimes intense artifacts when the plotting plane cuts through bonds. Even so, it is possible to find a plotting plane referred to the six unsaturated carbon centers, in which there is evidence of a weak "homoaromatic" current (Scheme S4k) with features in common with the homotropenylium cation.[32]

7-Fluorocycloheptatriene. The two transition states found for 7-fluorocycloheptatriene are a [1,7] hydrogen shift and a [1,7] fluorine shift. Current–density maps for both show a

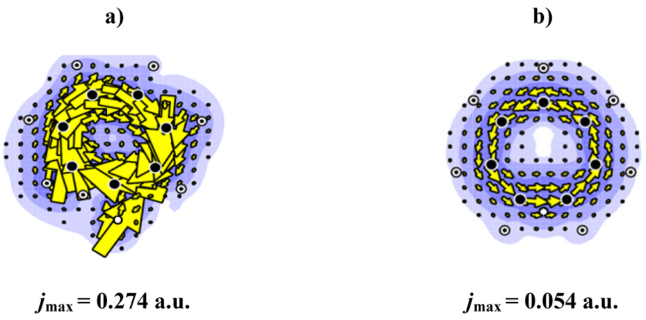
Scheme 12. π Current–Density Maps for [1,5] Hydrogen Shift in Cycloheptatriene Taken Using Two Different Planes[a]



[a] Key: (a) Illustration of the two planes as the yellow and blue planes. Taking the first yellow plane of carbon atoms C_1 to C_5, (b) the current map is calculated at 1 a_0 above the plane (out of the page) and (c) 1 a_0 below the plane (into the page). The second plane, the blue box, contains carbon atoms C_5, C_6, C_7, and C_1, and we show (d) the π current map calculated at 1 a_0 above the plane.

complete reversal of the respective [1,5] shifts in cyclopentadiene. Thus, in the present case, the H-shift TS has a paratropic (antiaromatic) ring current (Scheme 13a) and the F-shift TS has a weaker diatropic (aromatic) ring current (Scheme 13b). Nonplanarity of the reactant geometry is again a complicating factor for this case, but there is evidence for a homoaromatic diatropic ring current in the ground state (Scheme S4l). It is interesting that for both [1,5] H shift of cycloheptatriene and [1−7] F shift of 7-fluorocycloheptatriene, the barriers are significantly lower than for the [1,7] H-shift of 7-fluorocycloheptatriene (Table 1).

Scheme 13. **π Current−Density Maps for the Two Shifts in 7-Fluorocycloheptatriene: (a) [1,7] Hydrogen Shift (j_{max} of 0.274 au);[a] (b) [1,7] Fluorine Shift (j_{max} of 0.054 au)**



[a] This includes some large local currents from the fluorine; the π ring current is partially masked by the non-uniformity.

