Why Cyclooctatetraene Is Highly Stabilized: The Importance of "Two-Way" (Double) Hyperconjugation

Judy I. Wu,[†] Israel Fernández,[‡] Yirong Mo,[§] and Paul von Ragué Schleyer*,[†]

[†]Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States
[‡]Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense Madrid, 28040, Madrid, Spain
[§]Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, United States

Ⓢ *Supporting Information*

ABSTRACT: Despite its highly nonplanar geometry, the tub-shaped D_{2d} cyclooctatetraene (COT) minimum is far from being an unconjugated polyene model devoid of important π interactions. The warped skeleton of D_{2d} COT results in the large stabilization (41.1 kcal/mol) revealed by its isodesmic bond separation energy (BSE). This originates largely from the "two-way" hyperconjugation, back and forth across the C–C single bonds, between the CC/CH $\sigma(\sigma^*)$ and the C=C $(\pi^*)\pi$ orbitals. These hyperconjugative effects compensate for the substantial, but not complete, loss of π conjugation upon ring puckering. C–C single bond rotation of 1,3-butadiene involves a similar interplay between π conjugation and "two-way" double hyperconjugation and serves as a simple model for the inversion of D_{2d} to D_{4h} COT. The perpendicular rotational transition states of many other systems, e.g., the allyl cation, styrene, biphenyl, and ethene, are stabilized similarly by "two-way" hyperconjugation.

■ INTRODUCTION

Cyclooctatetraene (COT) is one of the decisive molecules in the history of chemistry. Its polyolefinic chemical properties[1,2] are quite unlike those of benzene. This discovery by Willstätter in 1911[1] rang the "death knell"[3] on Johannes Thiele's partial valence theory of aromaticity,[4] which predicted that all fully conjugated cyclic polyenes (annulenes) should display benzene-like aromatic behavior.

The strongly nonplanar tub-shaped (D_{2d}) COT ground state[2] is usually interpreted as being largely free from angle (and other) strain[5] and to be *decidedly nonaromatic*.[6,7] The twisting of the π system (the CCCC dihedral angles are nearly 60°) is widely regarded to effectively preclude conjugation: neither $4n + 2 \pi$ aromaticity nor $4n \pi$ electron antiaromaticity is present. Fowler et al. demonstrated the absence of a paratropic π ring current (which persisted surprisingly close to the minimum) in the (D_{2d}) COT ground state.[8] Hence, the energy of D_{2d} COT should be quite normal, i.e., neither destabilized nor stabilized. Pauling's rough estimate of only 5 kcal/mol[9] for the "resonance energy" of COT based on early experimental data supported this expectation.

In startling contrast, Polizer, et al. found that the isodesmic bond separation energy (BSE) of the D_{2d} COT minimum (eq 1, Scheme 1) is extremely large (41 kcal/mol).[10] Unexpectedly, tub-shaped D_{2d} COT is highly stabilized thermochemically! This qualitative conclusion is confirmed by the further comparisons in Scheme 1 with reference compounds that are stabilized by conjugation, hyperconjugation, and even aromaticity. The remarkably large stabilization of COT is nearly 2/3 that of benzene (BSE = 64.6 kcal/mol, eq 2a) and is over half that of styrene (77.3 kcal/mol, eq 2b),[11] the aromatic (and conjugated) C_8H_8 isomer of COT. Although diene systems like COT with highly twisted adjacent π orbitals are not expected to "conjugate" in the usual sense, the −2.3 kcal/mol energy of eq 3a reveals that the stabilization of D_{2d} COT is nearly the same

Scheme 1. Homodesmotic and Isodesmic Equations for Evaluating the Stabilization Energies of D_{2h} COT, Benzene, and Styrene[a]
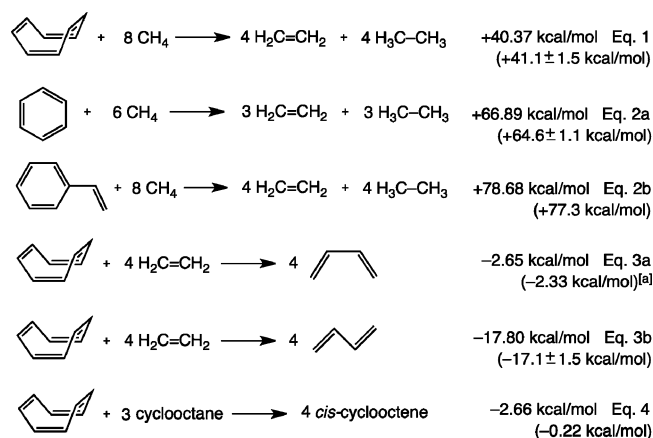
[a]All data were computed at the B3LYP/6-311+G** level (experimental evaluations, based on the heats of formation of molecules at 298 K, are in parentheses). [a]: Based on a 3.7 kcal/mol *syn–anti* energy difference.

as that of four *fully conjugated syn*-butadienes, and only modestly less than that of four (less appropriate) *anti*-butadiene models (eq 3b, −17.1 kcal/mol; also see ref 12). Equation 4 reveals that the stabilization of D_{2d} COT is nearly the same as 4 times the hyperconjugative stabilization of *cis*-cyclooctene (see ref 13). Politzer attributed the "considerable degree of stabilization" of COT "to limited π delocalization",[10] but this

does not explain the unexpectedly high stability of tub-shaped COT adequately.

