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The influence of the cyclic product's structure on the Diels–Alder transition state

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The concerted cycloaddition of ethylene and cyclopentadiene has been found with full geometry optimization and the STO-3G basis set to be synchronous with $E_a = 35$ kcal/mol, while the previously reported, partially optimized, concerted cycloaddition of butadiene and ethylene has been found to have a tendency towards asynchronism due to the nonsymmetrical structure of its transition state; this is due to the two conformations of the cyclohexene product, which also have been optimized, with the boat form being a transition state structure 5.3 kcal/mol above the half-chair structure.

Key words: Diels-Alder transition state — Cyclohexene conformations — Cyclopentadiene — Butadiene — Ethylene synchronism

It has been over a decade that the Diels–Alder reaction transition state (TS) has been studied theoretically by *ab initio* [1, 2] and semiempirical methods [3-5]. One of the major conclusions in our study [1] of the synchronous, concerted reaction pathway was that the TS structure is of C_1 symmetry wherein the ethylene adds to butadiene in a way that prefigures the half-chair conformation. This point, which was not mentioned in any of the reports which referenced our study [4a, 5], is crucial. It has been shown by McIver [6] that the commonly accepted path through the boat structure TS (of C_S symmetry) does not have the single negative eigenvalue of the second derivative force constant matrix which is required for TS structures. We found the nonsymmetric yet synchronous half-chair conformation to be at least 1 kcal/mol more stable than the boat form of the TS. In addition, Basilevsky [7] has shown diagrammatically that the point on a potential energy surface where the boat structure is maintained as the transition state represents a hyperbolic umbilic due to the two possible cyclohexene half-chair conformations. This problem is overcome if the TS already prefigures one or the other half-chair conformations, as our TS structure does.

We present here the results of a study which shows that the boat form of cyclohexene is itself a TS structure and the half-chair form is an equilibrium structure. In order to obviate the problem of this symmetry carryover from the cyclic structure to the cycloaddition TS, a cyclic product must be formed which is an equilibrium structure with C_S symmetry. Such a product is norbornene. Thus, we have calculated the equilibrium structure for 2-norbornene, cyclopentadiene, and ethylene and the TS structure for the synchronous, concerted pathway.

The geometric parameters of all structures were optimized such that no force was greater than 0.0002 a.u. for any parameter or atomic coordinate. The STO-3G minimal basis set was employed in the GAUSSIAN80 program [8]. Fig. 1 presents the optimized CC bond lengths and some dihedral angles for all structures, and Table 1 presents total energies in a.u. and energies relative to the half-chair cyclohexene and ethylene + cyclopentadiene.

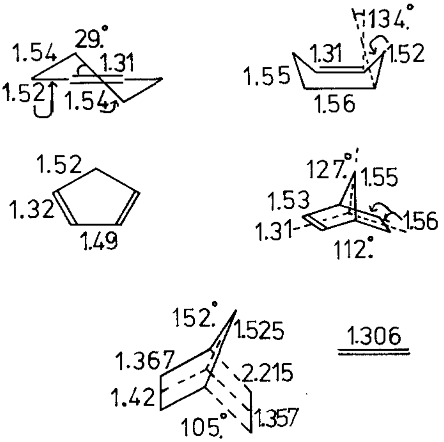

Fig. 1. The optimized CC bond lengths in Å and several dihedral angles

Table 1. Negatives of the total energies (a.u.) and energies relative to half-chair cyclohexene or ethylene + cyclopentadiene (kcal/mol)

	STO-3G	(rel)	(3-21G	(rel)	4-31G	(rel)
Cyclohexene:						
half-chair	230.261098	0.0				
boat	230.252673	5.3				
ethylene	77.073959	—	77.600988	—	77.922157	—
cyclopentadiene	190.457105	—	191.716313	—	192.512141	—
TS	267.475351	35	269.269000	30	270.373138	38
2-norbornene	267.660692	−80	269.368238	−32	270.466360	−20

The results show a barrier of 5.3 kcal/mol for the inversion of the half-chair conformation of cyclohexene through the boatlike TS. This value can be compared to the 6.9 kcal/mol found in our original work [1] and to 9.4 kcal/mol found in a SINDO work with force constant optimization [4b].

