

A Bispericyclic Transition Structure Allows for Efficient Relief of Antiaromaticity Enhancing Reactivity and Endo Stereoselectivity in the Dimerization of the Fleeting Cyclopentadienone

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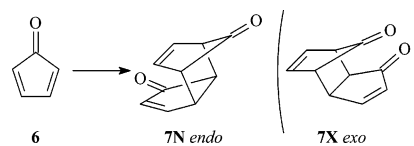
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Abstract: B3LYP/6-31G* calculations account for the enhanced reactivity and endo stereoselectivity in the dimerization of the fleeting antiaromatic cyclopentadienone. Secondary orbital interactions promote endo stereoselectivity and a full merging of 4+2 and 2+4 allowed paths in an endo bispericyclic transition structure. Electrostatic effects increase reactivity and selectivity but the driving force to enhanced reactivity is the loss of antiaromaticity in the dimerization TSs while enhanced selectivity derives from the more efficient relief of antiaromaticity in the bispericyclic array.

Secondary orbital interactions (SOIs) were introduced by Woodward and Hoffmann (WH) in 1965¹ and are widely used in interpreting the stereoselectivity of many cycloaddition reactions.² The SOI concept has nevertheless remained rather fuzzy and escaped a firm theoretical validation. Recently the existence of the SOIs has been even disputed.³

We have recently reported that the prototypal endo dimerization of cyclopentadiene, which served as a basis for the Alder's principle of the maximum accumulation of unsaturated centers⁴ and the WH SOIs as well, involves a rather unexpected bispericyclic transition structure (TS) **1** in which the 4+2 and 2+4 Diels–Alder (DA) cycloaddition paths **2** and **3** are fully merged.⁵ The shape of the bispericyclic TS did not support the classical WH SOI picture **4** and shows instead the remarkable influence of the less familiar but theoretically sound "next to next-neighbor" Salem–Houk (SH) SOI **5**⁶ involving the geminal 2+4 perimeter. In essence the bispericyclic TS **1** takes advantage of the stabilizing interactions of both the 4+2 and 2+4 cycloaddition paths owing to the modest

SCHEME 1



geometry deformation of the DA TS **2** required to exploit the SH SOIs.⁷



We wish to report here the more impressive case of merging of allowed paths in the dimerization of cyclopentadienone (CPDO), where a highly enhanced endo selectivity and reactivity is observed. CPDO is a classical fleeting intermediate that has attracted considerable attention from many workers because of the wide synthetic utility of cyclopentadienones and their theoretical interest and was thoroughly studied.⁸ The parent CPDO can be generated from a variety of precursors and efficiently trapped with DA reactions either as a diene or dienophile⁹ and could be observed in matrix studies at low temperature or under gas-phase conditions.¹⁰ In the absence of trapping agents, CPDO **6** dimerizes even at 40 K^{10a} affording exclusively the DA endo dimer **7N** (Scheme 1).

We have located the relevant points on the potential energy surface of the dimerization of CPDO at the B3LYP/6-31G* level,¹¹ which gives satisfactory geometries and reliable energies for pericyclic reactions and diradicals formation.¹² The electronic energies ΔE_e of the TSs and the adducts relative to the reactants are given

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TABLE 1. B3LYP/6-31G* Electronic Energies (ΔE_e) Relative to the Reactants (kcal/mol), Enthalpies (kcal/mol),^a Entropies (eu),^a Forming C...C Bond Lengths (Å), and Dipole Moments μ (D) of the TSs, Diradical Species, and Cycloadducts in the Dimerization of CPDO

	ΔE_e	ΔH	ΔS	C...C	μ
transition structures					
8N	2.4	3.7	-30.8	2.17 (2.80)	3.90
8X	10.1	11.2	-30.0	2.19 (2.60)	4.60
9^c	15.9	16.0	-25.2	2.14	0.00
11	-5.4	-3.4	-34.9	1.63 (2.66)	3.89
adducts					
7N	-32.8	-29.0	-34.4	1.57 (1.58)	3.45
7X	-32.7	-28.9	-34.5	1.57 (1.58)	4.60
10^c	-8.5	-6.9	-27.5	1.55	0.00