Electron diffraction[14−16] and reliable low temperature X-ray[17−19] analyses, as well as high level computations,[20] establish COT's highly nonplanar geometry (D_{2d} symmetry, φ = 56° CCCC dihedral angles) and the alternating CC bond lengths. The best available CC distances (C−C 1.470 Å, C=C 1.337 Å)[20] of D_{2d} COT also pose interpretive problems since they are closer to the 1.454 Å C−C and 1.338 Å C=C[21] distances in the, planar, fully π conjugated *anti*-butadiene, rather than to the 1.528 Å C−C and the 1.331 Å C=C lengths in ethane[22] and ethene.[21] Since the highly twisted D_{2d} COT framework precludes effective π conjugation, the COT CC lengths must reflect the operation of other stabilizing electron delocalization effects. Note that Dewar's hybridization argument,[23] that C sp²−C sp² bond lengths should be shorter than C sp³−C sp³ lengths, is applicable to COT and to butadiene in their various conformations.

The potential energy surfaces (PESs) of various COT states have been well investigated (Figure 1).[24] Briefly, planar D_{4h} and
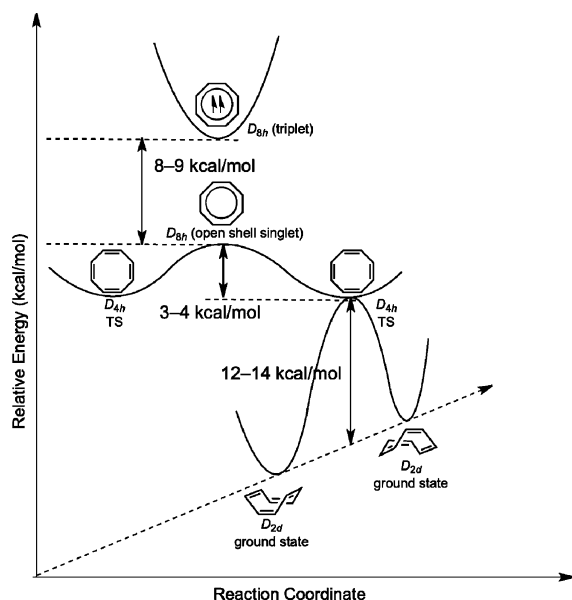

Figure 1. Schematic representation of the COT potential energy surface (PES) (adapted from ref 24 with permission and updated). Note that the singlet D_{8h} and D_{4h} TSs connect directly without an intervening intermediate and that the entire triplet PES, including the aromatic D_{8h} minimum,[29b] is higher in energy.

D_{8h} COT have optimum π conjugation but are only transition states.[25] The D_{8h} form is a typical "disjoint radical";[26,27] the open-shell D_{8h} singlet transition state (for π bond shifting)[28] is favored over the D_{8h} aromatic triplet state[29] minimum.[30] Evaluations of the dynamic tub-to-tub ring inversion process of D_{2d} COT based on NMR[31] and electron binding energy differences[32] revealed a 12−14 kcal/mol activation barrier via the bond-alternating (D_{4h}) singlet transition state (TS). Although the higher energy of the D_{4h} form has been attributed almost entirely to strain effects (rather than to antiaromaticity),[5] the energy of the D_{2d} ground state, the focus of our paper, has not been analyzed adequately before.

The 1,3-butadiene single bond rotation system provides the most basic model for the D_{2d} to D_{4h} inversion of COT. There are four twisted butadiene moieties in D_{2d} COT and four *syn*-

butadiene moieties in D_{4h} COT. Daudey et al. first proposed that perpendicular (*perp*-) butadiene is stabilized by hyperconjugation (among the aligned σ bond of one vinyl moiety and the adjacent π bond of the second C=C; see Figure 1 of ref 32 and Figure 4 below) by "the same order of magnitude" (8.9 kcal/mol) as π conjugation in planar *anti*-butadiene (10.4 kcal/mol), and that both these interactions shortened the C−C central bond by nearly the same amount.[33] Indeed, the electron densities at the C−C bond centers of *anti*- and *perp*-butadienes are very similar.[34] In the absence of π electron delocalization, Daudey et al. found that the equilibrium C sp²−C sp² distances of both *perp*-butadiene (1.541 Å) and *anti*-butadiene (1.521 Å) resembled the C sp³−C sp³ length of ethane (1.528 Å).[33] Feller et al.[35] proposed that the CC single bond of *perp*-butadiene (1.482 Å, from high level ab initio computations)[35] and of D_{2d} COT (1.470 Å)[20] modeled the length of a (nearly) "conjugation-free" C sp²−C sp² single bond, but they failed to note Daudey's hyperconjugation proposal.[33] George et al. suggested the use of *perp*-butadiene as a reference compound for evaluating the stabilization energies of conjugated hydrocarbons,[36] but did not consider the energetic effects of hyperconjugation, which compromises such procedures and negates their quantitative estimates.

