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Dominant Role of the π Framework in Cyclobutadiene

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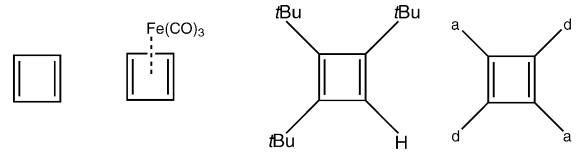
The extrinsic antiaromaticity of archetypal cyclobutadiene (CBD) is addressed with particular emphasis on the $\sigma-\pi$ separability problem. The destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ of CBD is obtained by appropriate homodesmotic reactions involving the open chain zigzag polyene(s). It is shown that $E(\mathrm{d})_{\mathrm{CBD}}$ does not depend on the electron correlation and the zero-point vibrational energy contributions, since they are small and of the opposite sign. Consequently, they cancel in the first approximation. Further, it turns out that $E(\mathrm{d})_{\mathrm{CBD}}$ can be estimated accurately enough with a very modest cc-pVDZ basis set at the Hartree−Fock (HF) level. The extrinsic antiaromatic destabilization $E(\mathrm{ean})_{\mathrm{CBD}}$ of CBD is deduced after extracting the angular strain energy estimated to be 32 kcal/mol. The resulting $E(\mathrm{ean})_{\mathrm{CBD}}$ value of 52 kcal/mol is in excellent agreement with the experimental thermodynamic data. If the $E(\mathrm{ean})_{\mathrm{CBD}}$ is estimated relative to two isolated C═C double bonds, then it assumes 38 kcal/mol, which is roughly 10 kcal/mol per one π electron. It is, therefore, safe to state that extrinsic antiaromaticity of CBD is larger than its angular strain. Although the σ and π electrons are coupled by a mutual Coulomb interaction $V_{\mathrm{ee}}^{\sigma\pi}$, several attempts of their decoupling is made by using three partitioning schemes: stockholder, equipartition, and standard π-electron theory recipe. The latter allocates the V_{nn} and $V_{\mathrm{ee}}^{\sigma\pi}$ terms to the σ- and π-electron frameworks, respectively. The nuclear repulsion term V_{nn} is dissected into σ and π components in the former two partitioning schemes by using stockholder criterion. It appears that the extrinsic antiaromatic destabilization $E(\mathrm{ean})_{\mathrm{CBD}}$ is determined by the π-electron framework according to all three partitioning models.

1. Introduction

The planar monocyclic $4n\pi$ annulene hydrocarbon systems were termed antiaromatic by Breslow[1] some forty years ago due to their extremely high reactivity and very low stability.[2] Indeed, it is very difficult to synthesize them and it took Herculean efforts of Pettit et al.[3] to prepare the first (CBD) system stabilized by complexation with iron tricarbonyl **2** (Scheme 1). This brilliant synthetic result was followed by preparation of the highly sterically protected CBD moiety by three tertiary butyl groups **3** by Masamune et al.[4] and production of some donor−acceptor (push−pull) substituted cyclobutadienes[5] as exemplified by **4** (Scheme 1), where "a" and "d" stand for COOEt and $\mathrm{N(Et)_2}$, respectively.

SCHEME 1



1 **2** **3** **4**

Further, the CBD fragment fused to large carbocycles[6] or to the aromatic benzene moiety like in benzo[1,2:4,5]dicyclobutadiene and [N]phenylenes[7] offered new insight into the interplay between the antiaromatic, nonaromatic, and aromatic bonding patterns. Finally, it appeared that a tandem of two CBD units provided essential building blocks in forming bridged superphanes, when complexed with the cobalt cyclopentadienyl fragments.[8] Evidently, the CBD ring serves as a versatile and interesting structural subunit possessing some extraordinary properties. A skillful experimental control of its reactivity has led to a large number of interesting molecular systems. Much of its chemistry and its theoretical description was reviewed recently.[9] CBD is a highly angularly strained compound, which is additionally destabilized by the 4π electrons according to the $4n\pi$ electron count (Hückel) rule.[10] It is, therefore, not unexpected that CBD triggered a longstanding discussion about the nature of its antiaromaticity. The early π-electron theories such as HMO[10] and Pariser−Parr−Pople[11] methods were in accordance with the idea of the inherent instability of the 4π electron cyclic network. On the other hand, some authors questioned the hypothesis of the intrinsically destabilizing effect of the 4π electrons.[12,13] In particular, Voter and Goddard[14] have shown by using the generalized resonating valence bond (GRVB) method that the transition structure (TS) of CBD had a delocalization energy of 21.8 kcal/mol compared to that of a single VB structure. This is compatible with our finding that the nondynamical π-electron correlation energy for the ground state (GS) and TS is $E(\mathrm{ND})_{\mathrm{GS}}^{\pi} = 42.8$ kcal/mol and $E(\mathrm{ND})_{\mathrm{TS}}^{\pi} =$ 64.8 kcal/mol, respectively, the difference being 22 kcal/mol. Since the corresponding dynamical correlation of the π electrons are 8.5 and 8.2 kcal/mol, respectively, it follows that the nondynamical π-electron correlation energy considerably stabilizes CBD in particular in its TS structure.[15] Our analysis performed at the HF level shows that the main reason for the

