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Merging and bifurcation of 4+2 and 2+4 cycloaddition modes in the archetypal dimerization of butadiene. A case of competing bispericyclic, pericyclic and diradical paths

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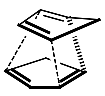
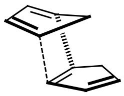
Abstract—The dimerization of butadiene has been explored by using DFT methods at the B3LYP level with the 6-311+G** basis set. A concerted bispericyclic TS for the *endo* pathway and a concerted pericyclic TS for the *exo* pathway are the lowest passes for the dimerization and occur at almost the same energy thus accounting for the lack of stereochemical preferences in the dimerization. Diradical paths involving two unswitched *transoid* butadiene moieties are competing and account for the formation of minor amounts of *trans*-1,2-divinyl cyclobutane and 1,5-cycloctadiene. © 2002 Elsevier Science Ltd. All rights reserved.

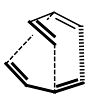
The origin of the *endo* stereoselection in Diels–Alder (DA) cycloadditions is still a matter of warm dispute and controversy and attracts continuing interest.[1] The monumental work of Alder and Stein led to establishment of the Alder's *endo* rule or principle of maximum accumulation of unsaturations.[2] In a seminal contribution in 1965[3] Woodward and Hoffmann (WH) traced to the Secondary Orbital Interactions (SOIs) the underlying factors of the Alder's rule and since then SOIs have become a fascinating and basic tenet for a few generations of organic chemists.[4] Despite their appeal the SOI escaped firm theoretical validations and conclusive evidence for their existence is still lacking.[1a,b]



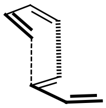
1 N



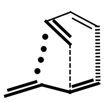
2 X



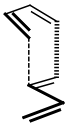
3 CN



4 CX



5 TN



6 TX

We have recently reported[5] that the maximum accumulation of unsaturated centers in the DA 4+2 *endo* dimerization of cyclopentadiene allows for the full exploitation of the 'next–nearest' Salem/Houk (SH) SOI[6] along the 2+4 perimeter; this results from the minimal structural deformations of the addends needed to take advantage of the SH SOI. The reaction takes then place through the bispericyclic and symmetrical transition structure (TS) **1**, where the 4+2 and 2+4 cycloaddition paths are fully merged, while the *exo* TS **2** lies 2.9 kcal/mol higher in energy. On going to the case of the parent acyclic butadiene, the role of a bispericyclic TS, if any, should be however less important since energy has to be supplied to distort the *transoid* butadiene into the reactive *cisoid* conformation of the diene moiety and also to switch the *transoid* (**T**) dienophile moiety into the *cisoid* (**C**) conformation needed for the bispericyclic array. Among the four possible TSs of the butadiene DA dimerization **3**–**6** one has then to expect a rather intricate and delicate balance of competing effects, deformation energies favoring **TN** and **TX**, SH SOIs favoring **CN** and WH SOI (dotted line in **5**) promoting **TN** and perhaps steric effects favoring the *exo* over the *endo* TSs.

At variance with the strict *endo* selection of cyclopentadiene, the dimerization of butadiene is experimentally known to take place without any stereochemical preference. The elegant studies by Stephenson and Klärner on the dimerization of *cis*,*cis*-1,4-dideutero-1,3-

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butadiene[7] are consistent with two main concerted *endo* and *exo* pathways of similar importance, along with minor diradical pathways leading to *trans*-1,2-divinylcyclobutane and 1,5-cyclooctadiene. Thermochemical estimates and previous theoretical calculations[8] show that concerted and diradical pathways are energetically quite close and differences are within 2–3 kcal/mol.

We have located the relevant points on the potential energy surface of the dimerization of butadiene at the B3LYP/6-31G* level,[9] which gives satisfactory geometries and reliable energies for pericyclic reactions and diradical formations,[10] but the higher level B3LYP/6-311+G** calculations were needed to give a more balanced description of the cycloaddition and diradical TSs of butadiene dimerization. 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. In Fig. 1 the B3LYP enthalpies are given along with the formulas. The lowest passes for the DA dimerization are the *endo* TS **CN** and the *exo* TS **TX**, which is 0.2 kcal/mol higher in energy. At a slightly higher energy lies TS **CX** (0.5 kcal/mol), while the WH TS **TN** is the highest pass (1.2 kcal/mol). The *anti trans*, *trans* diradical forming TS **tt-*out*** **7** and TS **tt-*in*** **8** lie essentially at the same energy of TS **CN** while the corresponding *anti* diradicals **9** and **10** lie 7 kcal/mol below TS **CN**. In the case of the *anti* **ct-*out*** and **cc-*out*** diradicals, the forming TSs **11** and **12** are lifted by 1.6 and 3.5 kcal/mol, respectively, with respect to the **tt** case while the corresponding diradicals **13** and **14** are less lifted, by 0.8 and 1.8 kcal/mol, respectively. Also shown is the Cope TS **15** at 24.3 kcal/mol above the addends and the cycloadduct **16**, which lies 28.8 kcal/mol below.