If hyperconjugation effects stabilize the perpendicular and twisted conformations of butadiene, they also should stabilize the D_{2d} COT ground state. Mulliken discussed this possibility for COT a half-century ago.[37] He noted in 1959 that the twisting of C−C bonds in D_{2d} COT "destroys π-conjugation, but creates first-order hyperconjugation at both ends of the C−C bond"; thus, "some resonance shortening is still expected."[36] Pitzer's even earlier work (in 1946) on the rotational barrier of styrene noted the possible stabilization of its perpendicular TS by hyperconjugation between the orthogonal vinyl and phenyl groups.[38] However, both these prescient observations seem to have eluded further attention in analyses of COT and related systems.[36]

We now evaluate the π delocalization effects involved in the $D_{4h} \rightarrow D_{2d}$ COT ring inversion and in the C−C bond rotation of butadiene computationally and answer the following questions: What is responsible for the large stabilization of the tub-shaped D_{2d} COT ground state? Do the C−C single bonds of D_{2d} COT and of *perp*-butadiene really represent "pure" C sp²−C sp² lengths?

■ METHODS

Block-localized wave function (BLW) computations,[39−41] employing the Xiamen Valence Bond (XMVB) program[42] (implemented in GAMESS-R5),[43] evaluated the vertical electron delocalization energies (BLW-DE) across the C−C single bonds of D_{2d} and D_{4h} COT, as well as *syn*-, *perp*-, and *anti*-butadienes. Due to the methodological and basis set limitations of the XMVB program, as well as the size of the COT species, all BLW-DE computations were performed at the HF/6-31G* level. Both D_{2d} and D_{4h} COT are closed-shell singlets with stable wave functions.[44] The BLW-DEs are based on the energy difference between a fully delocalized wave function (Ψ^{Del}) and an artificially localized wave function (Ψ^{Loc}). Since the BLW-DEs are derived by the Ψ^{Del} vs Ψ^{Loc} difference at the HF level, the effect due to the neglect of electron correlation is largely canceled (see ref 45). Ψ^{Loc} can be computed on the basis of either the geometry of the completely delocalized system (vertical BLW) or the geometry optimized

with the BLW constraint (adiabatic BLW). Both Ψ^{Del} and Ψ^{Loc} are optimized self-consistently.

Ψ^{Loc} is constructed by assigning electrons and primitive basis functions to particular subspaces of the molecule. This restricts the expansion of each block-localized molecular orbital (BL-MO) and artificially "disables" specific electron delocalization effects. In the various COT (and butadiene) conformations, the block-localized MOs corresponding to each of the HC=CH (or HC=CH$_2$, for butadiene) units only are expanded with the primitive basis functions of their carbons and hydrogens. This procedure, carried out consistently for all conformations of COT and of butadiene, precludes *all* electron delocalization (both π and σ, rather than just π) across the C−C single bonds and thus evaluates both hyperconjugation and conjugation effects together. Consequently, larger interaction energies result from this more general approach than just considering the π−π conjugation interactions, as in Daudey et al.'s paper.[33] Thus, for *anti*-butadiene, Daudey's π−π conjugation energy is 10.4 kcal/mol (our value is 9.2 kcal/mol, HF/6-31G*, using an equivalent localization scheme), whereas the HC=CH$_2$ blocking procedure (described above) gives 17.5 kcal/mol (HF/6-31G*), since both hyperconjugation and conjugation effects are evaluated.

The nonorthogonal partitioning of basis functions and BL-MOs, upon which the BLW method is based, has led to the criticism that nonorthogonal orbitals are ambiguous and the BLW method exaggerates the role of steric effects (thereby underestimating the delocalization energy).[39,46,47] However, we note that when a wave function is expressed with a Slater determinant, any localization scheme utilizing unitary transformations can convert delocalized canonical MOs to localized MOs. The latter have "tails" extending beyond the localized region due both to the orthogonalization constraint and to the effect of delocalization. Only the delocalization tails are responsible for the delocalization energy, the focus of our study. Since the removal of orthogonalization does not alter the total energy of the wave function, the energy change associated with the deletion of the delocalization tail is defined as the delocalization energy.

