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Electrostatic Acceleration of Electrocyclic Reactions by Metal Cation Complexation: The Cyclization of 1,3-*cis*-5-Hexatriene into 1,3-Cyclohexadiene and the 1,5-Hydrogen Shift in Cyclopentadiene. The Aromaticity of the Transition Structures

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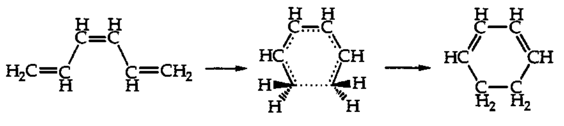
Abstract: Appreciable electrostatic acceleration of the cyclization of 1,3-*cis*-5-hexatriene to 1,3-cyclohexadiene by Li^+ complexation is predicted at theoretical levels where the computed kinetic parameters of the uncatalyzed reaction (E_a = 30,4−30,6 kcal/mol, $A = 6.1 \times 10^{11}$) agree with experiment ($E_a = 29{,}9 \pm 0{,}5$ kcal/mol, $A = (7{,}2 \pm 5{,}2) \times 10^{11}$). The calculated Li^+ electrostatic acceleration effect is very large, 9.2 kcal/mol (RMP4SDTQ) and 11,5 kcal/mol (Becke3LYP), even in this hydrocarbon system. A similar accelerating effect (10,9 kcal/mol, Becke3LYP) is found for the complexation by $Li(H_2O)^+$, a simple solvation model. These accelerations are due to the greater electrostatic stabilization of the transition structure than the ground state. The aromaticity of the 6-electron cyclization transition structure is characterized by its exalted magnetic susceptibility (Λ, −17,9 ppm cgs) and by upfield lithium chemical shift (−7,8) in the Li^+-complexed transition structure, computed by the IGLO method. The accelerations of various metal cations have been compared with the 8,0 kcal/mol effect for Li^+. The reductions of the 1,5-hydrogen shift barrier in cyclopentadiene are 4.7 kcal/mol for Na^+, 12.3 kcal/mol for Mg^{2+}, 13.7 kcal/mol for HBe^+, and 19.9 kcal/mol for Be^{2+}, with 8.0 kcal/mol for Li^+, respectively. The computed order of the cation acceleration is $Be^{2+} > HBe^+ \geq Mg^{2+} > Li^+ > Na^+$, comparable with the measured $Mg^{2+} > Li^+ > Na^+$.

Introduction

The cyclization of 1,3-*cis*-5-hexatriene (**1**) to 1,3-cyclohexadiene (**3**), a basic pericyclic reaction considered by Woodward and Hoffmann,[1] is now predicated to proceed more rapidly in an electrostatic field induced by the presence of metal cations.



1 **2** **3**

The unimolecular kinetics of this ring closure were determined experimentally by Lewis and Steiner[2] in the gas phase at 117−190 °C

$$k = (7.15 \pm 5.2) \times 10^{11} \exp[-(29{,}9 \pm 0.5)/RT]\ \mathrm{s}^{-1}$$

An *ab initio* RHF/6-31G* study of this cyclization[3,4] confirmed the concerted disrotatory reaction mechanism predicted by Woodward and Hoffmann.[1] However, the calculated activation energy (RMP2/6-31G*//RHF/6-31G*)[3] was 4.0 kcal/mol lower than the measured value. We show here that acceptable agreement is achieved at more sophisticated theoretical levels.

$LiClO_4$/diethyl ether and related Lewis acid systems, which catalyze Diels−Alder reactions dramatically, have been described extensively.[5] However, these accelerations have been ascribed to Lewis acid complexation of Li^+ to the heteroatom of the functional groups in the dienophile or in the diene components. Recently, we have predicted that Li^+ complexation accelerates pericyclic reactions in hydrocarbon systems which have no functional groups or heteroatoms, e.g. the degenerate Cope rearrangement in semibullvalene[6] as well as the 1,5-H shifts in cyclopentadiene and in 1,3-pentadiene.[7] The more polarizable transition structures are stabilized to a greater extent than the ground states by Li^+ complexation. We now report a similar effect on the cyclization of 1,3-*cis*-5-hexatriene to 1,3-cyclohexadiene and compare the electrostatic acceleration of the 1,5-H shift in cyclopentadiene by other metal cations, e.g. Na^+, Mg^{2+}, HBe^+, and Be^{2+}, vs Li^+.[7]

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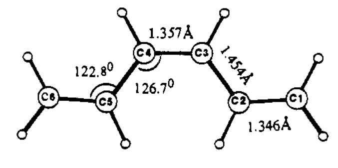
Computational Details

Geometries of all stationary points were optimized at RMP2(fc)/6-31G* using the Gaussian 92[8a] and Gaussian 94[8b] program packages and were characterized as minima or saddle points by calculation of the harmonic vibrational frequencies using analytical second derivatives (RHF/6-31G* frequencies were used for H_2O solvated lithium cation complexes). This gave the zero-point energies (ZPE), entropies (S), and thermochemical data. The computed ZPE's were scaled by an empirical factor of 0.93 (RMP2(fc)/6-31G*) or 0.89 (HF/6-31G*) to correct for the harmonic approximation.[9a,b] Single-point energies were determined at RMP4SDTQ/6-31G*[9a,b] and at Becke3LYP/6-311+G* (density functional theory, DFT) using the RMP2(fc)/6-31G* geometries.[9c,d] For the catalyzed 1,5-H shift in cyclopentadienes by Na^+, Mg^{2+}, HBe^+, and Be^{2+} metal cations, RMP2(fu) geometry optimizations and frequency calculations were carried out, and single-point energies were computed at RMP4SDTQ/6-311G**//RMP2(fu)/6-31G*.[9a,b] The activation enthalpies ($\Delta H^{\ddagger}$) are corrected for ZPE and thermal energies (vibrational, rotational, and transitional) at finite temperature.[9a,b] The activation energy (E_a) is equal to $\Delta H^{\ddagger} + RT$. Chemical shifts (δLi^+ and δH) and magnetic susceptibilities (χ) were computed on the correlated geometries using the IGLO (Individual Gauge for Localized Orbitals) method[10] with two basis sets: II [the Huzinaga 9s5p set for carbon (51111/2111, with d η = 1.0), 5s1p for hydrogen (311, with p η = 0.65), and 9s3p for Li (51111/3, with p η = 0.19, 0.75, 3.0)] and DZ [Huzinaga: 7s3p for carbon (4111,21), 3s for hydrogen (21)].