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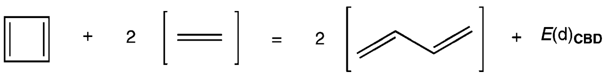
increase in energy in the transition state is due to a substantial increase in the nuclear repulsion term (by 43 kcal/mol), which is partially alleviated by a decrease in the electron−electron repulsion (by −16 kcal/mol). The energy of the TS is further diminished by the nondynamical correlation energy of 22 kcal/mol. Taking into account all energy terms including ZPVE contribution, one arrives at the TS energy barrier of 3.8 kcal/mol.[15] This is in good agreement with the experimental estimates.[16,17]

It is the aim of the present paper to shed more light on the role of σ and π electrons in determining antiaromaticity of CBD with particular emphasis on the $\sigma-\pi$ separability dilemma. For this purpose we shall examine the thermodynamic (energetic) data as a quantitative criterion of antiaromaticity, which can be utilized in two distinctly different ways. The first is given by enthalpies of hydrogenation of cyclobutene and CBD in a manner introduced by Kistiakowsky et al.[18] in studying the aromaticity of archetypal benzene. The other conceptual pathway is offered by the postulated homodesmotic reactions.[19] We shall adopt the latter approach, which compares the energetic decrease in stability of CBD relative to a linear zigzag polyene. In pursuing this goal, we shall examine the role of the electron correlation and show that antiaromaticity of CBD is essentially a consequence of its total Hartree−Fock energy. The latter will be analyzed in great detail and, anticipating forthcoming results, it can be said that antiaromaticity of CBD is a consequence of its π-electron features.

2. Theoretical Framework

The homodesmotic reaction quantitatively describing destabilization of the CBD ring system reads:



(1)

The destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ has two components: the angular strain $E(\mathrm{s})_{\mathrm{CBD}}$ and extrinsic antiaromaticity $E(\mathrm{ean})_{\mathrm{CBD}}$

$$E(\mathrm{d})_{\mathrm{CBD}} = E(\mathrm{s})_{\mathrm{CBD}} + E(\mathrm{ean})_{\mathrm{CBD}} \tag{2}$$

The extrinsic antiaromaticity is related to the fact that eq 1 implies the ring opening in *gedanken* reaction 1. It is contrasted with the intrinsic antiaromaticity $E(\mathrm{ian})_{\mathrm{CBD}}$ of the [4]-annulene, which is related to the rectangular ground-state geometry and its transformations to other planar structures, which preserve topology of the four-membered ring. This definition is analogous to the notions of intrinsic and extrinsic aromaticity of benzene.[15,20] This distinction is justified by the fact that intrinsic and extrinsic anti/aromaticities are caused by different energy terms implying that their physical origin is completely different. State of the art in the anti/aromaticity research is reflected to a great deal in a recent special issue of Chemical Reviews.[21] Let us focus on the $E(\mathrm{d})_{\mathrm{CBD}}$ defined by eq 1, which can be conveniently resolved into three components

$$E(\mathrm{d})_{\mathrm{CBD}} = E(\mathrm{HF})_{\mathrm{d}} + E(\mathrm{ND})^{\pi}_{\mathrm{d}} + E(\mathrm{D})^{\alpha}_{\mathrm{d}} + E(\mathrm{ZPV})_{\mathrm{d}} \tag{3}$$