Although the BLW method removes both the orthogonalization and delocalization tails by definition (intrinsically), the BL-MOs can be orthogonalized easily (e.g., if one prefers orthogonal orbitals where the tails would be ascribed solely to the orthogonalization constraint). Our computations focus on the localized state wave function, just as in the constrained density functional theory (CDFT) method.[48,49] Khaliullin et al.'s "absolutely localized molecular orbital" (ALMO) solution for nonorthogonal molecular orbitals provides individual orbital interactions in terms of MO perturbation theory.[50] ALMOs, in effect, are identical to BL-MOs. This endorses the BLW method, which was devised earlier.[41] We also note that the BL-MO relaxation (polarization or optimization) in the BLW method is an extension of the approaches adopted by Daudey et al.[33] and by Kollmar.[51] However, their approaches do not consider the optimization (polarization) of BL-MOs and give delocalization energies that deviate somewhat (10−20%) from BLW data (at different theoretical levels).

However, we do recognize the basis set dependence (which influences all computations to some extent) in BLW treatments.[52] This dependence intrudes mainly in the polarization stage. Thus, computed BLW-DE values typically fluctuate slightly from smaller basis sets to 6-311+G(d,p) and then decrease with larger bases. However, our extensive computa-

tions of the resonance energies of conjugated systems[52−55] demonstrated that the BLW method, when employed with midsized basis sets (e.g., 6-311+G(d,p)), give reasonably invariant values consistent with viable experimental evidence (see ref 56). Furthermore, it has been common practice for decades to minimize errors due to methodological imperfections by basing comparisons and interpretations on data computed at the same theoretical level. In addition, the general reliability of the BLW method is documented by its computed structural parameters, vibrational frequencies, and NMR data.[57,58] We are exploring ways to overcome or to alleviate the basis set dependence, e.g., by projecting large basis sets to a reduced space, which then is used for BLW computations.

NBO orbital deletions[59] carried out at the B3LYP/6-311+G** level (as implemented in Gaussian 03)[60] analyzed the conjugation vs hyperconjugation interplay involved in the $D_{4h} \rightarrow D_{2d}$ COT ring inversion (at $\varphi = 10°$ intervals) and the 1,3-butadiene C−C single bond rotation (at $\varphi = 30°$ intervals). The various COT and butadiene conformers were obtained by fixing the CCCC dihedral angles (φ) while allowing all other parameters to optimize freely. Conjugative interactions were evaluated by deleting the eight $\pi \rightarrow \pi^*$ donor−acceptor elements. The hyperconjugative interaction evaluations involved deleting the eight C−C $\sigma \rightarrow \pi^*$, eight $\pi \rightarrow$ C−C σ^*, eight C−H $\sigma \rightarrow \pi^*$, and eight $\pi \rightarrow$ C−H σ^* elements.

■ RESULTS AND DISCUSSION

Double Hyperconjugation in D_{2d} COT. Our comprehensive BLW and NBO analyses of the COT $D_{4h} \rightarrow D_{2d}$ COT ring inversion reveal that the remarkable stabilization of tub-shaped D_{2d} COT across the twisted C−C single bonds is due both to hyperconjugation and to residual (partial) π conjugation. Surprisingly, the very large computed total vertical BLW-DE between the four HC=CH units of D_{2d} COT, 56.9 kcal/mol, is almost the same as the 57.7 kcal/mol total vertical BLW-DE value for the fully π conjugated D_{4h} COT. The unexpectedly small difference (0.8 kcal/mol, between D_{2d} and D_{4h}) is due to the interplay between conjugation and hyperconjugation. Planar D_{4h} COT benefits from substantial π conjugation stabilization (despite its eight π electron antiaromatic character),[5] but this is balanced in D_{2d} COT because its twisted C−C single bonds promote *"two-way"* *(double) hyperconjugation* (see Figure 2). These results agree fully with the literature conclusions that the 12−14 kcal/mol $D_{4h} \rightarrow D_{2d}$ COT energy difference (see Figure 1) is due to steric (strain) rather than to electronic effects.[5] The NBO orbital deletion analyses support this interpretation. As depicted
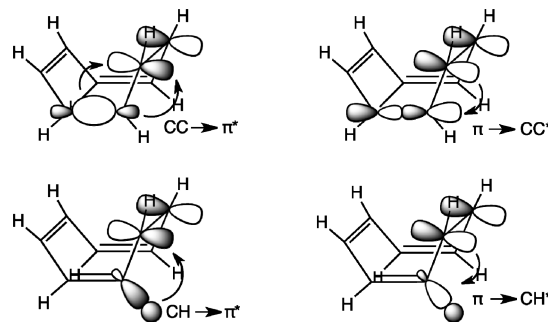

Figure 2. Schematic representation of *"two-way"* double hyperconjugation in D_{2d} COT.

