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An Unexpected Bispericyclic Transition Structure Leading to 4+2 and 2+4 Cycloadducts in the *Endo* Dimerization of Cyclopentadiene

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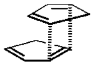
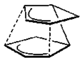
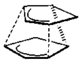
Received July 16, 2001; Revised Manuscript Received November 8, 2001

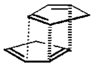
Secondary Orbital Interactions (SOIs) were introduced by Woodward and Hoffmann (WH) in 1965[1] and have gained wide acceptance in the interpretation of the various selectivities of pericyclic reactions.[2] Contemporary textbooks devote a chapter to the orbital symmetry rules and provide fascinating examples of the power of SOIs in accounting for the diverging *endo* and *exo* preference of the 4+2 and 6+4 cycloadditions, respectively. Despite their appeal the SOIs escaped however a firm theoretical validation and conclusive evidence for their existence is still lacking.[3]

We wish to report here a study of the dimerization of cyclopentadiene, which unexpectedly disclosed the origin of the *endo* selectivity and led to a simple rationalization that is quite different than usually thought. The cycloadditions of cyclopentadiene are perhaps the most classical and fruitful Diels−Alder (DA) cycloadditions.[4] The dimerization was extensively studied by Alder and Stein[5] and affords the *endo* dimer exclusively although on heating some *exo* isomer is formed.[5,6] The extraordinary stereoselection was the basis of the Alder's *endo* rule, mostly known as the "principle of the maximum accumulation of unsaturated centers".


1 DA


2 Cope


3 WK


4 WH SOI

In 1959 Woodward and Katz (WK) discovered the easy and stereospecific Cope rearrangements of *endo* dicyclopentadiene derivatives.[7] The strict relation and similarities of the cycloaddition Transition Structure (TS) **1** and the Cope TS **2** led WK to suggest a unifying picture for both transformations and to propose a two-stage mechanism for the cycloaddition path with the primary formation of a C⋯C bond between the ends of the diene system of the addends leading to a compressed diradicaloid TS **3**, whose branches are kept together by secondary attractive forces, in some way related to the bond shifts involved in the Cope rearrangement. After passage of the barrier the reaction "proceeds to the Cope TS and thence to the products". The precise topography of the energy surface between the two TSs could not be addressed and was viewed as an "irrelevant question". Soon after Berson argued that the precise topography of the two TSs was indeed essential in defining the one-step or two-step mechanism of the dimerization.[8] The topographical problem was never solved, since the WK picture was quickly superseded by the evanescent but conceptually sound WH SOIs,[1] depicted in **4** as a dotted line, as well as by the emerging evidence of concertedness in most pericyclic reactions.[9]

Table 1. B3LYP/6-31G* Electronic Energies (ΔE_e) Relative to the Reactants (kcal/mol), Enthalpies (kcal/mol), and Entropies (e.u.),[a] Forming C⋯C Bond Lengths (Å) of the TSs, Diradical Species, and Cycloadducts in the Dimerization of Cyclopentadiene[b]

	ΔE_e	ΔH	ΔS	C⋯C	ΔE_e(CASSCF)
5[c]	20.0 (19.7)	21.3 (21.0)	−26.4	1.56	33.5
6[c]	29.7 (25.3)	30.1 (25.7)	−28.0	1.94	44.6
7N[d]	19.4	21.0	−33.2	1.96 (2.90)	39.5[e]
7X[d]	22.2	23.9	−33.9	2.06 (2.51)	42.6[e]
8N	−16.3	−11.8	−38.3	1.57 (1.58)	−7.6[e]
8X	−17.4	−12.8	−38.2	1.57 (1.58)	−7.5[e]
9[d]	16.4	18.7	−38.0	1.64 (2.65)	36.2[e]

[a] Thermodynamic values at 298.15 K from unscaled vibrational frequencies in the harmonic approximation. [b] Cyclopentadiene, −194.101062 hartrees, correction to enthalpy $\Delta H = 60.90$, $S = 66.68$. [c] Fully optimized UB singlet diradicals; energies after spin correction[10c] are in parentheses. [d] UB and RB calculations gave identical results. [e] The CI coefficients (>0.88) and populations of the active orbitals indicate dominance of the ground configuration.