^a Thermodynamic values at 298.15 K from unscaled vibrational frequencies in the harmonic approximation. ^b Cyclopentadienone, -268.103660 hartrees, correction to enthalpy $\Delta H = 50.24$, $\Delta S = 69.14$, $\mu = 3.07$. ^c Fully optimized UB singlet diradicals.

in Table 1 along with the enthalpies, entropies, forming bond lengths, and dipole moments. In Figure 1 the B3LYP enthalpies are given along with their formulas, where **N** and **X** refer to the endo and exo stereochemistry, respectively.

As shown in the profile of Figure 1, the endo TS **8N** is by far the more favorable pass for the DA dimerization of CPDO and lies 3.7 kcal/mol above the reactants while the exo TS **8X** lies at 11.2 kcal/mol. The diradical forming TS **9** is located at even higher energy and leads to the corresponding anti diradical **10**. The exo and endo 4+2 cycloadducts **7X** and **7N** are 29 kcal/mol below the reactants, and the Cope TS **11**, which connects the (identical) endo adducts **7N** and **7N'**, lies 25.6 kcal/mol above the adducts.

The DA passes **8N** and **8X** correspond well to the bispericyclic and pericyclic TSs already described in the dimerization of cyclopentadiene. The merged TS **8N** is a first-order saddle point and chiral with C_2 symmetry and is depicted in Figure 2. The 1,1' bond, at the end of the diene moieties, is rather advanced (2.17 Å) while the symmetrical 4,2' and 2,4' bonds lag well behind and are still rather long (2.80 Å), giving the structure a highly asynchronous shape and a characteristic uncanny diradicaloid resemblance. The displacement vectors associated with the imaginary frequency of TS **8N** involve essentially the 1,1' C...C vibration with minute, but observable, in-phase vibrations of the long 2,4' and 4,2' C...C bond (Figure 2b). Accordingly, IRC calculations show that the reaction coordinate (RC) steps from TS **8N**

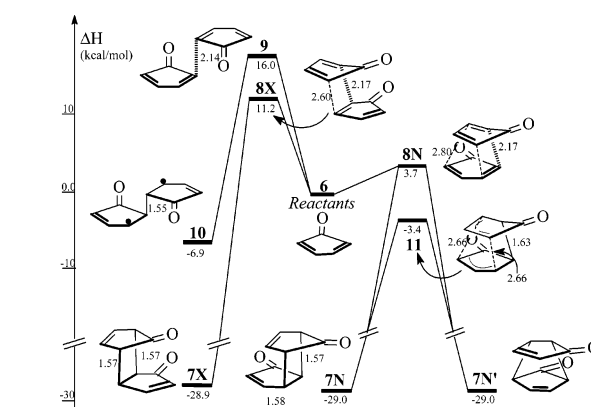


FIGURE 1. Transition structures, diradical intermediates, and DA cycloadducts in the CPDO dimerization. Numbers near the levels are enthalpies (in kcal/mol) relative to the reactants and numbers near the forming bonds are bond distances (in Å).

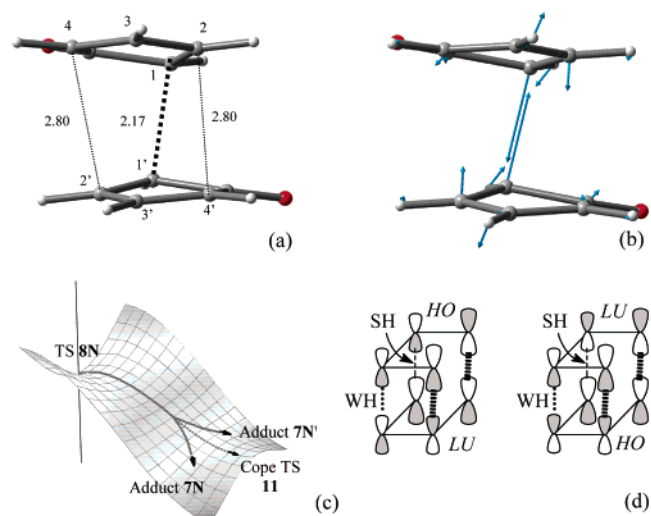


FIGURE 2. Geometric features (a) and displacement vectors (b) of TS **8N** and a 3D picture of RC of the dimerization path (c) where the dotted path refers to the crest toward Cope TS **11**. In the DA HO-LU interactions (d) the bold dashes refer to the primary interaction and the dashed and dotted lines to the SH and the WH SOIs, respectively.