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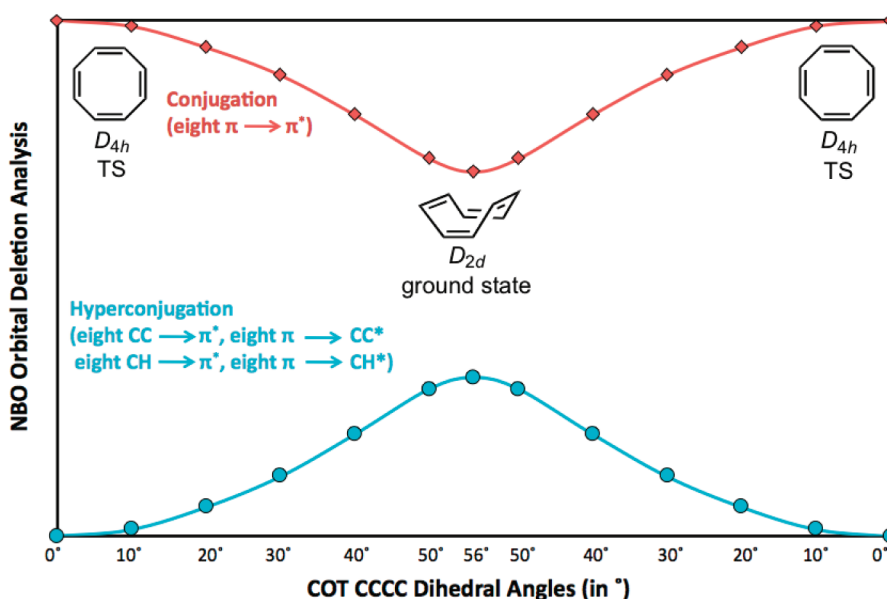dx.doi.org/10.1021/ct3000553 | *J. Chem. Theory Comput.* 2012, 8, 1280−1287

Figure 3. Schematic analysis of the COT inversion ($D_{4h} \rightarrow D_{2d} \rightarrow D_{4h}$) based on NBO orbital deletion data. Note the opposite effect of puckering on the conjugation ($\pi \rightarrow \pi^*$, red rhomboids) and hyperconjugation (CC/CH $\sigma \rightarrow \pi^*$ and $\pi \rightarrow$ CC/CH σ^*, blue circles) behavior.

qualitatively in Figure 3, the substantial $\pi \rightarrow \pi^*$ interactions in planar D_{4h} COT decrease moderately upon ring puckering, but are compensated fully by the developing double hyperconjugative interactions back and forth across the twisted C–C bonds between the CC/CH σ and C=C π orbital sets (also see Table S1 and Figure S1 in the Supporting Information). Note that the tricyclic isomer of COT (*syn*-tricyclo[4.2.0.0]-octa-3,7-diene) exhibits similar "through bond" orbital interactions among the vicinal π and C–C bonds.[61−63]

Although the energies of individual hyperconjugative interactions are generally smaller than conjugative effects, accumulation of the greater number of hyperconjugative interactions can give quite substantial total stabilization energies and influence the geometries of molecules (discussed below). Even staggered ethane is stabilized by hyperconjugation between the two methyl groups (by 8.7 kcal/mol at HF/6-31G*).[39]

"Two-way" (double) hyperconjugation is crucial for interpreting the energy and geometry of D_{2d} COT (as well as many other nonplanar molecules), but its importance has not been adequately recognized in the literature. Mulliken's 1959 considerations[36] should be stressed rather than ignored. The origin of hyperconjugation effects is qualitatively similar to π conjugation: both result in the energetic stabilization of molecules due to electron delocalization.[46]

1,3-Butadiene Rotation. As discussed above, the rotation around the C–C single bond of 1,3-butadiene[33,64] is the simplest model involving a conjugation/hyperconjugation interplay similar to that of the D_{2d} to D_{4h} COT inversion. Both *syn*-butadiene (C_{2v}, $\varphi = 0°$) and *anti*-butadiene (C_{2h}, $\varphi = 180°$) are stabilized by π conjugation across the C–C single bond, but *perp*-butadiene ($\varphi = 90°$) is stabilized by *"two-way" (double) hyperconjugation* across the twisted C–C bond (see Figure 4).

Consequently, the computed vertical BLW-DE between the HC=CH$_2$ units of *perp*-butadiene (12.2 kcal/mol) only is modestly smaller than the BLW-DEs of *syn*-butadiene (15.8 kcal/mol) and *anti*-butadiene (17.5 kcal/mol). Blends of conjugative and hyperconjugative interactions contribute to
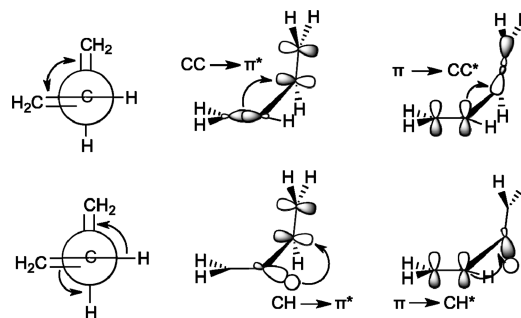

Figure 4. Schematic representation of "two-way" (double hyperconjugation) in *perp*-butadiene.

the stabilization energies of the intermediate butadiene conformations ($0° < \varphi < 180°$). The local *gauche*-butadiene minimum ($\varphi = 33°$; also see ref 65) benefits from partial π conjugation as well as from "two-way" (double) hyperconjugation.