where $E(\mathrm{HF})_{\mathrm{d}}$, $E(\mathrm{ND})^{\pi}_{\mathrm{d}}$, $E(\mathrm{D})^{\alpha}_{\mathrm{d}}$, and $E(\mathrm{ZPV})_{\mathrm{d}}$ signify the Hartree−Fock, the nondynamical π-electron correlation energy, and dynamical correlation energy, as well as the zero-point vibrational contribution, respectively. The superscript α stands for π and $(\pi) + \sigma$ corresponding to the π electron only or all valence $\sigma + \pi$ electrons dynamical correlation energy, respectively. Here, a label $(\pi) + \sigma$ denotes that the zeroth order wave function in the CASPT2 calculations is obtained by the CASSCF $(n, n)^{\pi}$ procedure as expounded below. It is important to keep in mind that all four energy components in eq 3 are obtained as a difference in the total energy of cyclobutadiene and two ethylenes against two *trans*-1,3-butadienes as required by eq 1. Generally, the Hartree−Fock (HF) energy has two contributions: $E(\mathrm{HF}) = E(\mathrm{HF})_{\mathrm{el}} + V_{\mathrm{nn}}$, where $E(\mathrm{HF})_{\mathrm{el}}$ and V_{nn} refer to the electronic energy and the nuclear repulsion, respectively. Assuming that the structural parameters are optimized at the HF level, we shall employ the virial theorem[22] stating that $E(\mathrm{HF}) = -E(\mathrm{T})_{\mathrm{HF}}$, where $E(\mathrm{T})_{\mathrm{HF}}$ denotes the kinetic energy of all electrons. It is well-known that the virial theorem holds for the exact HF wave functions and energies, or for approximate HF model provided all free parameters are optimized. However, in the case of approximate HF wave functions, e.g., due to the basis set incompleteness or unoptimized nonlinear parameters of atomic orbitals, one can stretch or compress coordinates of all electrons and nuclei by the scaling factor $\eta = -V(1)/2T(1)$, to restore the virial theorem.[23] The rectified kinetic and potential energies are $T(\eta) = \eta T(1)$ and $V(\eta) = \eta^2 V(1)$, respectively. Here, $T(1)$ and $V(1)$ denote the uncorrected kinetic and potential energies, respectively, obtained by the approximate HF wave function. In what follows, we shall employ corrected kinetic energy $T(\eta)$, which complies with the virial requirement. However, in doing so the stretching (or compressing) factor η will be dropped for the sake of simplicity.

Since the kinetic energy is a one-electron property, it can be rigorously separated into σ- and π-electron parts

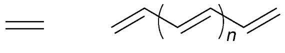
$$E(\mathrm{T})_{\mathrm{HF}} = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + E(\mathrm{T})^{\pi}_{\mathrm{HF}} \tag{4}$$

where $E(\mathrm{T})^{\sigma}_{\mathrm{HF}} = \sum_{i=1}^{\mathrm{occ}(\sigma)} 2\langle\psi_i|\nabla_i^2|\psi_i\rangle$ and $E(\mathrm{T})^{\pi}_{\mathrm{HF}} = \sum_{i=1}^{\mathrm{occ}(\pi)} 2\langle\psi_i|\nabla_i^2|\psi_i\rangle$.

Here the sums are extended over all doubly occupied σ-MOs and π-MOs, respectively. A distinct advantage of the kinetic energy over its potential energy counterpart is that a partitioning of the σ,π cross-terms and the nuclear repulsion V_{nn} is not necessary. They are implicitly included in the single electron MO kinetic energy terms in a disguised form. However, there are also some disadvantages because it would be erroneous to identify $-E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$ and $-E(\mathrm{T})^{\pi}_{\mathrm{HF}}$ kinetic energies with the total energy of the σ and π electrons of CBD, because the virial theorem does not hold separately for these two groups of electrons distinguished only by symmetry. This will be discussed in great detail later on. Next, we shall concentrate on the electron correlation effects. It is useful to discriminate between the nondynamical or static correlation energy, which is a consequence of the (pseudo)degenerate MO levels, and the dynamical correlation energy arising from the instantaneous relative positions of electrons in their permanent motion. The former will be calculated for the π electrons applying the complete active space (CASSCF) formalism.[24,25] The nondynamical component of the π-electron correlation is obtained by