toward the Cope TS **11** with only minor changes of the long C...C bond until reaching a valley-ridge inflection point¹³ (at a $C_1\cdots C_{1'}$ distance of 1.92 Å) where the distortive antisymmetric C...C/C...C vibration (which is the imaginary frequency of the Cope TS **11**) 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 **7N** and **7N'**. The Frontier orbital (FO) rationalization of merging⁵ is shown in Figure 2d for the simple case of the parent butadiene system. The highly favorable SH SOIs promote merging of the 4+2 and 2+4 allowed paths, whose cooperation strengthens the 1,1' bond.

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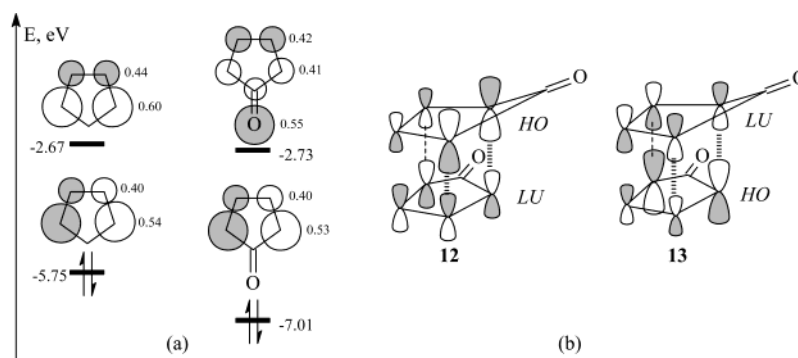


FIGURE 3. The FOs of cyclopentadiene and CPDO (a) and the DA *HOMO-LUMO* interactions **12** and **13** in CPDO dimerization (b). Numbers near the levels are the B3LYP orbital energies in eV and numbers near the orbitals are STO3G//B3LYP coefficients. Bold dashes in **12** and **13** specify the primary interactions along the 4+2 DA perimeter with the upper addend serving as diene while dashed lines refer to the SH SOIs.

The most striking results in the dimerization of CPDO are, however, the enhanced reactivity and stereoselectivity. With respect to cyclopentadiene the endo and exo enthalpic DA barriers decrease from 21.0 and 23.9 kcal/mol to 3.7 and 11.2 kcal/mol, respectively, while the exo–endo difference, namely the stereoselectivity, increases dramatically from 2.9 to 7.5 kcal/mol. A comparison of the geometrical features of the dimerization TSs supports the larger influence of the SOIs in the case of CPDO. With respect to cyclopentadiene, TS **8N** occurs earlier since the length of the stronger $C_1\cdots C_{1'}$ forming bond increases from 1.97 to 2.17 Å. The lengths of the long and weaker bonds show instead a decrease from 2.90 to 2.80 Å, well consistent with the more influential SOIs in the CPDO dimerization.

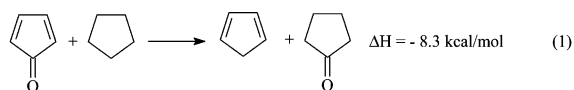
How to account for the enhanced reactivity and selectivity of CPDO? It is usually assumed^{9c,10a} that the increased reactivity in the CPDO dimerization is related to the reduced *HOMO-LUMO* gap in CPDO owing to a sizable *LUMO* lowering, which results from mixing of the low-lying π^*_{CO} orbital and the *LUMO* of the diene moiety. The inductive influence of the C=O group causes, however, a remarkable lowering of the CPDO *HOMO*, too, as documented by PES studies.^{10b,14}