NBO orbital deletion analysis of the butadiene C–C bond rotation (Figure 5) reveals the interrelationship between the stabilization due to conjugation (red rhomboids) and the stabilization due to hyperconjugation (blue circles). The substantial $\pi \rightarrow \pi^*$ interactions present in the planar *syn* and *anti* forms (at the left and right sides of Figure 5) fall off dramatically in the nonplanar conformations (in the middle of Figure 5), but are largely recovered by hyperconjugation back and forth across the twisted C–C bond (see Figure 5 and Table S2 in the Supporting Information). Hence, the experimental *anti → gauche* butadiene C–C bond rotational barrier (5.9 kcal/mol)[66] is much lower than the computed BLW-DE of *anti*-butadiene (17.5 kcal/mol), since the twisted conformations (including the rotation TS) are stabilized by "two-way" double hyperconjugation.

Our findings confirm Daudey et al.'s conclusions that hyperconjugation effects in the perpendicular form of butadiene appear to be "of the same order of magnitude as π conjugation."[33]
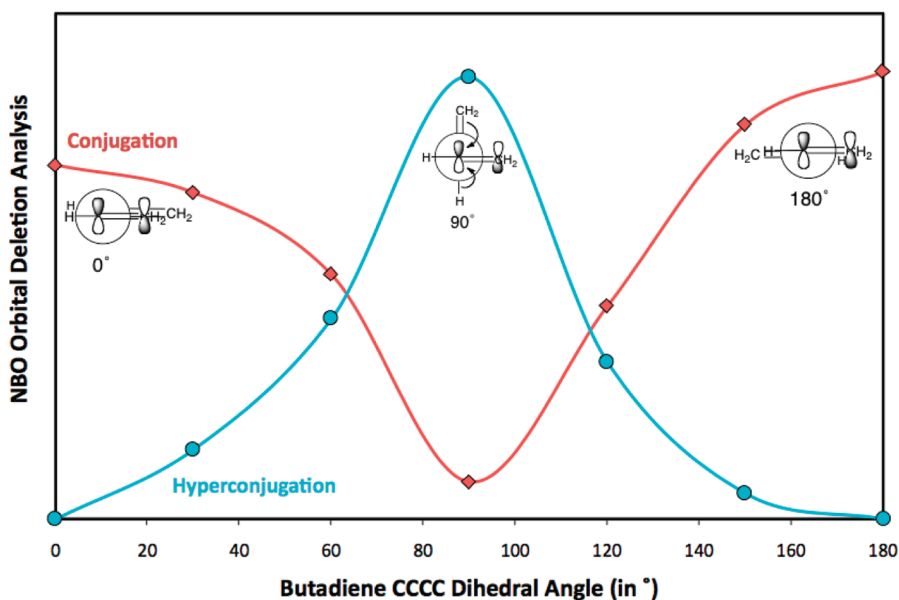
Figure 5. Schematic analysis of the 1,3-butadiene C−C bond rotation (syn → perp → anti) based on NBO orbital deletion data. Note the opposite effect of twisting on the conjugation ($\pi \to \pi^*$, red rhomboids) and hyperconjugation ($\pi \to \sigma$ C−C*, $\pi \to \sigma$ C−H*, σ C−C $\to \pi^*$, σ C−H $\to \pi^*$, blue circles) behavior.

Effects of "Two-Way" (Double) Hyperconjugation on C sp²−C sp² Single Bond Lengths.

"Two-way" double hyperconjugation influences not only the energies but also the geometries of molecules. Although both nonplanar D_{2d} COT and *perp*-butadiene[36] have been proposed as "conjugation-free" models,[35] both benefit energetically from substantial double hyperconjugation and some "resonance shortening [of the C−C bonds] is expected."[37] Hence, the shorter C−C distances of COT (1.470 Å) and of *perp*-butadiene (1.482 Å), compared to the C sp³−C sp³ length of ethane (1.528 Å) (see Table 1, best

Table 1. Computed HF/6-31G* Geometries (with and without BLW Constraint for π Delocalization between the HC≡CH/HC≡CH₂ Units) and the Best Available Literature Data for the C−C Distances (in Å) of D_{2d} COT, *anti*-Butadiene, and *perp*-Butadiene

	COT (D_{2d})	*anti*-butadiene	*perp*-butadiene	ethane
best available literature data	1.470[a]	1.454[b]	1.482[c]	1.528[d]
HF/6-31G* (no BLW constraint)	1.478	1.458	1.489	1.527
HF/6-31G* (with BLW constraint)	1.519	1.522	1.533	1.565
ΔC−C (before and after BLW)	0.041	0.064	0.044	0.038

[a]Reference 20. [b]Reference 21. [c]Reference 35. [d]Reference 22.

available literature data), do not represent "conjugation-free" C sp²−C sp² bond lengths as Feller et al. proposed.[35]