$$E(\mathrm{ND})^{\pi} = E(\mathrm{HF}) - E(\mathrm{CASSCF}(n, n)^{\pi}) \tag{5}$$

where we define the correlation energy here and use it thereafter as a positive quantity for convenience, although it is intrinsically negative thus describing stabilization of the molecular systems. In formula 5, the numbers of active π electrons and active π-MOs are denoted by (n, n) in the same order. The dynamical correlation energy will be estimated by the second-order perturbation theory within the CASPT2 framework.[26,27] We shall



5 **6** - **13** for *n* = 0 - 7

Figure 1.

consider first the dynamical correlation energy of π electrons only according to

$$E(\mathrm{D})^{\pi} = E(\mathrm{CASSCF}(n, n)^{\pi}) - E(\mathrm{CASPT2}^{\pi}) \qquad (6)$$

where exclusively π electrons are involved in the PT2 procedure. In the second step, we shall include all valence σ and π electrons in the perturbational calculation. The corresponding dynamical correlation is denoted $E(\mathrm{D})^{(\pi)+\sigma}$ and is given by

$$E(\mathrm{D})^{(\pi)+\sigma} = E(\mathrm{CASSCF}(n, n)^{\pi}) - E(\mathrm{CASPT2}^{(\pi)+\sigma}) \quad (7)$$

In both cases the initial zeroth-order wave function is provided by the CAS SCF $(n, n)^{\pi}$ calculation. The choice of the basis set functions is very important. We shall make use of Dunning's correlation-consistent split-valence sets cc-pVLZ, where L denotes multiple zeta functions.[28] Dunning's basis sets introduce improvements in the total energy in a controlled manner, thus offering themselves for various extrapolation recipes in attempts to estimate the infinite basis set (IB) values.

A useful procedure in obtaining IB correlation energies applicable in large systems was proposed by Truhlar et al.,[29] which made possible employment of very efficient cc-pVDZ and cc-pVTZ basis sets without a significant loss in accuracy. Truhlar's approach was utilized in development of the additivity formulas for the π-electron correlation energy in planar systems.[30]

All calculations are carried out by using Gaussian 98,[31] MOLCAS[32] and MOLPRO[33] programs.

3. Results and Discussion

3.1. Linear Polyenes. Since the linear zigzag polyenes will serve as the nonaromatic set of reference compounds, let us consider them first. To test the additivity of Hartree−Fock kinetic energy components $E(\mathrm{T})^{\sigma}$, $E(\mathrm{T})^{\pi}$, and their sum $E(\mathrm{T})_{\mathrm{t}}$, where we dropped subscript HF for simplicity, the HF calculations have been carried out for systems **5**−**13** depicted in Figure 1 by optimizing their geometries and the obtained kinetic energies were fitted by bilinear relationships

$$E(\mathrm{T})^{\sigma} = k_{\mathrm{C}}^{\sigma} n_{\mathrm{C}} + k_{\mathrm{H}}^{\sigma} n_{\mathrm{H}} + \mathrm{const}_1 \qquad (8)$$

and

$$E(\mathrm{T})^{\pi} = k_{\mathrm{C(inn)}}^{\pi} n_{\mathrm{C(inn)}} + k_{\mathrm{C(out)}}^{\pi} n_{\mathrm{C(out)}} + \mathrm{const}_2 \qquad (9)$$

In formula 8, n_{C} and n_{H} denote numbers of C and H atoms in the polyene, respectively. The weighting parameters k_{C} and k_{H} describe the average σ contribution of each carbon and hydrogen atom, respectively, to the total HF energy. In considering the π part of the kinetic energy, we distinguish two types of carbon atoms: the inner (═CH─) and the outer (or terminal, ═CH$_2$) ones belonging to the ends of linear chains. These two carbon atoms represent two distinctly different structural groups. The quality of the extremely simple relations 8 and 9 is very high as evidenced by the data presented in Table 1. The results refer to cc-pVDZ and cc-pVTZ basis sets, since the use of larger sets is precluded in sizable polyenes such as **12** and **13**. It appears that the regression relation based on the number of C and H atoms vs the kinetic energy of polyenes is optimal ($R^2 = 1$). Further, the average absolute deviation (AAD) and the maximum absolute deviation (MAD) values of only 0.4 and 0.8 kcal/mol, respectively, found for both basis sets are more than satisfactory.