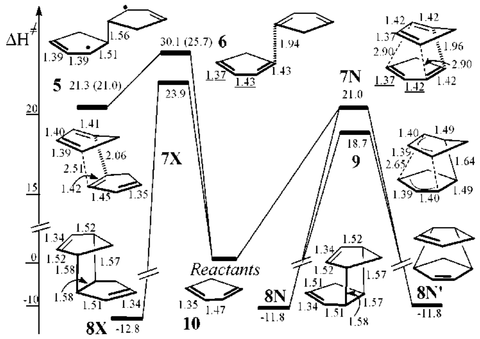


Figure 1. Transition structures, diradical intermediates. and DA cycloadducts in the cyclopentadiene dimerization. Numbers near the levels are enthalpies (in kcal/mol) relative to the reactants and numbers near the forming bonds are bond distances (in Å).

We have located the relevant points on the potential energy surface of the dimerization of cyclopentadiene at the B3LYP/6-31G* level, which gives satisfactory geometries and reliable energies for pericyclic reactions and diradical formations.[10] The electronic energies ΔE_e of the TSs and the adducts relative to the reactants are given in Table 1 along with the enthalpies, entropies, and forming bond lengths. The last column shows the ΔE_e of CASSCF(8,8)/6-31G* calculations on B3LYP geometries for comparison. In Figure 1 the B3LYP enthalpies are given along with the formulas. The lowest passes for the DA dimerization are the *endo* TS **7N** (21.0 kcal/mol) and the *exo* TS **7X**, which is 2.9 kcal/mol higher in energy, while the diradical forming TS **6** occurs at remarkably higher energies, 9.1 kcal/mol above TS **7N** and 4.7 kcal/mol after spin correction.[10c] The diradical **5** lies essentially at the same energy of TS **7N**, while the Cope TS **9** is 2.3 kcal/mol below TS **7N**. The *exo* adduct **8X** is 12.8 kcal/mol below the reactants and is 1.0 kcal/mol more stable than the more strained *endo* cycloadduct **8N**. The CASSCF results agree qualitatively but show the known[10a,c] bias in favor of the diradical species as well as the overestimation of the barrier heights.

The most remarkable feature is however the shape of the lowest DA barrier **7N**. While the *exo* TS **7X** still corresponds to a case of asynchronous DA cycloaddition, asynchronicity is significantly magnified in the *endo* TS **7N**, which shows up chiral with C_2 symmetry and similar to the WK imaginative picture **3** (Figure 2).

10.1021/ja016622h CCC: $22.00

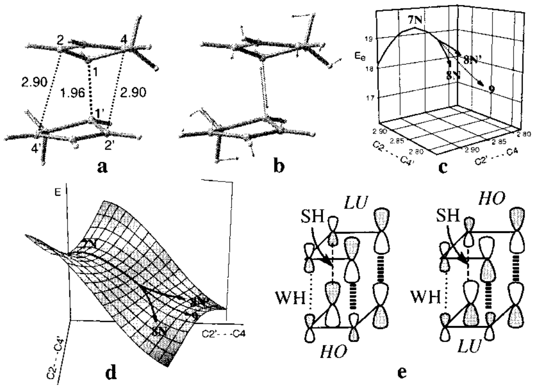


Figure 2. Geometric features (a) and displacement vectors (b) of TS **7N**, the RC (c) of the dimerization path, and (d) a 3D picture of the surface. The dotted path refers to the crest toward Cope TS **9**. In the DA *HO-LU* interactions (e) the bold dashes refer to the primary interaction and the dashed and dotted lines to the SH and the WH SOIs, respectively.

Structurally TS **7N** resembles the diradical forming TS **6** in many respects. The length of the forming C···C bond in **7N** is 1.96 Å, almost identical with that of **6,** and the degree of structural reorganization of the diene moieties toward the allyl structures is quite similar, as shown by the comparable lengths of the incipient allyl moieties, which are underlined in Figure 1.