Various types of calculations given in the Supporting Information show the lowering of both the CPDO FOs with respect to cyclopentadiene as well as the low polarization of CPDO *LUMO*, which shows similar coefficients on the diene carbons. The B3LYP FOs of cyclopentadiene and CPDO are depicted in Figure 3 and show that the *HOMO-LUMO* gap of CPDO is actually larger than that of cyclopentadiene. Clearly, according to FO principles,^{2a,15} this increased gap cannot account for the enhanced reactivity since stabilization energy and FO gap are inversely proportional. The FOs of CPDO could accommodate, at least in part, the endo selectivity of CPDO as shown in the *HOMO-LUMO* interactions **12** and **13** (Figure 3b). Each interaction provides maximal stabilization to a different 4+2 and 2+4 cycloaddition mode and merging offers a unique opportunity of sharing the best stabilizations of the two different paths. When viewed more canonically, a single cycloaddition mode, e.g.

the one indicated by the bold dashed bonds in **12** and **13**, is assisted by the strong SOI apparent in one of the two interactions, in the case at hand in **13**.

In the framework of the Salem–Klopman treatment of organic reactivity^{2a,6a} the enhanced effects could derive from favorable Coulombic terms. Indeed CPDO is a highly polar compound ($\mu = 3.07$ D) and sizable electrostatic effects should manifest in the dimerization TSs. An evaluation of the Coulombic term has been made by using the Mulliken charges and gives a Coulombic attraction between the addends of 1.0 and 0.6 kcal/mol in TSs **8N** and **8X**, respectively. Although the Coulombic attractions are in the right direction, their sizes account for only a minor part of the enhanced effects.

Which is then the main origin of the enhanced effects? We trace the enhanced reactivity and selectivity in the dimerization of CPDO to its well-known antiaromatic nature¹⁶ and to the loss of antiaromaticity in the cycloaddition TSs. We have evaluated the enthalpic difference between CPDO and cyclopentadiene deriving from aromaticity effects with the isodesmic reaction 1,¹⁷ which gives a reaction enthalpy of -8.3 kcal/mol at the B3LYP/6-31G* level. When raising the energies of the CPDO



reactants by 2×8.3 kcal/mol, we can compare the profiles of the CPDO and cyclopentadiene on a common energy scale, as depicted in Figure 4. Since the lowering of the dimerization barriers of CPDO is due in part to electrostatic effects, which are negligible in the case of cyclopentadiene, we have taken away in Figure 4 the stabilization of TS **8X** and **8N** ascribable to electrostatic effects by shifting upward the energy levels by 0.6 and 1.0 kcal/mol, respectively, to focus mainly on the antiaromaticity changes. The dimerization profile of CPDO

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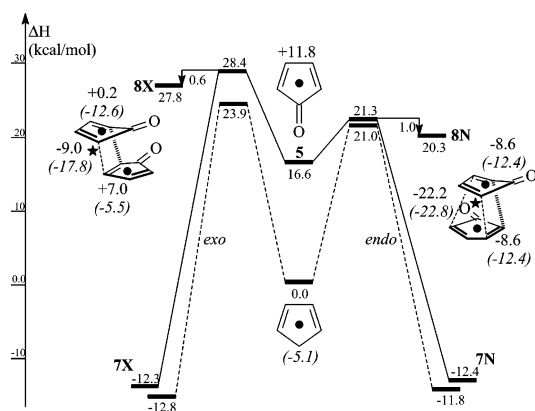


FIGURE 4. Profiles of the dimerization of CPDO (full lines) and cyclopentadiene (dashed lines) with a common energy scale based on the isodesmic eq 1; arrows indicate the stabilization of the TS **8X** and **8N** ascribable to electrostatic effects by the amounts given in kcal/mol. Ghost atoms for the calculation of the NICS were placed at the centers of the ring of the addends (dots) and at the central points of the DA basement (stars) and the NICS values are given nearby. The corresponding NICS values for the cyclopentadiene TSs are given in italics between parentheses.

shows satisfactorily the relief of antiaromaticity on going from the addends to the cycloadducts. It is gratifying to notice that the latter compounds, which are devoid of the aromaticity effects of the reactants, lie at energies comparable to the cycloadducts of cyclopentadiene.