TABLE 1: Weighting Parameters Describing Several Kinds of the Average Atomic Kinetic Energies Entering Formulas 8 and 9 for the Set of Open Chain Linear Polyenes $C_{2n}H_{2n+2}$ Calculated within the Hartree−Fock Approximation (in a.u.)[a]

	$E(\mathrm{T})_{\mathrm{HF}}^{\sigma}$	$E(\mathrm{T})_{\mathrm{HF}}^{\pi}$	$E(\mathrm{T})_{\mathrm{HF}}^{\sigma}$	$E(\mathrm{T})_{\mathrm{HF}}^{\pi}$
atoms	cc-pVDZ		cc-pVTZ	
hydrogen				
k_{H}^{σ}	0.59550		0.60360	
carbon				
k_{C}^{σ}	36.85899		36.86075	
$k_{\mathrm{C(inn)}}^{\pi}$		0.99331		0.99316
$k_{\mathrm{C(out)}}^{\pi}$		0.96979		0.96398
AAD	0.4	0.3	0.3	0.3
MAD	0.7	0.8	0.7	0.8
R^2	1.00000	1.00000	1.00000	1.00000

[a] The average (AAD) and maximum absolute deviations (MAD) from the additivity are given in kcal/mol.

Finally, it appears that the additive constants in (8) and (9) are virtually zero, which is conceptually an important result. Whereas the additivity of the bond energies in polyenes was known for a long time since Dewar and Gleicher's pioneering paper in 1965 related to PPP and HMO methods,[34] the underlying additivity features of the π-electron correlation energies in polyenes were disclosed only recently.[15,35] The calculated $E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$, and $E(\mathrm{D})^{(\pi)+\sigma}$ correlation energies for polyenes **5**−**10** are displayed in Table 2. It will appear in what follows that the correlation energies and their various components ($E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$, etc.) are in fact additive for any basis set employed here including results referring to complete basis sets obtained by interpolation, thus indicating that this is a very persistent, robust and general characteristic of the electron correlation in polyenes. Since the $E(\mathrm{D})^{(\pi)+\sigma}$ dynamical correlation energies are obtained for the zeroth order CASSCF$^{\pi}$ wave function complemented by the second-order PT2 calculation including all valence $\pi + \sigma$ electrons, it follows that the total electron correlation for a particular polyene is given by

$$E(\mathrm{corr})_{\mathrm{t}} = E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma} \qquad (10)$$

The total valence electrons correlation energies are easily deduced from the data in Table 2 and therefore they are not explicitly presented. The additivity constants k appearing in formulas 11−13

$$E(\mathrm{ND})^{\pi} = k(\mathrm{ND})_{\mathrm{C(inn)}}^{\pi} n_{\mathrm{C(inn)}} + k(\mathrm{ND})_{\mathrm{C(out)}}^{\pi} n_{\mathrm{C(out)}} \qquad (11)$$

$$E(\mathrm{D})^{\pi} = k(\mathrm{D})_{\mathrm{C(inn)}}^{\pi} n_{\mathrm{C(inn)}} + k(\mathrm{D})_{\mathrm{C(out)}}^{\pi} n_{\mathrm{C(out)}} \qquad (12)$$

$$E(\mathrm{D})^{(\pi)+\sigma} = k(\mathrm{D})_{\mathrm{C}}^{(\pi)+\sigma} n_{\mathrm{C}} + k(\mathrm{D})_{\mathrm{H}}^{(\pi)+\sigma} n_{\mathrm{H}} \qquad (13)$$

are shown in Table 3. The set of molecules **5**−**10** is rather small, because the complexities in calculating $E(\mathrm{D})^{(\pi)+\sigma}$ increase very fast with the size of a polyene. Nevertheless, this set is sufficiently large for illustrative purposes, because it is well-known by now that the additivity concept works very well.[15,30,35] It is, therefore, not unexpected that performance of formulas (11−13) is excellent too (Table 3).