The data in Fig. 1 fit the experimental results rather satisfactorily, showing that two passes at comparable energy are available to the butadiene DA dimerization, namely the SH SOI assisted *endo* TS **CN** and the least sterically hindered *exo* TS **TX**, which account for the lack of stereoselectivity in the butadiene cycloaddition.[11] Comparable in energy, but presumably still underestimated by the calculations at this theoretical level, are two passes for diradical formation, TS **tt-*out*** **7** and TS **tt-*in*** **8**, which provide an entry into the flat tetramethylene manyfold (the twixtyl or caldera),[12] where fast internal rotations interrelate the various conformations and slower collapses to *trans*- and *cis*-1,2-divinyl cyclobutane take place.[13] Under the reaction

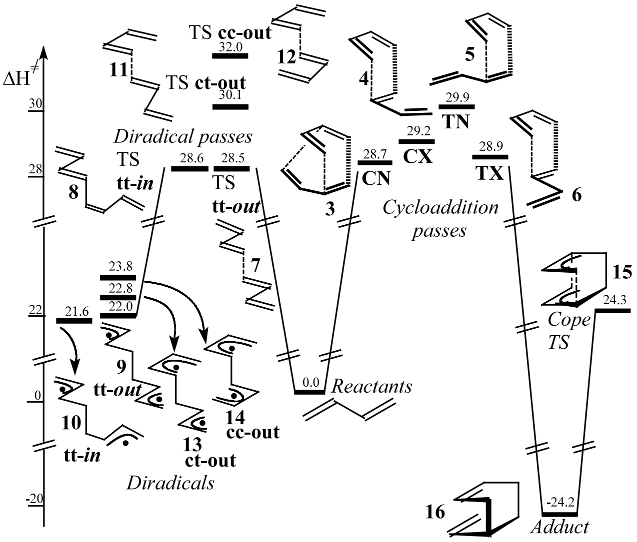

Figure 1. Transition structures, diradical intermediates and DA cycloadducts in the butadiene dimerization. Numbers near the levels are enthalpies in kcal/mol relative to the reactants and numbers near the forming bonds are bond distances in Å.

Table 1. B3LYP/6-311+G** 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 cycloadduct in the dimerization of butadiene[b]

	ΔE_e[c]	ΔH[d]	ΔS	C···C
CN 3[e]	27.1 (24.7)	28.7 (0.0)	−29.6	1.94, 2.99, 2.99
CX 4[e]	27.6 (24.8)	29.2 (0.5)	−29.7	1.97, 2.70
TN 5[e]	28.5 (25.5)	29.9 (1.2)	−29.6	2.08, 2.46
TX 6[e]	27.4 (24.5)	28.9 (0.2)	−29.1	2.02, 2.54
TS **tt-*out*** **7**[f]	28.1 (24.9)	28.5 (−0.2)	−21.0	1.91
TS **tt-*in*** **8**[f]	28.2 (25.0)	28.6 (−0.1)	−23.6	1.91
tt-*out* **9**[f]	20.9 (16.3)	22.0 (−6.7)	−21.6	1.56
tt-*in* **10**[f]	20.6 (16.1)	21.6 (−7.1)	−22.0	1.56
TS **ct-*out*** **11**[f]	29.5 (26.5)	30.1 (1.4)	−23.5	1.92
TS **cc-*out*** **12**[f]	31.3 (28.4)	32.0 (3.3)	−23.3	1.94
ct- *out* **13**	21.6 (17.3)	22.8 (−5.9)	−21.7	1.56
cc-*out* **14**[f]	22.4 (18.3)	23.8 (−6.9)	−21.1	1.57
Cope **15**[e]	22.0 (17.5)	24.3 (−4.4)	−37.2	2.48, 2.48
Adduct **16**	−28.8 (−35.2)	−24.2 (−52.9)	−33.6	

[a] Thermodynamic values at 298.15 K from unscaled vibrational frequencies in the harmonic approximation.

[b] *s-trans*-Butadiene, −156.040798 hartrees, correction to enthalpy $\delta H = 56.68$, $S = 66.12$; *s-cis*-butadiene: $\Delta E_e = 3.50$.