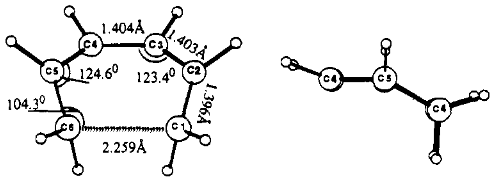
Results and Discussion

(a) Cyclization of 1,3-*cis*-5-Hexatriene (1) to 1,3-Cyclohexadiene (3). The RMP2(fc)/6-31G* geometries of 1,3-*cis*-5-hexatriene (**1**), the cyclization transition state (**2**), and 1,3-cyclohexadiene (**3**) are shown in Figure 1. The calculated absolute and relative energies are given in Tables 1 and 2. According to the RMP2(fc)/6-31G* frequency calculations, both **1** (C_{2v}) and **3** (C_2) are minima and **2** (C_s) is the transition structure: the only imaginary frequency corresponds to the concerted disrotatory approach of the two terminal CH_2 groups.

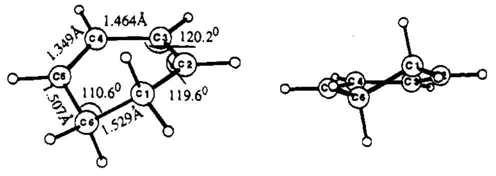
As shown in Figure 1, **1** has typical single and double CC bond lengths along the conjugated chain (1.346, 1.454, and 1.357 Å). The C1−C6 separation, 5.780 Å in **1**, decreases to 2.259 Å in transition structure **2**. Comparable CC separations have been computed for many concerted and synchronous pericyclic transition structures;[4] the Diels−Alder reactions of ethylene with cyclopentadiene (2.227 Å) and with 1,3-butadiene (2.285 Å)[11a] are examples. The other C−C bond lengths of 1.396−1,404 Å in **2** are very close to the benzene distance of 1.395 Å (MP2-(fc)/6-31G*) and to the values in many aromatic transition structures (for example, for the 1,5-H shifts in cyclopentadiene and in 1,3-pentadiene,[4,7] the 1,7-H shift in 1,3,5-heptatriene,[11b] as well as the Cope rearrangement in semibullvalene[6] and in 1,5-hexadiene[11c]). Hence, the geometry is in accord with the description of **2** as an aromatic transition structure.[12]



1, C_{2v}



2, C_s



3, C_2

Figure 1. The RMP2(fc)/6-31G* geometries of 1,3,5-hexatriene (**1**), cyclization transition structure **2**, and 1,3-cyclohexadiene (**3**).

Table 1. Calculated Total Energies (in au), Zero-Point Vibrational Energies (ZPE), and the Thermal Energies (E_{th}, kcal/mol at 400 K), as well as the Number of Imaginary Frequencies (NIMAG) for **1**, **2**, and **3**

no.	symm	RMP2(fc) /6-31G*	ZPE[a] (NIMAG)	E_{th} (400 K)	RMP4SDTQ /6-31G*[b]	Becke3LYP /6-311+G*[b]
1	C_{2v}	−232.559 79	70.2(0)	83.3	−232.648 13	−233.450 60
2	C_s	−232.517 03	70.5(1)	82.5	−232.599 83	−233.401 98
3	C_2	−232.593 62	72.7(0)	84.6	−232.678 38	−233.471 25

[a] RMP2(fc)/6-31G* values scaled by 0.93, sec ref 9. [b] Using RMP2(fc)/6-31G* geometries.

Table 2. Computed Activation Entropies ($\Delta S^{\ddagger}$, cal/(mol K)), Activation Energies (E_a) and Reaction Enthalpies (ΔH, kcal/mol) as well as Frequency Factor (A) Compared with the Measured Values for the Cyclization of **1** to **3**

	RMP2(fc) /6-31G*	RMP4SDTQ /6-31G*[a]	Becke3LYP /6-311+G*[b]	expt[c]
$\Delta S^{\ddagger}$ (A)	−5.2 (6.1 × 10^{11})			−4.9 ((7.2 ± 5.2) × 10^{11})
E_a	26.9	30.4	30.6	29.9 ± 0.5
ΔH	−20.0	−17.8	−11.8	−17.5[d]

[a] RMP4SDTQ/6-31G*//RMP2(fc)/6-31G* + ZPE(RMP2(fc)/6-31G*, 400 K). [b] Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + ZPE-(RMP2(fc)/6-31G*). [c] Reference 2. [d] Estimated using Benson increments, see ref 13.

The calculated 1,3,5-hexatriene cyclization barriers of 30,4 kcal/mol [RMP4SDTQ/6-31G*//RMP2(fc)/6-31G* + ZPE-

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(RMP2(fc)/6-31G*, 400 K)] and 30.6 kcal/mol [Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + ZPE (RMP2(fc)/6-31G*, 400 K)] agree very well with experiment, $E_a = 29.9 \pm 0.5$ kcal/mol.[2] Even the computed activation entropy ($\Delta S^{\ddagger}$, −5.2 kcal/(mol K)) and frequency factor ($A = 6.1 \times 10^{11}$) are in accord with the experimental[2] values of −4.9 cal/(mol K) and $(7.15 \pm 5.2) \times 10^{11}$ s^{-1}. This demonstrates the ability of the ab initio and DFT levels employed here to reproduce the kinetic data (Table 2). The reaction enthalpy of −17.8 kcal/mol (RMP4SDTQ) agrees well with the estimated −17.5 kcal/mol by using the Benson[13] hydrocarbon increments, and the Becke3LYP/6-311+G* value of −11.8 kcal/mol is, however, 6.0 kcal/mol lower than the RMP4SDTQ result.