It is clear that the nondynamical correlation energy $E(\mathrm{ND})^{\pi}$ reflects properties of the π-MO manifold. The same holds for the π-electron dynamical correlation energies $E(\mathrm{D})^{\pi}$. In contrast, the dynamical correlation energy of σ and π electrons $E(\mathrm{D})^{(\pi)+\sigma}$ cannot be partitioned into σ and π components in a clear-cut

TABLE 2: Nondynamical and Dynamical Correlation Energies of π Electrons and the Dynamical Correlation Energies of All Valence Electrons for Zig-Zag Polyenes, Obtained in Same Order by CASSCF$^{\pi}$/bs//HF/bs, CASPT2$^{\pi}$/bs//HF/bs and CASPT2$^{(\pi)+\sigma}$/bs//HF/bs, where bs Stands for cc-pVDZ and cc-pVTZ Basis Sets[a]

basis set	cc-pVDZ			cc-pVTZ			IB		
energy	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$
ethylene	17.1	3.6	157.0	16.7	4.9	195.1	16.7	5.8	218.3
butadiene	33.5	9.1	304.4	32.7	12.0	377.2	32.7	13.9	421.4
hexatriene	49.9	14.7	452.1	48.8	19.3	559.6	48.8	22.2	624.8
octatetraene	66.4	20.4	600.0	64.8	26.7	742.2	64.9	30.6	828.3
decapentaene	82.7	26.1	747.9	81.3	34.1		81.4	39.0	
dodecahexaene	99.2	31.8	895.9	97.4			97.6		

[a] Energies obtained for the infinite basis sets are denoted by IB (in kcal/mol).

TABLE 3: Weighting Parameters Yielding the Average Atomic Correlation Energies Appearing in eqs (1−11), in kcal/mol

basis set	VDZ			VTZ			IB		
energy	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{D})^{(\pi)+\sigma}$
$k(\mathrm{ND})^{\pi}_{\mathrm{C(inn)}}$	8.21			8.08			8.10		
$k(\mathrm{ND})^{\pi}_{\mathrm{C(out)}}$	8.55			8.29			8.27		
$k(\mathrm{D})^{\pi}_{\mathrm{C(inn)}}$		2.82			3.66			4.16	
$k(\mathrm{D})^{\pi}_{\mathrm{C(out)}}$		1.75			2.39			2.84	
$k(\mathrm{D})^{(\pi)+\sigma}_{\mathrm{C}}$			69.43			84.89			94.25
$k(\mathrm{D})^{(\pi)+\sigma}_{\mathrm{H}}$			4.46			6.30			7.43
AAD	0.0	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
MAD	0.1	0.1	0.3	0.1	0.1	0.1	0.2	0.1	0.1
R^2	1.00000	0.99998	1.00000	0.99999	0.99996	1.00000	0.99999	0.99997	1.00000

TABLE 4: Various Contributions to the Antiaromatic Destabilization of Cyclobutadiene $E(\mathrm{d})_{\mathrm{CBD}}$ in kcal/mol, According to Homodesmotic Reaction 1[a]

basis set	$E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$	$E(\mathrm{T})^{\pi}_{\mathrm{HF}}$	$E(\mathrm{T})^{\mathrm{t}}_{\mathrm{HF}}$	$E(ND)^{\pi}$	$E(\mathrm{D})^{\pi}$	$E(\mathrm{corr})^{\pi}_{\mathrm{t}}$	$E(\mathrm{D})^{(\pi)+\sigma}$	$E(corr)_{\mathrm{t}}$	ZPVE	$E(\mathrm{d})_{\mathrm{CBD}}$
cc-pVDZ	−191.9	108.3	−83.6	−7.3	1.8	−5.5	3.8	−3.5	4.0	84.1
cc-pVTZ	−185.8	103.3	−82.5	−7.0	2.3	−4.7	3.9	−3.1	4.0	83.4
cc-pVQZ	−181.1	98.9	−82.2	−6.8	2.4	−4.4	4.1	−2.7	4.0	83.5
cc-pV5Z	−177.5	95.4	−82.0	−6.7			4.0	−2.7	4.0	83.3
cc-pV6Z	−176.6	94.6	−82.1						4.0	83.4
IB	−176.6	93.7	−82.9	−6.7			3.0	−2.7	4.0	84.4