As previously reported for olefinic hydrogens [9], they do not remain in the same plane as the C—C=C—C atoms if they are not impelled to do so by achieving a higher order of symmetry for the molecule. Thus the optimized dihedral angles for the olefinic hydrogens are: half-chair cyclohexene (C_2, 0.468°)[1], boat cyclohexene (C_S, 0.267°)[1], norbornene (C_S, 4.140° endo), TS (C_S, 8.227° Endo), and cyclopentadiene (C_{2v}, 0°). The dihedral angle for C—C=C—C in half-chair cyclohexene is 0.093°.

Since open chained species are not treated as well variationally as cyclic species when employing minimal basis sets, one expects the cycloaddition reaction energy of −80.7 kcal/mol to be too low. The energy for each species involved in the cycloaddition reaction has been recalculated with the 3-21G and 4-31G split valence basis sets while using the STO-3G optimized geometries (Table 1). The heats of reaction are found to be −32 and −20 kcal/mol, respectively, and the activation barriers are 30 and 38 kcal/mol, respectively. The STO-3G activation energy for cycloaddition is precisely 34.950 kcal/mol, the accuracy of which is limited by the theoretical method.

Regardless of the value for the activation barrier due to a particular basis set, the synchronous, concerted cycloaddition of ethylene and cyclopentadiene is found to have a transition state when using the STO-3G set. The question of whether this is the minimum energy pathway can only be answered with an exploration of the two step hypersurface using a method which includes extensive electron correlation and with reoptimization of the synchronous pathway using the same theoretical method.

The question of synchronism in concerted reactions and the loss of it when using substituents is not new [10]. In their study of 1,3 dipolar cycloadditions, Leroy and Sana proposed a measure of the tendency towards asynchronism when the two new bonds are arbitrarily constrained to form synchronously [11]. The asynchronism tendency, A is obtained by taking the weighted difference of the rates of evolution of the two bonds *AB* and *CD* being formed in the activated complex:

$$A(AB/CD)=\frac{T_{AB}(R^{\neq})-T_{CD}(R^{\neq})}{T_{AB}(R^{\neq})+T_{CD}(R^{\neq})}\times 100, \quad (1)$$

where the evolution T of a bond at any point on the reaction path is:

$$T_{AB}(R)=\frac{\mathrm{E}_{AB}(R)-\mathrm{E}_{AB}(\text{reactant})}{\mathrm{E}_{AB}(\text{product})-\mathrm{E}_{AB}(\text{reactant})}\times 100, \quad (2)$$

and E_{AB} is the energy of bond *AB* calculated with the following formula using

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[1] Bent out of the C—C=C—C plane in the opposite direction from the CH_2 directly across

the Mulliken population P_{AB} (constants are for CC bonds [11]):

$$E_{AB}=216.722\ P_{AB}^3-263.308\ P_{AB}^2+53.653\ P_{AB}. \tag{3}$$

Due to the plane of symmetry present in the TS for the cyclopentadiene plus ethylene addition, the populations of the two new bonds are equal, thus giving equal bond energies and no asynchronism. Using the bond energies for butadiene plus ethylene that we reported in Ref. [1a] for the TS (11.0 and 10.8 kcal/mol), the asynchronism tendency is 2.8%. This is due to the absence of any symmetry as the half-chair form is prefigured in the TS. Since the presence of substituents which do not keep C_s symmetry for the cyclopentadiene plus ethylene addition will cause P_{AB} to be different from P_{CD}, there will always be asynchronism in these cases, though they still may be concerted. Work is in progress to study the influence of substituents on the amount of asynchronism.

Added Note: A recent study [12] has shown the Cope reaction of two allyl radicals to form cyclohexene-1,4 diyl to be synchronous only when a flexible basis set and multiconfigurational rather than two configurational SCF wave functions are used. As noted by these authors, the STO-3G basis set overemphasizes the formation of σ bonds at the expense of Π type radicals. Since the present reaction pathways do not contain radicals, the above objection against the STO-3G basis-set can not be made. It has already been found [13], however, that the use of a two-configurational wave function will bias the TS towards a product-like structure in the Diels-Alder reaction.

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