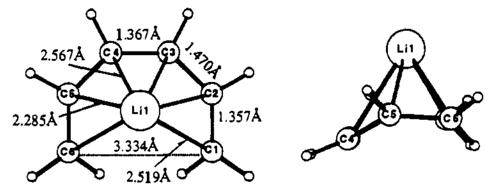
Assuming the transition state to be a diradical, the nonconcerted cyclization of 1,3,5-hexatriene was estimated to require an activation energy of ca. 42−45 kcal/mol by Doering et al.[14] Hence, the (**1** → **3**) energy of concert,[15] 12−15 kcal/mol, is much lower than those of the 1,5-H and 1,7-H shifts (40 and 60 kcal/mol,[7,11b] respectively), but near the energy of concert (13.7 kcal/mol) estimated for the Diels−Alder reaction of cyclopentadiene with ethylene.[11a,15] Thus, cyclization transition structure **2** also fulfills the energetic criterion of aromaticity.[12]

(b) Acceleration of 1 → 3 Cyclization by Li⁺ Complexation. The RMP2(fc)/6-31G* geometries of the Li^+ complexes, **4**−**7**, are shown in Figure 2 to facilitate comparison with **1**−**3** (Figure 1). The calculated absolute and relative energies of **4**−**7** are summarized in Tables 3 and 4.

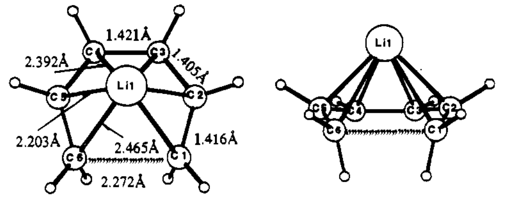
The most stable Li^+−**1** complex (**4**) adopts a conformation in which Li^+ coordinates with all three double bonds; the Li^+−C separations are 2.519, 2.285, and 2.567 Å. In comparison with the extended conformation of **1**, the C_1−C_6 separation is shortened to 3.334 Å. Li^+ complexation lengthens by 0.01 Å on the double and conjugated single CC bonds.

As in the Li^+ catalyses of the 1,5-H shifts in cyclopentadiene and in 1,3-pentadiene,[7] we examined two possible C_s complexes of transition structure **2** with Li^+, **5** and **6**. As shown in Figure 2, the Li−C distances are the major differences between **5** and **6**. Since corresponding Li−C separations are shorter in **5** (2.465, 2.203, and 2.392 Å) than in **4**, Li^+ interacts better with the transition state than with the ground state. In **6**, Li^+ coordinates mainly with C3,4 (2.278 Å); the Li−C1,6 and Li−C2,5 distances, 3.319 and 3.007 Å, are too long for effective interaction. The RMP4SDTQ/6-31G*//RMP2(fc)/6-31G* complexation energies are −26.6 (**4**), −35.7 (**5**), −24.7 (**6**), and −28.7 (**7**) kcal/mol (the corresponding Becke3LYP/6-311+G*//MP2(fc)/6-31G* values are: −29.3 (**4**), −40.6 (**5**), and −34.9 (**7**) kcal/mol).

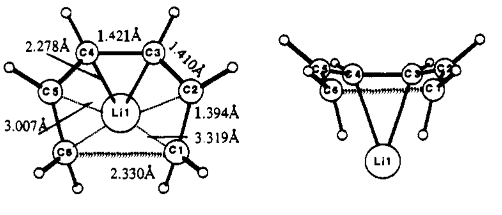
The RMP2(fc)/6-31G* frequency calculations show **4** and **7** to be minima on the potential energy surface and **5** to be a transition structure (NIMAG=1). However, with two negative frequencies (NIMAG=2) **6** is a higher order stationary point. Moreover, **5** is 11 kcal/mol more stable than **6**, due evidently to the greater Li−C separations in **6** than in **5**. The calculated activation energy (via **5**) and reaction exothermicity for the conversion of **4** into **7** are 21.2 and −20.3 kcal/mol (RMP4SDTQ) and 19.1 and −17.9 kcal/mol (Becke3LYP, Table 4), respectively. In comparison with reaction of **1** to give **3** (via **2**), the cyclization barrier is reduced due to Li^+ complexation by 9.2 kcal/mol (RMP4SDTQ) and 11.5 kcal/mol (Becke3LYP).



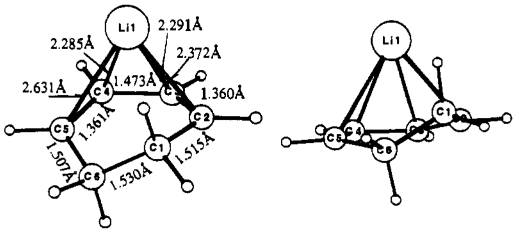
4, C_s



5, C_s



6, C_s



7, C_1

Figure 2. The RMP2(fc)/6-31G* geometries of Li^+ complexes **4**, **5**, **6**, and **7**.

Table 3. Calculated Total Energies (in au), Zero-Point Vibrational Energies (ZPE), and the Thermal Energies (E_{th}, kcal/mol at 400 K) and the Number of Imaginary Frequencies (NIMAG) for **4**−**7**

no.	symm	RMP2(fc) /6-31G*	ZPE[a] (NIMAG)	E_{th} (400 K)	RMP4SDTQ /6-31G* [b]	Becke3LYP /6-311+G* [b]
4	C_s	−239.853 67	72.0 (0)	86.4	−239.941 04	−240.782 17
5	C_s	−239.824 49	72.2 (1)	85.5	−239.907 29	−240.751 59
6	C_s	−239.804 96	71.2 (2)	83.4	−239.889 64	
7	C_1	−239.890 36	73.8 (0)	87.2	−239.974 56	−240.811 74
Li⁺					−7.250 49	−7.284 92

[a] RMP2(fc)/6-31G* values scaled by 0.93, see ref 9. [b] Using RMP2(fc)/6-31G* geometries.

