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π4s + π2s Cycloadditions: Allyl Anions Plus Ethylene

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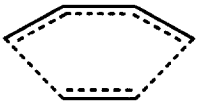
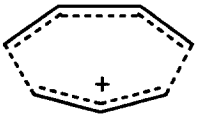
Abstract: *Ab initio* calculations failed to locate the expected transition structure with Cs symmetry for the concerted π4s + π2s cycloaddition of allyl anion with ethylene. Unsymmetrical structures were found that satisfied the normal criteria for first order saddle points, *i.e.* one imaginary frequency. Similarly, cycloadditions between ethylene with 2-fluoroallyl anion, 2-azaallyl anion CH_2=N-CH_2(-), and the lithium-complexed 2-azaallyl system CH_2=N-CH_2Li failed to generate first order transition structures with Cs symmetry. Calculations at the MP2(FC)/6-311++G(d) level show that allyl anion prefers a structure with C2 symmetry as opposed to the classical (planar) C2v structure.

Diels-Alder reactions are considered the prototypal example of π4s + π2s cycloaddition reactions. Frontier orbital formalism elegantly describes these reactions as synchronous processes involving continuous electronic orbital overlap from ground state components over a transition structure to form products.[1a] Although computational analyses of these transition structures have led to a variety of structural descriptions, some involving synchronous bond-making, some involving stepwise bond-making, the consensus favors synchronous bond formation at least for symmetrical systems.[1] A typical transition structure calculated for the combination of ethylene with butadiene (MP2/6-31G*) has Cs symmetry and incipient C---C bonds lengths equal to 2.285 Å. Frontier orbital theory leads to comparable expectations for the two related π4s + π2s combinations involving 1,3-dienes plus allyl cations and allyl anions plus ethylenes.[2] Indeed, some examples of these reactions have been reported, at least two of which were reported to be stereospecific.[3]



Diels-Alder TS

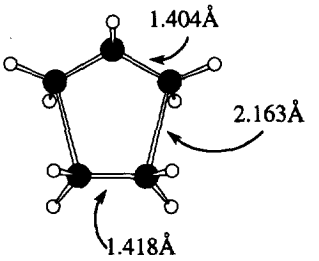


Butadiene +
Allyl Cation TS

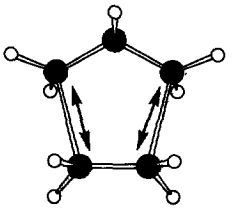
Allyl Anion +
Ethylene TS

Recently, de Pascual-Teresa and Houk studied the butadiene-allyl cation reaction using *ab initio* methods (RHF and MP2/6-31G* basis sets) and reported that they could find only stepwise mechanisms for the cycloaddition.[4] Although a stationary point corresponding to the above Cs structure was located (C---C bond lengths of 2.318 Å), this structure was characterized as a *second* order saddle point by vibrational frequency analysis (two imaginary frequencies). Lower energy open-chain structures were found that were characterized as true transition structures. Although this finding in of itself does not negate the validity of frontier orbital analysis, the inability to locate a synchronous transition structure at *any* energy level is disturbing.

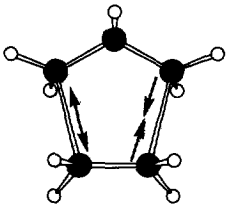
In conjunction with our computational studies on cycloreversion reactions[5] we examined the course of the cycloaddition reaction between allyl anion and ethylene in an effort to locate a transition structure with synchronous bond making at the ends of the allyl system. Our initial calculations[6] at the RHF/6-31++G(d) level led to the structure with Cs (envelope) symmetry shown below which was characterized by vibrational analysis as a second-order saddle point. The larger imaginary frequency (-658 cm^{-1}) is associated with the Cs reaction path. The smaller one (-334 cm^{-1}) is symmetry breaking and leads to a structure with C1 symmetry. We were unable to locate a symmetrical (Cs) first-order saddle point.



Cs Stationary Point
Energy (hartrees): -194.400311
RHF/6-31++G(d)

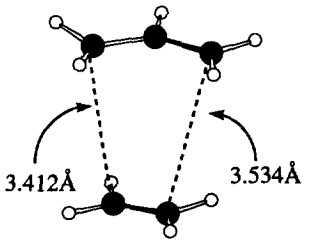


$\bar{\upsilon}$ i = -659 cm^{-1}

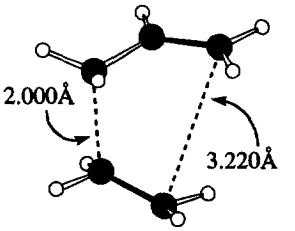


$\bar{\upsilon}$ i = -335 cm^{-1}

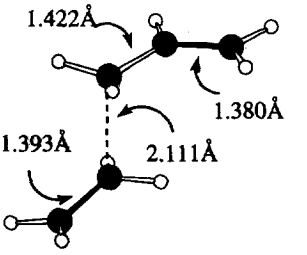
When the symmetry restriction is removed, a first-order transition state with C1 symmetry is generated that is 18.4 kcal/mol lower in energy than the Cs structure. Similar results were obtained at the MP2/6-31G(d) level; the Cs (E=-195.066868 h) structure displayed two imaginary frequencies (-291 cm^{-1}, -32 cm^{-1}) and the C1 transition structure only one. At the MP2/6-31+G(d) level we found two imaginary frequencies (-336 cm^{-1}, -167 cm^{-1}) for the Cs stationary point (E=-195.107273 h) and one for the C1 structure.