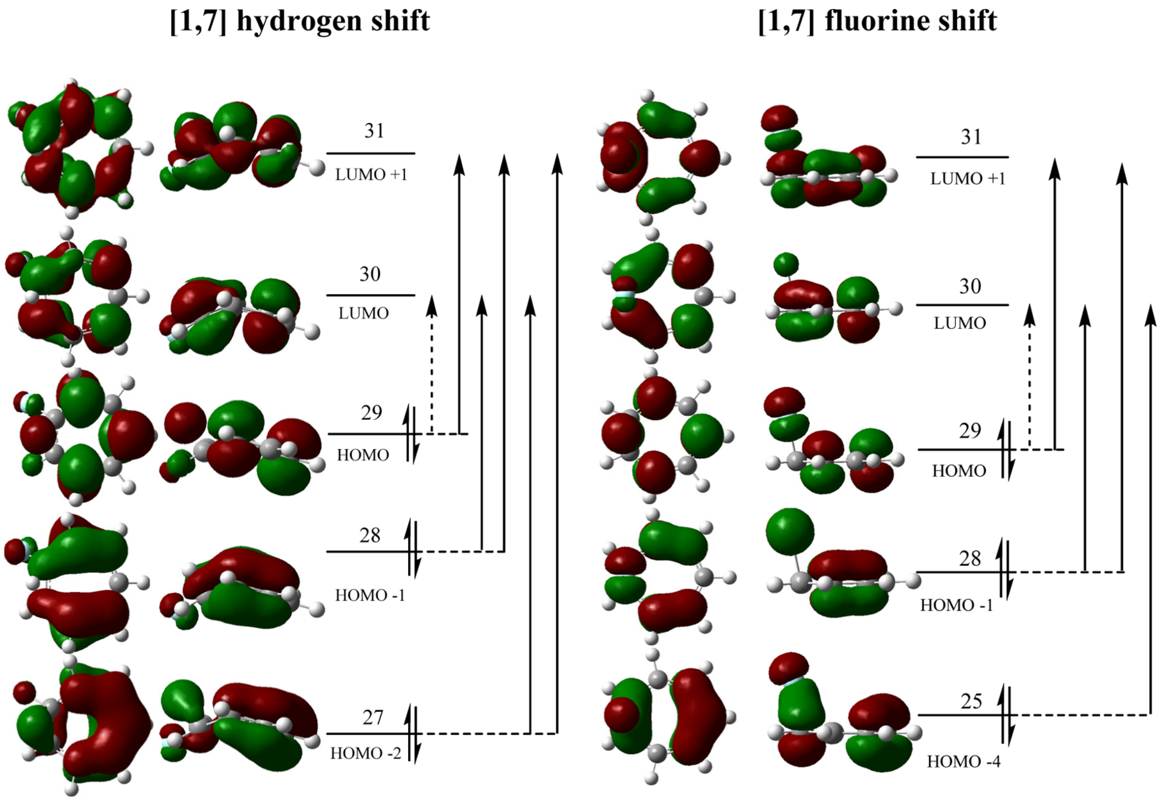
This reversal in currents offers a striking rationalization of the trends in the barrier heights discussed previously. H atom migration has an activation enthalpy of 28.6 kcal/mol for the diatropic TS ([1,5] shift in 5-fluorocyclopentadiene) and 83.7 kcal/mol for the paratropic TS ([1,7] shift in 7-fluorocycloheptatriene). F atom migration has an activation enthalpy of 48.0 kcal/mol for the paratropic TS ([1,5] shift in 5-fluorocyclopentadiene) and 28.3 kcal/mol for the diatropic TS ([1,7] shift in 7-fluorocycloheptatriene).

The ring current directions for the [1,7] TSs have a ready explanation in an orbital scheme. The frontier orbitals and energy levels for the two TSs are shown in Scheme 14.

The orbitals can be interpreted as before by the combination of the π/π* manifold of the ring with orbitals for the migrating atom (one for H, two for F), again using a C_s pseudosymmetry. The cycloheptatriene ring now has π MOs with Λ = 0−3. For the H-shift, the 5 × 5 symmetric interaction block produces three bonding contributions with Λ = 0, 1, and 2 parentage, of which the HOMO has Λ = 2 (orbital 29). The 3 × 3 block retains the bonding Λ = 1 orbital, with the Λ = 2 orbital forming the LUMO (orbital 30) of the TS. The conclusion from the selection rules is clear: the dominant HOMO−LUMO transition has ΔΛ = 0 and gives rise to a strong paratropic current. This is partially canceled by weaker diatropic contributions, again as in the manner of planar COT or the TS for the [1,5] F shift in cyclopentadiene.

The corresponding analysis of the F migration proceeds along the same lines. The symmetric 5 × 5 interaction block still gives three bonding combinations of the parentage Λ = 0 to 2, with a Λ = 2 HOMO (orbital 29). The antisymmetric block,

Scheme 14. **Orbital Breakdown for the [1,7] Hydrogen and [1,7] Fluorine Shifts in 7-Fluorocycloheptatriene[a]**


[1,7] hydrogen shift

[1,7] fluorine shift

[a] Dashed arrows indicate transitions possible via non-nodal change transitions and solid arrows denote transitions possible via nodal change transitions. Only transitions with a significant contribution to the resulting current are shown.

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now a 4 × 4 problem, again gives two bonding combinations of $\Lambda = 1$ parentage (orbitals 26, not shown in Scheme 14, and 28) and two antibonding combinations with parentage $\Lambda = 2$, forming the LUMO (orbital 30), and $\Lambda = 3$ (orbital 32, highlighting a high energy π-orbital not shown in Scheme 14). At first sight, the selection rules seem to contradict the observed current in Scheme 13. However, the paratropic contribution from the HOMO to LUMO transition is weak and is canceled out by diatropic contributions from other excitations, such as HOMO to LUMO+1. In contrast, the HOMO current for the H-shift is dominated by the HOMO−LUMO excitation leading to the strong paratropicity.