The accelerations of the 1,5-H shifts in cyclopentadiene and in 1,3-pentadiene by Li^+ complexation were attributed to electrostatic interactions; replacement of Li^+ by a positive charge (+) in the same position gave similar results.[7] The present investigation of the acceleration of the 1,3,5-hexatriene cyclization confirms this finding. Replacement of Li^+ by a positive charge (+) at the same position (r = 1.604 Å, the distance between Li^+ and the C2−C5 midpoint, Figure 2) resulted in a catalytic effect of 11.2 kcal/mol, close to the value (9.2 kcal/mol) for the Li^+ effect. Hence, the main contributions also come from the electrostatic interactions. The degenerate Cope rearrangement in semibullvalene is another example.[6] Moreover, shortening the distance (r) to the positive charge (+) from 1.604 to 1.204 Å decreases the activation energy from 18.4 to 3.2

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Table 4. Computed Activation Energies (E_a) and Electrostatic Catalytic Effects (ΔE_{cat})^a as well as Reaction Enthalpies (ΔH, kcal/mol) for the Li^+ Complexed Cyclization of **4** → **7**

	RMP2(fc) /6-31G*	RMP4SDTQ /6-31G*^{b}	Becke3LYP /6-311+G*^{c}
E_a [ΔE_{cat}] **4** → **5**	18.3 [−8.6]	21.2 [−9.2]	19.1 [−11.5]
E_a [ΔE_{cat}] **4** → **6**	29.5 [2.6]	30.3 [−0.1]	
ΔH **4** → **7**	−22.3	−20.3	−17.9

^{a} ΔE_{cat} is the difference between the calculated activation energies with and without Li^+ complexation. ^{b} RMP4SDTQ/6-31G*//RMP2(fc)/6-31G* + ZPE (RMP2(fc)/6-31G*, 400 K). ^{c} Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + ZPE (RMP2(fc)/6-31G*, 400 K).

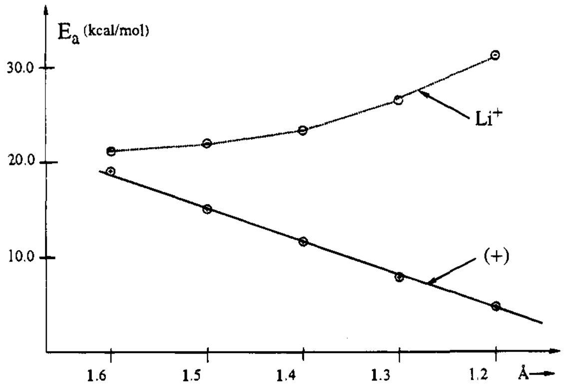

Figure 3. Calculated activation energies (RMP4SDTQ/6-31G*//RMP2-(fc)/6-31G*) as functions of the distance of Li^+ and of a positive charge (+) to the middle point of C_2-C_5 separation.

kcal/mol. In contrast, when the Li^+ distance is shortened from 1.604 to 1.204 Å, the activation energy increases from 21.3 to 31.0 kcal/mol (RMP4SDTQ/6-31G*//RMP2(fc)/6-31G*) (Figure 3). This difference is due to the greater repulsive interaction of the Li^+ cation with the carbon skeleton in the transition structure.

(c) Magnetic Criterion of Aromaticity of the Cyclization Transition State. The magnetic criteria of aromaticity, the shielding and deshielding effects of various nuclei as well as the diamagnetic susceptibility and magnetic anisotropy exaltation, result from "ring current effects".[16,17] The shielding of δLi^+, when π-complexed to aromatic compounds,[6,7,18] should be noted in the present context. In a new application, we have used the magnetic criteria to help characterize the aromaticity of pericyclic transition states.[6,7,11] Table 5 summarizes the calculated and experimental activation energies (E_a), the energies of concert (E_{con}),[15] the acceleration effects by Li^+ (ΔE_a), the Li^+ chemical shifts in the transition structures (δLi^+), and the magnetic susceptibility exaltations without and with Li^+ complexation. The reactions characterized in this manner include the degenerate Cope rearrangement in semibullvalene[6] and in 1,5-hexadiene,[11c] the cyclizations of 1,3,5-hexatriene and of 1,3,5,7-octatetraene,[11d] the 1,5-H shifts in cyclopentadiene and in 1,3-pentadiene,[7] and the 1,7-H shift in 1,3,5-heptatriene,[11b] as well as the Diels–Alder reaction of ethylene with butadiene and with cyclobutadiene.[11a]

While the magnetic properties of transition states cannot be measured experimentally, they can be computed effectively, e.g. by the IGLO method. Moreover, the change of the magnetic susceptibilities along the reaction coordinate (taken as the C1–C6 separation, Figure 4) can be explored.[11a,d] The geometries of the discrete points with various C1–C6 distances were optimized at RMP2(fc)/6-31G* and used for IGLO/DZ//RMP2-(fc)/6-31G* computations.

Figure 4 shows that both the calculated magnetic susceptibility (χ) and the relative energy have maxima near $r = 2.3$ Å along the reaction coordinate. This distance is in the typical range of such C–C separations in the transition structures of pericyclic reactions.[4,11] Transition structure **2** does possess aromatic character; both educt and product have *appreciably smaller* magnetic susceptibilities.