[a] The electron correlation calculations for the cc-pV6Z basis set were not feasible, whereas the CASPT2 calculations for the cc-pV5Z did not converge. The total correlation energy $E(\mathrm{corr})_{\mathrm{t}}$ is given by $E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$.

way. Concomitantly, the same holds for for the total valence shell correlation energy $E(\mathrm{corr})_{\mathrm{t}} = E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$. However, this is not of particular significance for the interpretation of the antiaromaticity in CBD, as it will be shown in the next section. As a final comment let us mention that the inner-core electron correlation energies are not considered, since it was tacitly assumed that they are strictly additive thus canceling in eq 1. This assumption is plausible and the inner-shell electrons were frozen in the electron correlation calculations.

3.2. Cyclobutadiene. *3.2.1. Energetic Account.* The basis for quantitative thermodynamic estimate of antiaromaticity is provided by homodesmotic reaction 1. The energetic data are given in Table 4. Let us focus on some numerical aspects of the results. Perusal of the presented numbers shows that kinetic energy contribution $E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$ of the σ electrons to $E(\mathrm{ean})_{\mathrm{CBD}}$ is converged at the cc-pV6Z basis set. On the other hand, the kinetic energy of the π electrons is with this basis set still off by 1 kcal/mol. Further, it is well established by now that the nondynamical correlation energy is highly insensitive to the quality of the employed basis. Consequently, it is not surprising that $E(\mathrm{ND})^{\pi}$ contribution to $E(\mathrm{d})_{\mathrm{CBD}}$ is increasing in a very close range from −7.3 to −6.7 kcal/mol as the basis sets gain in flexibility in going from cc-pVDZ to cc-pV5Z functions. It is gratifying that a reasonable value is obtained already for a modest cc-pVTZ basis set. On the other hand, the dynamical correlation energy is extremely dependent on the basis set and yet the contributions of both $E(\mathrm{D})^{\pi}$ and $E(\mathrm{D})^{(\pi)+\sigma}$ energies to $E(\mathrm{d})_{\mathrm{CBD}}$ exhibit a remarkable insensitivity (Table 4), which is apparently a consequence of a very well balanced homodesmotic reaction 1 employed in studying antiaromaticity. As a result, the total correlation energy $E(\mathrm{corr})_{\mathrm{t}}$ increases rather slowly from −3.5 to −2.7 kcal/mol for basis sets extending from the cc-pVDZ to highly refined cc-pV5Z basis set, respectively. Similarly, the ZPVE is practically independent of the basis set, which is obviously a consequence of the very simple additivity property of this quantity.[36−38] It can be estimated quite accurately by the HF/cc-pVDZ model, if a customary scaling factor 0.89 for DZ basis functions is employed. This model is utilized here and the estimated contribution of ZPVE to the $E(\mathrm{d})_{\mathrm{CBD}}$ destabilization energy is 4 kcal/mol. It follows that a combined $E(\mathrm{corr})_{\mathrm{t}}$ + ZPVE effect on $E(\mathrm{d})_{\mathrm{CBD}}$ is rather small being in the range between 0.5 and 1.3 kcal/mol depending on the basis set used. In any case it can be safely concluded that the electron correlation and ZPVE contributions practically cancel in the first approximation. Hence, the first important corollary of the present calculation is that $E(\mathrm{d})_{\mathrm{CBD}}$ is determined by the HF energies of molecules involved in eq 1.

Further, the total kinetic energy $E(\mathrm{T})^{\mathrm{t}}_{\mathrm{HF}}$ is almost independent of the employed basis although its $E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$ and $E(\mathrm{T})^{\pi}_{\mathrm{HF}}$ components are strongly dependent on the basis functions. It is encouraging that very simple cc-pVDZ set yields $E(\mathrm{d})_{\mathrm{CBD}}$ value via the kinetic energy and virial theorem, which is only by 0.7 kcal/mol larger than the infinite basis set estimate. Moreover, the former value is by 0.8 kcal/mol lower than the IB estimate of $E(\mathrm{d})_{\mathrm{CBD}}$ including both $E(\mathrm{corr})_{\mathrm{t}}$ and *ZPVE* contribution implying that we can continue our analysis by focusing on the HF/cc-pVDZ results.