$\bar{\upsilon}$ i = -538 cm^{-1}
C1 Stationary Point
RHF/6-31++G(d)
Energy: -194.429606 h



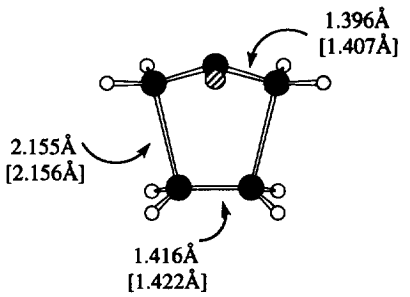
$\bar{\upsilon}$ i = -248 cm^{-1}
C1 Stationary Point
MP2/6-31G(d)
E=-195.069507 h

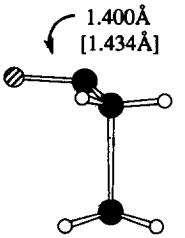


$\bar{\upsilon}$ i = -266 cm^{-1}
C1 Stationary Point
MP2/6-31+G(d)
E=-195.114309 h

Three other π4 s + π2s combinations were also examined: 2-fluoroallyl anion, 2-azaallyl anion, and lithium 2-azaallyl anion plus ethylene. These examples were chosen because they more closely resemble experimentally observed reactive combinations that have an electron-withdrawing group or atom associated with the π4 component. The allyllithium:ethylene system is electrically neutral and even more closely resembles typical Diels-Alder reactants. In the event, the calculated Cs structures paralleled those with the unsubstituted system fairly closely. In each case the only stationary points found were the second order saddle points shown below.

Fluoroallyl anion + ethylene:





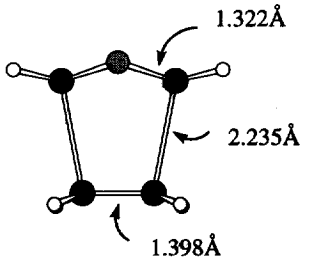
Cs Stationary Point

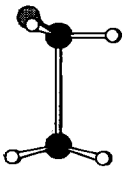
HF/6-31++G(d)
[MP2/6-31+G(d)]

$\bar{\upsilon}$ i = -699, -307 cm^{-1}

[$\bar{\upsilon}$ i = -346, -157 cm^{-1}]

2-Azaallyl anion + ethylene:

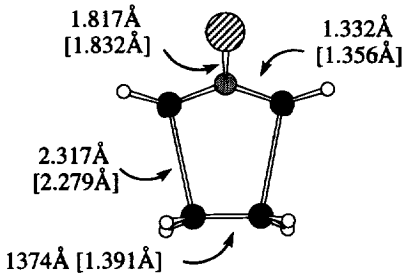


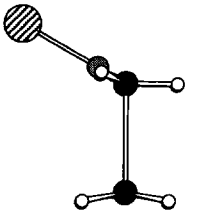


Cs Stationary Point
HF/6-31++G(d)

$\bar{\upsilon}$ i = -533, -270 cm^{-1}

Lithium 2-Azaallyl anion + ethylene





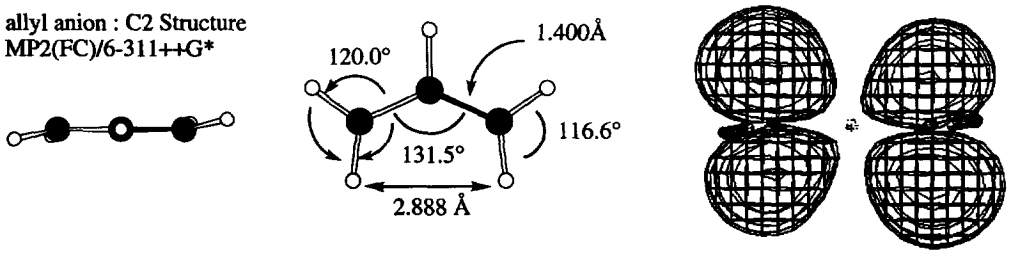
Cs Stationary Point
HF/6-31++G(d)
[MP2/6-31+G(d)]

$\bar{\upsilon}$ i = -574, -73 cm^{-1}

[$\bar{\upsilon}$ i = --374, -109, -35 cm-1]

Others[1,8] have pointed out that simple frontier molecular orbital considerations are inadequate to explain both the energetics and the regiochemistry of Diels-Alder reactions. In the cases at hand, it may be that the closed shell repulsions of inner orbitals gives rise to prohibitively high anti-bonding terms that override the bonding expected for the HOMO-LUMO terms. In addition, it may be of importance to note that the ordering of the energy levels of the occupied orbitals in these systems differs from that associated with typical ethylene/butadiene systems: χ_1 and χ_2 of allyl anion lie above π for ethylene.[7] This could lead to crossing of orbitals of the same symmetry during early stages of the reaction.[8] These results are not necessarily in contradiction to the experimental findings of stereospecific additions since the second bond could be formed more rapidly than bond rotation. In any event, these examples signal the possibility that there may be more subtle factors that control the "allowedness" of cycloaddition reactions. We are continuing to investigate this reaction with higher level methods, *e.g.* MCSCF, that have been recommended for pericyclic reactions.[1e,1f]

Incidental to these calculations we found that the allyl anion prefers a C2 symmetry at the MP2(FC)/6-311++G* level (E=-116.868175 h).[9,10] The C2v (planar) structure at this level represents a second order saddle point (E= -116.867502h ; υi = -598.0, -584.2 cm^{-1}). It is not unlikely that the C2v form is destablized due to repulsion caused by the through-space interactions of the orbitals at C_1 and C_3 and/or H---H repulsion.[11]



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7. Eigenvalues at the MP2(FC)/6-311+G(d) level are: π (-0.37441); χ_1 (-0.19717); χ_2 (-0.01530). Eigenvalues at the MP2(FC)/6-311++G(d) level are: π (-0.37436); χ_1 (-0.19580); χ_2 (-0.01926).

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