We reexamined the magnetic properties of the stationary points, e.g. educt (**1**), transition structure (**2**), and product (**3**), at the higher IGLO/II//RMP2(fc)/6-31G* level. As shown in Figure 5, the proton chemical shifts in **1** and **3** are normal. In transition structure **2**, the chemical shifts for H's on C3,4 increase from 5.8 to 7.0, while the latter is close to the benzene value (7.2 ppm) calculated at the same level, the δH's at C2,5 (5.8–6.6) and at C1,6 (5.2–5.3) in **1** are deshielded to 4.6 and 3.0 in **2**. These changes are significant but the upfield shifts are smaller than those for the 1,7-H shift transition structure in 1,3,5-heptatriene[7] and in the transition structures of Diels–Alder reactions.[11a] In contrast, the calculated total magnetic susceptibility ($\chi = -76.5$) is much larger for the cyclization transition state **2** than for **1** (−59.1) or **3** (−58.3). The magnetic susceptibility exaltation (Λ, relative to **1**) of −17.4 may be compared with the benzene value (−13.4) and with Λ's for the set of other pericyclic reactions summarized in Table 5. As expected, the magnetic susceptibility difference between **1** and **3** is quite small, 0.8 ppm cgs.

Evidence of the ring current effects in the Li^+ complexed aromatic transition structure (**5**) also is indicated by the IGLO upfield chemical shift of Li^+, −7.6, which is even larger than that computed for cyclopentadienyllithium, −5.7 (−8.6 measured in THF at 25 °C),[18] and for the Li^+–benzene complex (−6.6), but like that of the transition state of the 1,5-H shift in 1,3-pentadiene (−7.7).[7] In contrast, the calculated $\delta(Li^+)$'s in **4** and **7** are normal (−0.5 to 2.1 ppm).[6] The computed magnetic susceptibility exaltation (Λ, relative to **4**) of −17.1 characterizes the aromaticity of the Li^+-complexed cyclization transition structure **5**.

(d) Acceleration of 1,5-H Shift in Cyclopentadiene (CPD) by Na^+, Mg^{2+}, HBe^+, and Be^{2+}. Besides the Li^+ accelerating effects observed experimentally in diethyl ether, Li^+, Ba^{2+}, Mg^{2+}, and Na^+ accelerate Diels–Alder reactions in acetone and acetonitrile solutions.[5e,k] For example, Righetti et al.[5e] have

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(20) Due to the cost of computer time, we have carried out only the HF/6-31G* frequencies for **12** and **13**; the ZPE's are 87.2 (**12**, NIMAG=0) and 87.6 kcal/mol (**13**, NIMAG=1).

Table 5. The Calculated and Experimental Activation Energies (E_a), the Energies of Concert (E_{con}), the Acceleration Effects by Li^+ (ΔE_a), the Li^+ Chemical Shifts in the Transition Structures (δLi^+), and the Magnetic Susceptibility Exaltations without (H.C.) and with Li^+ Complexation (Li^+-comp.) of a Set of Pericyclic Reactions

reactions	E_a calc (expt)	E_{con}	ΔE_a	δLi^+	Λ(GS-TS) H.C.(Li^+ complexation)
Cope rearrangement in semibullvalene[a]	4.1 (4.8 ± 0.2)	51[b]	4.8	−10.8	−21.8 (−17.6)
1,5-H shift in cyclopentadiene[c]	27.5 (24.3 ± 0.5)	50	8.0	−5.6	−8.9 (−9.0)
1,5-H shift in 1,3-pentadiene[c]	36.9 (36.3 ± 0.5)	40	5.2	−7.7	−9.9 (−13.2)
cyclization of 1,3,5-hexatriene[d]	30.4 (29.9 ± 0.5)	12−15	9.2	−7.8	−17,4 (−17.1)
1,7-H shift in 1,3,5-heptatriene[e]	19.7 (20.8 ± 0.7)	60			−23.1 (−)
Cope rearrangement in 1,5-hexadiene[f]	35.8 (34.4 ± 0.5)	22.1			−19.9 (−)
butadiene + ethylene[g]	22.4 (23.6)	5.7			−19.3 (−)
cyclopentadiene + ethylene[g]	17.5 (17.5)	13.7			−17.7 (−)
cyclization of 1,3,5,7-octatetraene[h]	15.0 (17.0)	20			−12.6 (−)

[a] Reference 6. [b] The difference between the concerted activation energy and the energies of two allyl radicals determinated by Doering.[14c] [c] Reference 7. [d] This work. [e] Reference 11b. [f] Reference 11c. [g] Reference 11a. [h] Reference 11d.

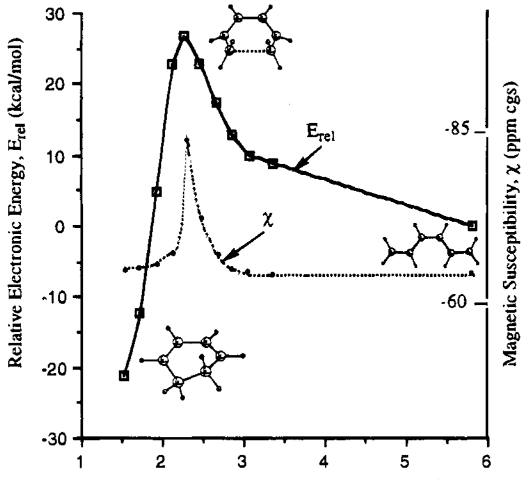
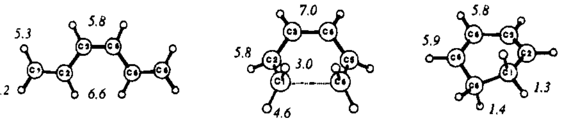


Figure 4. Relative electronic energies E_a (RMP2(fc)/6-31G*) and magnetic susceptibilities χ as a function of the reaction coordinate (C1−C6 distance).