Our BLW results agree with Daudey et al.'s finding that "the origin [of the C−C central bond shortening in butadiene] is mainly due to π conjugation in the planar *s-trans* (*anti-*) conformation while hyperconjugation largely compensates the lack of π conjugation in the perpendicular form and leads to a similar shortening of the central bond."[33] The C−C single bonds of D_{2d} COT are shortened similarly, i.e., by double hyperconjugation and residual π conjugation across the C−C single bonds. Remarkably, the fully optimized HF/6-31G* C−

C distances of COT (1.478 Å), *anti*-butadiene (1.458 Å), and *perp*-butadiene (1.489 Å) increase to much longer C sp²−C sp² bond distances (1.519, 1.522, and 1.533 Å, respectively, see Table 1) when computed under localized BLW constraint (Ψ^{Loc}, i.e., no electron delocalization across the C−C single bonds). Clearly, both nonplanar D_{2d} COT and *perp*-butadiene[36] are not appropriate "conjugation-free" models![35] Based on the same BLW procedure (precluding electron delocalization across the C−C single bond), the ethane C sp³−C sp³ length also increases (from 1.527 to 1.565 Å). Along with conjugation[37] and hybridization[23] effects, hyperconjugative interactions[33] participate in the shortening of C−C single bond lengths.

Other Molecules with Double Hyperconjugation.

The structures and energies of many molecules also are influenced importantly by "two-way" (double) hyperconjugation. Besides COT, the D_{2d} minima of allene (Figure 6c), triplet ethylene
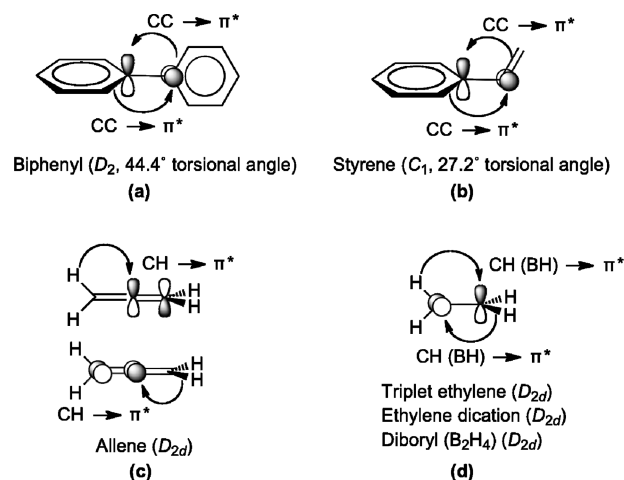

Figure 6. Schematic representations of "two-way" (double) hyperconjugation in biphenyl (D_2), styrene (C_1), allene (D_{2d}), triplet ethylene (D_{2d}), ethylene dication (D_{2d}), and diboryl (D_{2d}).

(C_2H_4, Figure 6d), the ethylene dication ($C_2H_4^{2+}$, Figure 6d), and diboryl (B_2H_4, Figure 6d), as well as many twisted conjugated molecules and polyenes with nonplanar equilibrium structures, e.g., biphenyl (D_2, 44.4° torsional angle, Figure 6a), styrene (C_1, 27.2° torsional angle, Figure 6b), and many nonplanar Möbius and the higher Hückel annulenes, also are subject to "two-way" (double) hyperconjugation.

Importantly, rotational barriers do not provide satisfactory estimates of conjugative and hyperconjugative interaction energies in planar molecules, since the corresponding transition structures also are stabilized.[33,37,38,67−69] For example, the stabilization of the allyl cation by conjugation (i.e., from the filled π orbitals to the adjacent CH_2 empty p orbital) is partially compensated by the large hyperconjugation effects in its 90° twisted TS.[69] Similarly, the nearly equivalent rotational barriers of biphenyl (D_2, ca. 44.4 ± 1.4[70] CCCC dihedral angle) to its fully planar D_{2h} (1.6 kcal/mol, experiment) and to its highly twisted D_{2d} (perpendicular benzene rings) (1.4 kcal/mol, experiment) TSs illustrates the importance of double hyperconjugation.[71−73] According to the classical explanation, planar D_{2h} biphenyl is fully conjugated but it suffers from steric repulsion between the two sets of "bay" hydrogens and thus is only a rotation TS (see ref 74 for the controversial "H−H bonding" interpretation). However, this does not explain why the rotation barriers via both the D_{2h} and D_{2d} TSs are so low.

Although the biphenyl D_2 minimum benefits from partially developed π conjugation and double hyperconjugation, the D_{2h} and D_{2d} rotational TSs benefit from optimal π conjugation and double hyperconjugation, respectively. Hence, the BLW-based evaluations of the π only interactions between the two benzene rings of both the D_{2h} (8.8 kcal/mol) and D_{2d} (7.5 kcal/mol) biphenyl rotation TSs are very similar. Note that not only CH but also CC σ bonds can be effective hyperconjugation donors[75] as Mulliken[37] and Pitzer[38] recognized long ago.