[c] B3LYP/6-31G* electronic energies in parentheses.

[d] Enthalpies relative to TS **CN 3** in parentheses.

[e] UB and RB calculations gave identical results.

[f] Fully optimized UB singlet diradicals.

conditions the latter is converted into 1,5-cyclooctadiene through an easy Cope rearrangement.[14]

TS **CN 3** is a first order saddle point of the bispericyclic variety, similar to the *endo* TS **1** of the cyclopentadiene dimerization,[5] and is depicted in Fig. 2. The 1,1′ bond, at the ends of the butadiene moieties, is rather advanced (1.94 Å) while the symmetrical 4,2′ and 2,4′ bonds lag well behind and are still rather long (2.99 Å), giving to the structure a highly asynchronous shape and an uncanny diradicaloid resemblance. The TS **CN** is chiral with C2 symmetry and IRC calculations show that the reaction coordinate (RC) steps from TS **CN** maintaining the C_2 symmetry with only minor changes in the long C···C bonds. On the product side the RC steps at the beginning toward the Cope TS but on the way the distortive antisymmetric C···C/C···C vibration (which is the imaginary frequency of the Cope TS **15**) becomes negative and breaks the C_2 symmetry causing a bifurcation[15] in two different paths (Fig. 2b), which are equivalent through a binary rotation axis. At variance with the cyclopentadiene case, the inflection point occurs almost immediately after the TS is passed, at a 1,1′ bond distance of 1.90 Å, presumably because of the higher flexibility of the acyclic butadiene moieties in the bispericyclic array. The bispericyclic shape and high asynchronicity of TS **CN** can be accounted for with the quite simple Frontier Orbital (FO) rationalization shown in Fig. 2c. The highly favorable SH SOIs lead to a merging of the 4+2 and 2+4 allowed paths, whose cooperation strengthens the 1,1′ bond.

The other available cycloaddition pass, TS **TX 6**, corresponds to the least hindered approach of the addends and looks like a normal asynchronous DA cycloaddition. The **tt** diradical forming TSs **8** and **9** have the expected geometries as well as the **ct** and **cc** diradical forming TSs, which are lifted owing to the cost of the conformational switch of the addends.

Although the computational results do parallel the experimental findings, the unexpected location of the remaining two cycloaddition TSs **CX** and **TN** raise some perplexities. Why should the unassisted TS **CX** be so low, in spite of the cost of the conformational switch? Alternatively, why is TS **TN** so high, in view of the possible stabilization through the classical WH SOIs? Do the WH SOIs really exist?

A careful examination of the geometrical features of the cycloaddition TSs discloses the likely origin of these perplexing locations. At variance with the TSs of the cyclopentadiene dimerization, the forming bonds between the butadiene moieties in the dimerization TSs are significantly twisted away from the coplanar arrangement. In TS **CN** the butadiene moieties are twisted inside by 20.3° and in TS **CX** and **TX** are twisted outside by 20.9 and 13.9°, respectively, while in TS **TN** no sizeable twisting is observed (Fig. 3). The inside twisting of **CN** can be ascribed to the necessary adjustment to take advantage of the SH SOI, while the outside twistings of the *exo* TSs **CX** and **TX** suggest the relief of steric strain around the 1,1′ shorter forming