On looking at the TSs, the CPDO profile of Figure 4 suggests a remarkable but partial loss of antiaromaticity in TS **8X** and an almost complete loss in the bispericyclic TS **8N**. Delocalization into the cycloaddition perimeter of TS **8X** offers a convenient opportunity for the relief of antiaromaticity, while the bispericyclic TS **8N** offers a magnified opportunity of delocalization into the two merged cycloaddition perimeters.

Aside from the features of the energetic criterium adopted above, the nucleus-independent chemical shifts (NICS) support the interpretation and give a more detailed account of the cyclic delocalization in the TSs and the aromatic and antiaromatic character it imparts to the addends. These magnetic indicators of aromaticity have been developed by Schleyer et al.¹⁸ and applied to prototypal pericyclic TSs to demonstrate their cyclic aromatic delocalization.^{18b} The NICS values are given near the formulas in Figure 4 and have been evaluated with B3LYP/6-31G* calculations at the geometrical center of the rings of the addends (dots) and at the central point of the DA basement (stars) defined by the 2 dienophile carbons and the 2 central diene carbons. This location of the starred centers is convenient for the comparison of delocalizations in the exo and endo TSs because of an almost perfect coincidence in the endo TSs with the geometrical centers of the bispericyclic arrays and the centers of the merged twin DA basements.

Negative values of the NICS indicate aromatic and positive values antiaromatic character. The NICS of

CPDO is positive^{16a} (+11.8 ppm), denoting antiaromaticity, and decreases in the CPDO subunits of TS **8X** (+0.2; +7.0), the major effect (+0.2) being on the diene component owing to its heavier involvement in the cyclic delocalization of the cycloaddition TS. The effect is larger in TS **8N**, where both the (identical) CPDO subunits attain respectable aromatic values (−8.6) because of the efficient delocalization in the bispericyclic array. In the case of the slightly aromatic^{18c} cyclopentadiene the NICS is negative (−5.1) and decreases in the exo TS (−12.6; −5.5) in a manner analogous to the CPDO case. Somewhat surprisingly in the endo TS the (identical) cyclopentadiene subunits show a decrease (−12.4), which remains, however, behind that of the exo diene subunit (−12.6). This apparent anomaly reflects subtle differences in the endo TSs of CPDO and cyclopentadiene. As already noted in discussing the SOIs, the bispericyclic array is more asynchronous in the case of cyclopentadiene than in the case of CPDO. The increase of asynchronicity in the bispericyclic array of cyclopentadiene gets along with a reduced cyclic delocalization, which is monitored by the NICS values.

The NICS values at the central points of the DA basement are all negative denoting aromatic cyclic delocalization and impressively parallel the ordering deduced from the energetic comparison of Figure 4. The aromatic cyclic delocalization in TS **8X** is minimal (−9.0) and increases in the cyclopentadiene exo TS (−17.8) while the endo TSs show higher and similar aromaticities, TS **8N** (−22.2) and the cyclopentadiene endo TS (−22.8). The NICS values at the geometrical centers of the bispericyclic arrays are only slightly larger, −22.3 and −23.1, respectively, and support nicely the almost complete loss of antiaromaticity in TS **8N**.

In summary, the SH SOI model accounts for the venerable Alder's principle of maximum accumulation of unsaturated centers in the dimerization of cyclopentadiene and applies to the dimerization of CPDO as well. In the latter case, favorable electrostatic interactions somewhat increase reactivity and selectivity but the driving force to enhanced reactivity is the attending loss of antiaromaticity in the cycloaddition TSs while enhanced selectivity derives from the more efficient relief of antiaromaticity in the bispericyclic array of TS **8N**. Besides energetic comparisons, NICS values impressively support the changes in the cyclic aromatic delocalization in the cycloadditions and account well for subtle differences in the TSs.

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Supporting Information Available: FOs of cyclopentadienone and cyclopentadiene; geometries of transition structures and adducts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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