The planar and perpendicular 1,3-disilabutadiene forms (as well as those of other sila-substituted butadiene analogs) also are stabilized by conjugation and by hyperconjugation, respectively.[76] Apeloig, et al. concluded that "rotational barriers are not an accurate tool for approximating π-REs, because factors such as differences between rotamers in hyperconjugation, steric congestion, and so forth, can reduce (or increase) the barrier significantly and complicate the interpretation."[76] Hence, the computed vertical BLW-DEs (HF/6-31G*) between the two π bonds of *anti*- (11.3 kcal/mol), *syn*- (8.2 kcal/mol), and *perp*- (9.8 kcal/mol) 1,3-disilabutadiene do not differ much and explain the rather low rotational barriers of such species. Interestingly, 1,3,5,7-tetrasilacyclooctatetraene, the tetrasila-analog of COT, has a planar rather than tub-shaped minimum.[77]

CONCLUSIONS

Although planar D_{4h} COT is stabilized considerably by π conjugation (despite its four π electron character), tub-shaped D_{2d} COT is far from being an unconjugated polyene model devoid of important π interactions. Instead, "two-fold" (double) hyperconjugative interactions across the twisted C−C bonds of D_{2d} COT stabilize its twisted conformation considerably and compensate for the reduction in π conjugation relative to D_{4h} COT. As a consequence of the shortening due to numerous hyperconjugative interactions, the C−C single bond lengths of D_{2d} COT and of *perp*-butadiene do *not* represent those of "pure" (i.e., unconjugated) C sp²−C sp² bonds. The neglect of "two-way" (double) hyperconjugation has serious consequen-

ces in interpreting the energies and geometries of COT, butadiene, biphenyl, and many other molecules with nonplanar equilibrium structures. Our paper in preparation addresses such examples in detail.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
NBO orbital deletion data of the conjugation and hyperconjugation interactions involved in the inversion of COT (Table S1) and the C−C bond rotation of 1,3-butadiene (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: schleyer@chem.uga.edu.

Notes
The authors declare no competing financial interest.

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(5) Compared to the parent D_{2d} minimum, the higher energies of D_{4h} and D_{8h} COT are due to the effects of ring strain. The much wider 135° CCC angles in planar D_{4h} and D_{8h} COT (but not the 126.5° in tub D_{2d} COT) deviate significantly from the CCC angles in appropriate hydrocarbon models (e.g., 125.1° in the allyl radical,

124.3° in C_{2h} butadiene, and 124.7° in propene). Pierrefixe and Bickelhaupt also noted that the H's are forced to be closer together in D_{4h} than in D_{2d} COT. See: Pierrefixe, S. C. A.; Bickelhaupt, F. M. *J. Phys. Chem. A* **2008**, *112*, 12816−12822. Despite the experimentally observed upfield ^{1}H chemical shifts of planar COT derivatives (δ = 3.6−4.6 ppm, compared to the parent D_{2d} COT δ = 5.68 ppm), the large positive NICS value at the ring center of D_{4h} COT, and its strong computed paratropic ring currents, estimates of the antiaromatic destabilization energy of D_{4h} COT based on molecular mechanics (See: Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* **1973**, *29*, 2519−2523. Roth, W. R.; Lennartz, H. W.; Vogel, E.; Leiendecker, M.; Oda, M. *Chem. Ber.* **1986**, *119*, 837−843.) and various isomerization reactions (See: Wannere, C. S.; Moran, D.; Allinger, N. L.; Hess, B. A. Jr.; Schaad, L. J.; Schleyer, P. v. R. *Org. Lett.* **2003**, *17*, 2983−2986. Schleyer, P. v. R.; Pühlhofer, F. *Org. Lett.* **2002**, *4*, 2873−2876. Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317−1331.) gave very small values (1− 3 kcal/mol). Allinger et al. found that the $D_{2d} \rightarrow D_{4h}$ COT inversion barrier was dominated by angle bending and an increase in van der Waals energy, and thus "there was no need to invoke 'anti-aromatic destabilization' of the planar D_{4h} TS" (See: Nevins, N.; Lii, J. H.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 695−729. Allinger, N. L. In *Molecular Structure: Understanding Steric and Electronic Effects From Molecular Mechanics*; John Wiley and Sons, Inc.: Hoboken, NJ, 2010; Chapter 5, pp 115−116.).

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(13) This is ca. 37.3 kcal/mol, based on the hyperconjugation stabilization of propene (5.5 kcal/mol, 44 kcal/mol for four *cis*-cyclooctenes) (See: Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R. *Chem.—Eur. J.* **2007**, *13*, 7731−7744 , for propene stabilization.) and the strain energies of *cis*-cyclooctene (6.0 kcal/mol), cyclooctane (10.3 kcal/mol), and COT (0) (See: Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419−2438). Equation 4 is an evaluation based on the experimental heats of formation of COT (71.13 kcal/mol, from http://cccbdb.nist.gov/), cyclooctane (−29.7 kcal/mol, from Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986), and *cis*-cyclooctene (−4.57 kcal/mol, from Schmitz, L. R.; Chen, Y. R. *J. Comput. Chem.* **1994**, *15*, 1437− 1445).

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