Despite its diradicaloid appearance TS **7N** is a first-order saddle point leading to the cycloadduct **8N** along a concerted path. The displacement vectors associated with the imaginary frequency of TS **7N** involve essentially the 1,1′ C···C vibration with minute, but observable, in-phase vibrations of the long 2,4′ and 2′,4 C···C bonds (Figure 2b). Accordingly, IRC calculations show that the Reaction Coordinate (RC) steps from TS **7N** maintain the C_2 symmetry, with only minor changes of the long C···C bonds. On the product side the RC steps at the beginning toward the Cope TS **9** but on the way the distortive antisymmetric C···C/C···C vibration (which is the imaginary frequency of the Cope TS **9**) becomes negative, too, and breaks the C_2 symmetry, causing a bifurcation in two different paths, which are equivalent through a binary rotation axis and point resolutely toward the equivalent 4+2 and 2+4 cycloadducts **8N** and **8N′** (Figure 2c,d). Thus the B3LYP calculations provide a precise topography of the energy surface after passage of the DA barrier. No metastable intermediates could be located along the RC, which avoids the Cope TS **9**.

The remaining subtle question concerns the origin of the long C···C bonds of TS **7N**. Is the WK picture **3** an adequate description? At variance with the WK picture the allyl moieties are not fully developed and model calculations show that two incipient allyl fragments frozen at the geometry of TS **7N** do not attract each other sizably relative to the same fragments kept far away.[11] Moreover the interaction is distortive, as usual for the Cope topology, e.g. in the Cope TS **9**. A likely alternative, wholly consistent with the symmetrical and associative vibrations of Figure 2b, is a bispericyclic TS, just as the one sketched in formula **7N,** where the 4+2 and 2+4 cycloaddition paths have fully merged. The long C···C bonds of Figure 2a are then the (weaker) primary interactions of two DA cycloadditions whose perimeters share the stronger primary interactions. Only after passage of the barrier **7N** and on approaching the Cope TS **9** does the distortive character of the Cope topology mix in and the RC split.

The occurrence of a concerted bispericyclic TS with a diradicaloid appearance in the case of cyclopentadiene is not fully surprising. Because of the large polarization of the frontier orbitals (FO) toward the ends of the diene moiety, the cycloaddition tends to be asynchronous as shown, e.g., in TS **7X**. In the case of the *endo* approach additional stabilization can be recovered with only minor structural deformations by fully exploiting the less familiar but highly favorable Salem/Houk[12] (SH) SOIs (Figure 2e), which leads to a merging of both the geometrically possible 4+2 and 2+4 allowed paths. In the bispericyclic TS the cooperative action of the 4+2 and 2+4 processes strengthens further the C···C bond formation at the ends of the diene moieties and increases asynchronicity but still retains some concertedness.

In summary, the *endo* DA TS **1** of cyclopentadiene dimerization is admirably suited to take advantage of the maximum accumulation of unsaturated centers because of the large SH SOIs and the minimal structural deformations required to exploit them.[13] Although a part of the enthalpic difference between TSs **7N** and **7X** has to be ascribed to destabilization of **7X** due to steric repulsion between the methylene and the *exo* allyl moiety,[3a] the shape of TS **7N** testifies to the presence of significant attractive secondary forces assisting the *endo* approach. It is worth noting that the SH SOI model nicely accounts for the observed increase of *endo* preference with increasing reactivity of cycloaddends.[14]

In a previous study[15] on the dimerization of methacrolein we have reported a similar case of merging. We adopted the Alder's term crypto-diradical to describe the diradicaloid TS and a WK picture analogous to **3** to account for the long bonds. The bispericyclic nature of the TS was not immediately recognizable and we could not appreciate the far-reaching potential of the bispericyclic array.

Acknowledgment. Financial support by MURST, University of Pavia (FAR), and CILEA is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and energies of optimized geometries shown in Figure 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA016622H