This apparent paradox is explained by inspection of the forms of the two HOMO orbitals. In the TS for the H-shift, the clear $\Lambda = 2$ character (i.e., four lobes separated by two nodal lines) of the orbital come from the participation of the H s-orbital on the upper face of the ring (compare the top and side views of the MO in Scheme 14). The HOMO−LUMO overlap on this face gives rise to the dominant paratropic current. In the TS for the F shift the HOMO has mixed character, with only three lobes on the upper face. The F-derived orbital is not participating in the region of the ring. The LUMO has typical $\Lambda = 2$ character, and so the HOMO−LUMO overlap is not of strict $\Delta\Lambda = 0$ character on either of its faces. The weak paratropicity of this excitation is then overwhelmed by the diatropic contributions. Hence, the reversal of current between the two TSs is a result of the poorer spatial overlap and energetic mismatch for F and C 2p-orbitals, rather than an effect of symmetry alone.

Cyclopropene. The lack of planarity in the cyclopropene systems again leads to a contentious current−density analysis. In the case of the [1,3] hydrogen shift in both cyclopropene and 3-fluorocyclopropene, the ring has undergone such large distortions in the TSs that conclusive proof of aromaticity is not possible. At best, the results weakly *imply* aromaticity in the case of the TS for the [1,3] hydrogen shift in cyclopropene. But in the case of the hydrogen shift in 3-fluorocyclopropene π current-density maps are uninterpretable. This could also be due in part to the difficulty in accurate partitioning into π and σ orbitals.

In the case of the [1,3] fluorine shift in 3-fluorocyclopropene, current map interpretation is again difficult. This could be due to the difficulty in π and σ orbital partitioning. On the other hand, the relatively low activation enthalpy; the geometry of the TS with no long bond; the large charge separation found for the TS, and formal analogy with the 7-fluorocycloheptatriene system permit the suggestion of some aromatic, cyclopropenyl cation character in this TS. Overall, no clear ring current is observable through any of our calculations and we cannot confidently conclude that any shift in cyclopropene proceeds through an aromatic or antiaromatic TS.

CONCLUSIONS

Computational evidence, including activation enthalpies, NPA charge distributions, and ring-current evaluations, confirm the aromaticity of the transition states for the orbital-symmetry allowed, suprafacial [1,5] hydrogen, alkyl, silyl, and boryl shifts of 5-substituted cyclopentadienes and for a few other ring-substituted cyclopentadienes as well. The [1,5] fluorine shift in 5-fluorocyclopentadiene has, on the other hand, an antiaromatic, paratropic ring current owing to the cyclopentadienyl cation character in this TS and, thus, a much higher activation enthalpy than the other [1,5] shifts.

Calculations on the [1,3] hydrogen and fluorine shifts in cyclopropene and fluorocyclopropenes reveal behavior strikingly different from that of the cyclopentadienes: The hydrogen shifts have high barriers and TSs in which a ring C−C bond is largely broken. But the fluorine shift is relatively easy and has no broken C−C bond in the TS. We suggest that this TS has aromatic, cyclopropenyl cation character based on its calculated properties, listed above, although a definitive ring current could not be identified for these TSs.

Studies on [1,7] shifts in cycloheptatrienes show similar but enhanced behavior of this sort. The suprafacial [1,7] hydrogen shift is forbidden by orbital-symmetry considerations and has a very high barrier in both cycloheptatriene and 7-fluorocycloheptatriene. However, the suprafacial [1,7] fluorine shift has a low activation enthalpy, a diatropic ring current, and hence, aromatic cycloheptatrienyl cation character in the TS. The [1,3] and [1,7] fluorine shifts show that expectations based on the Woodward−Hoffmann rules can be subverted should unusual stabilization of the TS be possible.

Calculations support the idea that geometric distortions of the cyclic moiety in the TS have only small effects on aromaticity (see Appendix A of the Supporting Information) but that charge separation can be a powerful determinant for such character.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01261.

> Details of the computational approaches; Appendix A; electronic energies, zero-point vibrational energies, and imaginary frequencies of transition states; Cartesian coordinates for obtained structures; selected geometric parameters; current−density maps for the fluorine shift in 3-fluorocyclopropene the fluorine shift in 7-fluorocycloheptatriene and the hydride shift in cyclopentadiene (PDF)

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