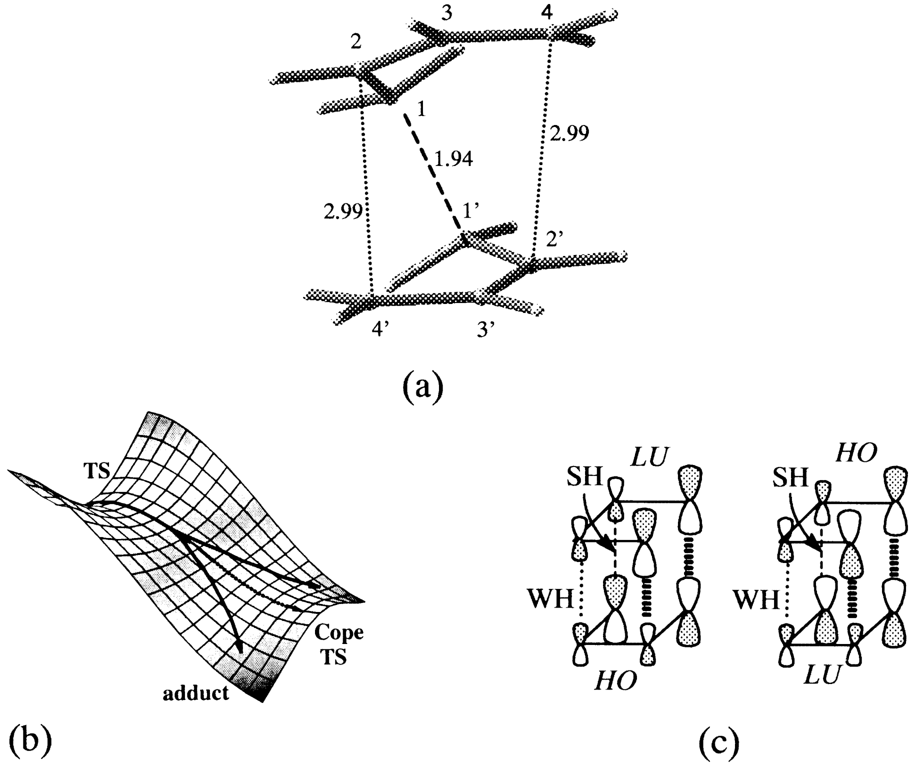

Figure 2. Geometric features and forming bond lengths in Å of the *endo* dimerization TS **CN** (a) and a 3D picture of the RC of the dimerization path (b). The dotted path refers to the crest toward Cope TS. In the DA *HO-LU* interactions (c) the bold dashes refer to the primary interaction, the dashed and dotted lines to the SH and the WH SOIs, respectively.

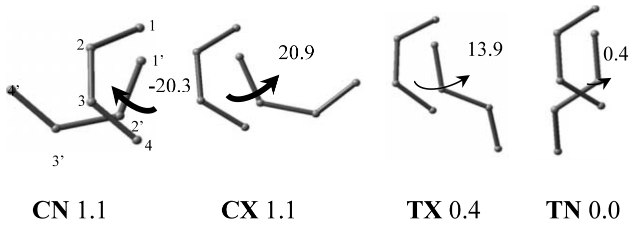

Figure 3. Twisting effects in the cycloaddition TSs. Arrows indicate the twisting of the dienophile moieties and the numbers near the arrows give the dihedral angles 1/1′/2′/4. Numbers near the TS labels are the stabilization energies in kcal/mol associated with the twisting motions.

bond as well as the relief of the closed shell repulsion between the addends, which is a large component of the DA barrier.[16] The outside twisting reduces the repulsive interactions and the FO stabilizing interactions as well, allowing for the attainment of a minimum compromise geometry.

An estimate of the energy changes associated with the twisting motions can be provided by calculations with the constraints of maintaining the primary bondings on the same plane, i.e. by setting the dihedral angle between the ends of the diene and the dienophile carbons equal to zero. Model calculations at the B3LYP/6-31G* level with these constraints show a remarkable lift of the electronic energies of the TSs by the amounts given in Fig. 3 and in the case of TS **CN**, the disruption of the bispericyclic array, which is converted into a rather normal asynchronous DA TS. While in the case of TS **CN** the inside twisting is necessary for the attainment of the lower lying bispericyclic array, whose stabilization more than compensates the cost of the inside motion, the outside twisting of the *exo* TS **CX** remarkably provides almost the same energetic effect while the effect on TS **TX** is lesser. Despite the ‘opening’ of the *exo* TSs **CX** and **TX**, they remain pericyclic and well below the reference *anti* **cc** and **ct** diradical forming TSs. Finally in the case of the WH TS **TN** no significant twisting is observed, since the inside and the outside twistings are expected to increase significantly the closed shell repulsions without any attending increase of the FO interactions. No significant energetic advantage can then be attributed to the WH SOIs, at least in the case at hand.[17]

In summary the DA dimerization of butadiene takes place through the bispericyclic *endo* TS **CN** and the pericyclic *exo* TS **TX**, which occur at almost the same energies. The former pathway takes advantage of the stabilizing SH SOI while the latter has the least steric hindrance. Interestingly enough this simple picture accommodates fairly well the observed[7b] sharp increase of *endo* stereoselection in the dimerization of *cis*,*cis* 1,4-dideuterobutadiene under high pressure, owing to the more compact *endo* TS **CN**. Diradical paths are competing through the TSs *anti* **tt-*out*** and **tt-*in***. These passes involve two unswitched *transoid* butadiene moieties, accounting for the formation of minor amounts of *trans*-1,2-divinyl-cyclobutane and 1,5-cyclooctadiene, and are presumably underestimated at the theoretical level used here.

The merging and the bifurcation of the cycloaddition paths should depend on the substitution patterns of butadienes and the study of the substituent effects will be pursued in due course.

Acknowledgements

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