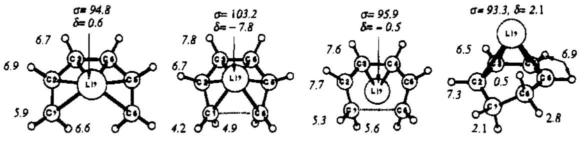
	1, C_{2v}	2, C_s	3, C_2
χ(dia, para, n.l.)	(-75.5, +10.9, +2,5)	(-81.9, +6.5, -1.1)	(-69.2, +6.8, +4.1)
χ(tot.)	-59.1	-76.5	-58.3
Λ	0.0	-17.4	+0.8

Figure 5. IGLO calculated magnetic susceptibilities χ (ppm cgs), magnetic susceptibility exaltation Λ (relative to **1**), and ^1H chemical shifts for 1,3,5-hexatriene (**1**), the cyclization transition structure (**2**), and 1,3-cyclohexadiene (**3**) (IGLO/II//RMP2(fc)/6-31G*).

reported an Mg^{2+} > Ba^{2+} ≥ Li^+ > Na^+ order of catalytic effects of the cation perchlorates on the rates of different Diels−Alder reactions in acetone solution. Fukuzumi and Okamoto[5k] observed the magnesium perchlorate catalyzed Diels−Alder reactions of anthracenes with *p*-benzoquinone derivatives in MeCN. These prompted us to study the accelerating effects of Na^+, Mg^{2+}, HBe^+, and Be^{2+} theoretically. Since our earlier investigation of the 1,5-H shift in cyclopentadiene by Li^+ found only accelerating effects when Li^+ and the migrating H are on the opposite side of the five-carbon skeleton,[7] we only investigated the Na^+, Mg^{2+}, HBe^+, and Be^{2+} catalytic effects in similar situations.

Table 6 summarizes the calculated zero-point vibrational energies (ZPE), the thermal energies (E_{th}, kcal/mol), the number of imaginary frequencies (NIMAG), the high-level total energies (in a.u.), the activation entropies ($\Delta S^‡$), and the activation energies as well as the catalytic effects for the 1,5-H shift with and without metal cation complexation. The RMP2(fu)/6-31G* optimized geometries of the complexed ground states (CPD-M^{n+}: **8** (Na^+), **9** (Mg^{2+}), **10** (HBe^+), and **11** (Be^{2+})) and of the transition state complexes (TS-M^{n+}: **8a** (Na^+), **9a** (Mg^{2+}), **10a** (HBe^+), and **11a** (Be^{2+})) are shown in Figure 7.

All the CPD−metal cation complexes (**8**−**11**) are minima (NIMAG=0, MP2(fu)/6-31G*) whereas **8a**−**11a** (the 1,5-H transition structure complexes) have NIMAG = 1 (Figure 7). The two methylene hydrogens, equivalent in CPD, are designated H_{cis} and H_{trans} with regard to the metal cation in the ground state complexes (**8**−**11**). The calculated Wiberg bond indexes (WBI[9a]) of C−H(cis) and C−H(trans) as well as the natural



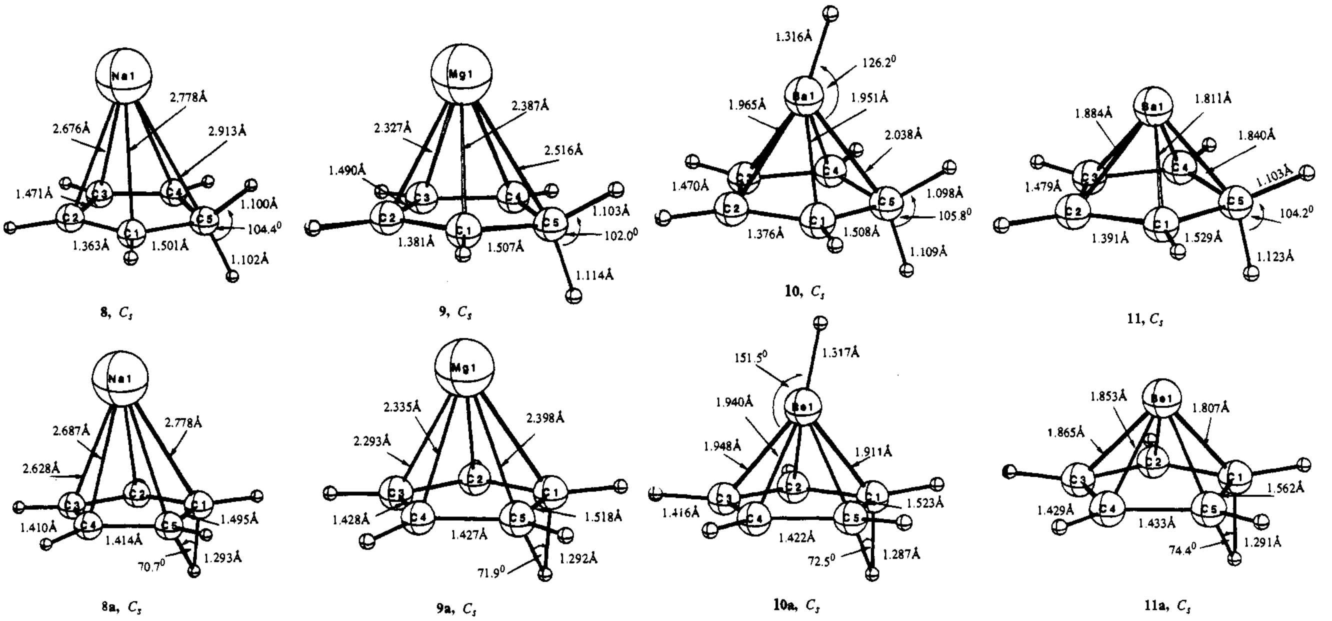
	4, C_s	5, C_s	6, C_s	7, C_1
χ(dia, para, n.l.)	(-72.9, +10.7, +2.7)	(-83.0, +6.5, -0.1)	(-82.7, +8.7, -0.7)	(-70.3, +7.8, +4.4)
χ(tot.)	-59.5	-76.6	-74.7	-58.1
Λ	0.0	-17.1	-15.2	+1.4

Figure 6. IGLO calculated magnetic susceptibilities χ (ppm cgs), magnetic susceptibility exaltation Λ (relative to **1a**), and ^1H chemical shifts for the Li^+ complexes **4**, **5**, **6**, and **7** (IGLO/II//RMP2(fc)/-6-31G*).

Table 6. Calculated Total Energies (au), Activation Entropies (ΔS^o, cal/(mol K)), Zero-Point Energies (ZPE, kcal/mol), Thermal Energies (E_{th}, kcal/mol), Activation Energies (E_a, kcal/mol), and Catalytic Effects (ΔE_{cat}, kcal/mol) for the 1,5-H Shift in Cyclopentadiene Complexed by Na^+, Li^+, Mg^{2+}, HBe^+, and Be^{2+}

M		RMP2(fu)/6-31G* ZPE (NIMAG, E_{th})[a]	RMP4SDTQ /6-311G**[b]	$\Delta S^‡$ (500 K)	E_a[c]	ΔE_{cat}[d]
Na^+	**8**	59.7 (0, 66.7)	−355.306 48	−2.1	22.3	−4.7
	8a	57.8 (1, 64.1)	−355.268 92			
Mg^{2+}	**9**	59.7 (0, 66.3)	−392.596 19	−2.1	14.7	−12.3
	9a	58.1 (1, 64.3)	−392.571 18			
HBe^+	**10**	65.5 (0, 72.3)	−208.642 20	−2.6	13.3	−13.7
	10a	64.2 (1, 70.5)	−208.619 76			
Be^{2+}	**11**	60.5 (0, 66.4)	−207.553 84	−2.1	7.1	−19.9
	11a	59.5 (1, 64.9)	−207.541 58			
Li^+[e]		60.2 (0, 66.8)	−200.898 70	−2.3	19.0	−8.0
		58.4 (1, 64.1)	−200.798 33			
X[e]		58.9 (0, 64.7)	−193.608 97	0.01	27.0	0.0
		56.8 (1, 61.8)	−193.562 42			

[a] At 500 K. [b] Using the RMP2(fu)/6-31G* geometries. [c] At RMP4SDTQ/6-311G**//RMP2(fu)/6-31G* + E_{th} (RMP2(fu)/6-31G*, 500 K). [d] Energy difference between the calculated activation energy with and without metal cation complexation. [e] X indicates the parent reaction without metal cation complexation, see ref 7.


8, C_s 9, C_s 10, C_s 11, C_s

8a, C_s 9a, C_s 10a, C_s 11a, C_s

Figure 7. The RMP2(fc)/6-31G* geometries for the cyclopentadiene metal cation complexes **8** (Na^+), **9** (Mg^{2+}), **10** (HBe^+), and **11** (Be^{2+}) and the corresponding transition structures (**8a**, **9a**, **10a**, and **11a**).

Table 7. The RHF/6-31G*//RMP2(fu)/6-31G* Wiberg Bond Indexes (WBI) for C−H(cis) and C−H(trans) and the Natural Charges (NPA) for H(cis), H(trans), and Metal Cations (M) in the CPD−M Complexes

		WBI		NPA		
complexes	P.G.	C−H(cis)	C−H(trans)	H(cis)	H(trans)	M
CPD[a]	C_{2v}	0.897	0.897	0.249	0.249	
CPD−Li^+ [a]	C_s	0.892	0.833	0.266	0.332	0.967
CPD−Na^+ (**8**)	C_s	0.899	0.850	0.255	0.312	0.978
CPD−Mg^{2+} (**9**)	C_s	0.870	0.766	0.313	0.422	1.859
CPD−BeH^+ (**10**)	C_s	0.861	0.780	0.328	0.383	0.858
CPD−Be^{2+} (**11**)	C_s	0.838	0.687	0.366	0.477	1.759

[a] Taken from ref 7.

Table 8. The RHF/6-31G*//RMP2(fu)/6-31G* Wiberg Bond Indexes (WBI) for C−H(m), Natural Charges (NPA) for H(m), and Their Differences to the Corresponding Values without Metal Cations as well as the Natural Charge for Metal Cations (M) in the 1,5-H Transition State Complexes

	P.G.	C−H(m)	Δ(C−Hm)	H(m)	Δ(H(m))	M
TS[a]	C_s	0.410	0.000	0.359	0.000	
TS−Li^+ [a]	C_s	0.379	−0.013	0.493	0.143	0.967
TS−Na^+ (**8a**)	C_s	0.386	−0.024	0.420	0.061	0.982
TS−Mg^{2+} (**9a**)	C_s	0.384	−0.026	0.418	0.059	1.876
TS−BeH^+ (**10a**)	C_s	0.396	−0.014	0.396	0.037	0.870
TS−Be^{2+} (**11a**)	C_s	0.348	−0.062	0.511	0.152	1.759

[a] Taken from ref 7.

charges[19] of H(cis), H(trans), and the metal cations are given in Table 7 for the ground states and in Table 8 for the transition states.

In **8**−**11**, the C−H_{trans} bonds are longer than the C−H_{cis} bonds and the WBI for C−H_{trans} bonds are smaller than those for C−H_{cis} bonds. On the other hand, H_{cis}'s are less positively charged than H_{trans}'s. These indicate that the C−H_{trans} bonds are more polarized and activated by metal cation complexation than the C−H_{cis} bonds. Hence, the migration of H_{trans}, as expected, should be easier than that of H_{cis}.

In the transition structure complexes (**8a**−**11a**), the WBI of the critical C−H(m) bonds are smaller than in the transition state without attached metal ions, and the migrating H(m)'s in the transition state metal complexes are more positive charged.

Table 9. Calculated Total Energies (in au) and the Activation Energy (E_a, in kcal/mol) for $Li^+(H_2O)$ Complexed 1,3,5-Hexatriene (**12**) and the Cyclization Transition State (**13**)[a]

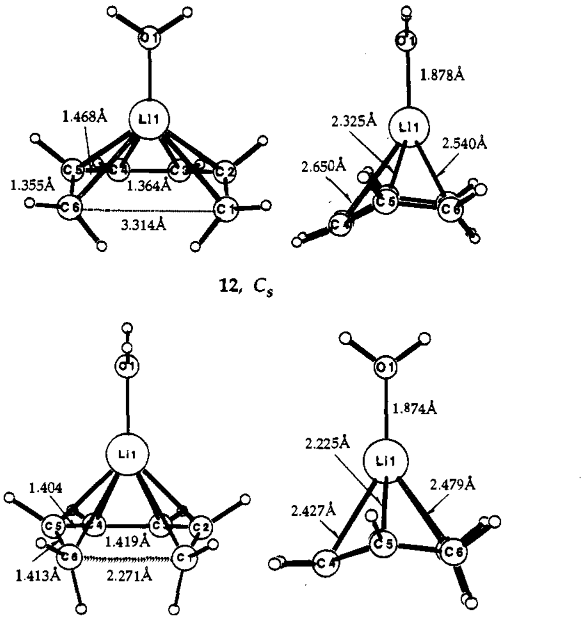
	RMP2(fc)/6-31G*	Becke3LYP/6-311+G* [b]
12	−316.10661	−317.27397
13	−316.07928	−317.24312
E_a	17.5	19.7[c]

[a] Reference 20. [b] Using the MP2(fc)/6-31G* geometries. [c] At Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + ZPE(RHF/6-31G*).

The activation energies (E_a) (Table 6, at RMP4SDTQ/6-311G**//RMP2(fu)/6-31G* + Eth(RMP2(fu)/6-31G*, 500 K)) are lower with metal cation complexation than without. The catalytic effects (ΔE_{cat}) are as follows: 4.7 (Na^+), 8.0 (Li^+), 12,3 (Mg^{2+}), 13.7 (HBe^+), and 19.9 kcal/mol (Be^{2+}). The activation energies ($\Delta S^{\ddagger}$) of the metal cation complexed reactions are also more negative with than without complexation. Thus, the 1,5-H shift in cyclopentadiene is accelerated, not only by Li^+, but also by Na^+, Mg^{2+}, HBe^+, and Be^{2+}. The computed order of cation activity, $Be^{2+} > HBe^+ \geq Mg^{2+} > Li^+ > Na^+$, may be compared with the experimental order of Righetti et al.,[5e] $Mg^{2+} > Ba^{2+} \geq Li^+ > Na^+$.

(e) Influence of Solvent Complexation. How does solvation influence these metal cation accelerations? Solvation is a spontaneous process from the gas phase into the medium. For a chemical reaction, not only the educt and product but also the transition state are solvated, and the solvation energies are however different. If the solvation energy for the transition state, E_{solv}(ts), is larger (more negative) than that for the ground state, E_{solv}(gs), the activation energy is reduced and the reaction will be accelerated. In contrast, if E_{solv}(ts) is smaller (less negative) than E_{solv}(gs), the activation barrier is raised and the reaction will be lowered, respectively. Based on these findings, we computed the cyclization barrier of 1,3,5-hexatriene complexed with a solvated lithium cation [$Li(H_2O)^+$] instead of with Li^+ only (Table 9).

The RMP2(fc)/6-31G* optimized geometries of the $Li(H_2O)^+$ complexed 1,3,5-hexatriene (**12**) and the cyclization transition structure (**13**) are shown in Figure 8. Relative to the Li^+ complexes **4** and **5**, the main effect of the H_2O solvation is to increase the Li−C distances somewhat, more in **12** than in **13** (Figure 8).



12, C_s

13, C_s

Figure 8. The RMP2(fc)/6-31G* optimized geometries of the $Li(H_2O)^+$ complexed 1,3,5-hexatriene (**12**) and the cyclization transition structure (**13**).

The calculated activation energy [Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + ZPE(RHF/6-31G*] of 19.7 kcal/mol is 10.9 kcal/mol lower than the corresponding value without Li^+ complexation (30,6 kcal/mol, Table 2) and close to the value with Li^+ complexation (19,1 kcal/mol, Table 4). Thus, complexation of one H_2O molecule has little effect. The main problem in realizing this predicted accelerating reaction is to choose a medium in which the Li^+ cation is relatively free from counterion (no nucleophilic) and solvent molecules. Thus, the "free" lithium cation can interact with the educt and more strongly with the transition state to accelerate reactions.

Conclusion

As predicted by Woodward and Hoffmann,[1,4] the cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene is disrotatory and concerted. The experimental kinetics are reproduced very well at the ab initio RMP4SDTQ/6-31G*//RMP2(fc)/6-31G* + E_{th}(RMP2(fc)/6-31G*, 400 K) and the Becke3LYP/6-311+G*//RMP2(fc)/6-31G* + E_{th}(RMP2(fc)/6-31G*, 400 K) levels. The aromaticity of the transition structure fulfills various criteria of aromaticity; geometric (quite uniform bond lengths), energetic (large energy of concert), and magnetic (upfield chemical shift of Li^+ and exalted magnetic susceptibility in the transition state). The very large Li^+ electrostatic acceleration effect (9.2 kcal/mol, RMP4SDTQ; 11.5 kcal/mol, Becke3LYP) in this hydrocarbon system is due to the greater electrostatic stabilization of the transition structure than the ground state by metal cation complexation. Complexation of Li^+ by one H_2O molecule has little effect, and more extensive solvation was not modeled. The electrostatic accelerating effect of the 1,5-H shift in cyclopentadiene by the Li^+ cation also is produced by complexation of Na^+, Mg^{2+}, HBe^+, and Be^{2+}. The computed order of cation acceleration agrees with an experimental sequence, e.g. $Mg^{2+} > Li^+ > Na^+$ (for a related reaction).[5e]

The results should encourage experimentalists to find conditions or catalysts which will produce the large accelerating effects for hydrocarbon systems predicted by our computations.

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