3.2.2. Role of the Potential Energy Terms. The virial theorem stating that $E(\mathrm{HF}) = -E(\mathrm{T})^{\mathrm{t}}_{\mathrm{HF}}$ means that all information about the interactions between the electrons, the nuclei and electrons and between the nuclei themselves given by the V_{ee}, V_{ne}, and V_{nn} terms, respectively, are included in the negative total kinetic energy. However, this information is hidden and in particular the kinetic energies $-E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$ and $-E(\mathrm{T})^{\pi}_{\mathrm{HF}}$ cannot help alone in discussing the relative roles of the σ- and π-electrons in determining the antiaromatic destabilization. Hence, we shall examine the total HF energy in a form

$$E(\mathrm{HF}) = E(\mathrm{T})^{\mathrm{t}}_{\mathrm{HF}} + V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{nn}} \tag{14}$$

The first potential energy term is easily resolved into σ and π components since $(1/r_{\mathrm{ne}})$ is one-electron operator yielding $V_{\mathrm{ne}} = V^{\sigma}_{\mathrm{ne}} + V^{\pi}_{\mathrm{ne}}$. In contrast, V_{ee} and V_{nn} involve two-electron and no-electron operators, respectively, and consequently cannot be dissected into σ and π contributions in an unequivocal way. Thus the highly desired $\sigma-\pi$ separability, discussed many times over decades, has no exact solution and the question is only whether there is an acceptable partitioning from the common sense point of view. Let us consider the electron repulsion term V_{ee} first

$$V_{\mathrm{ee}} = V^{\sigma\sigma}_{\mathrm{ee}} + V^{\pi\pi}_{\mathrm{ee}} + V^{\sigma\pi}_{\mathrm{ee}} \tag{15}$$

The σ and π electrons are coupled through their mutual Coulomb interaction term $V^{\sigma\pi}_{\mathrm{ee}}$. We notice that the number of σ electrons is always significantly higher than π electrons and intuitively one should apportion larger share of the $V^{\sigma\pi}_{\mathrm{ee}}$ term to the former subgroup of electrons. It is useful to invoke for that purpose the stockholder principle, which was introduced by Hirschfeld[39] in discussing the problem of the electron density of atoms in molecules. Following his idea, let us assume that we have two point charges Z_{A} and Z_{B}. Their Coulomb repulsion is given by

$$V = [Z_{\mathrm{A}}Z_{\mathrm{B}}/r_{\mathrm{AB}}] = V_{\mathrm{A}} + V_{\mathrm{B}} \tag{16}$$

which can be resolved in two contributions each proportional to the corresponding point charge. It is easily found that

$$V_{\mathrm{A}} = \zeta_{\mathrm{r}}(Z_{\mathrm{A}}/r_{\mathrm{AB}}) \text{ and } V_{\mathrm{B}} = \zeta_{\mathrm{r}}(Z_{\mathrm{B}}/r_{\mathrm{AB}}) \tag{17}$$

where $\zeta_{\mathrm{r}} = Z_{\mathrm{A}}Z_{\mathrm{B}}/(Z_{\mathrm{A}} + Z_{\mathrm{B}})$ is the reduced charge. Employing the stockholder criterion one can partition $V^{\sigma\pi}_{\mathrm{ee}}$ into two components

$$V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{sigma}) = (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{ee}} \text{ and } V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{pi}) = (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{ee}} \tag{18}$$

where n_{σ}, n_{π}, and N denote numbers of the σ and π electrons and their total number, respectively. Here and heretofore sigma and pi given within parentheses denote terms obtained by some decomposition scheme. Dissection of the nuclear repulsion term V_{nn} is an even more delicate problem, since it does not explicitly depend on electrons. However, the V_{nn} term is determined through the features of Born−Oppenheimer potential energy surface and hence depends implicitly on the distributions of both σ and π electrons. Starting from this point view one can establish one-to-one correspondence between each proton in the nucleus and an electron in a neutral atom. Since we consider CBD and some neutral linear hydrocarbons, we can apportion $5|e|$ and $1|e|$ positive charge to the σ and π nuclear charge components in each carbon atom, respectively. The hydrogen atom protons belong of course to the σ-framework. It is now easy to separate V_{nn} into three contributions $V_{\mathrm{nn}} = V^{\sigma\sigma}_{\mathrm{nn}} + V^{\pi\pi}_{\mathrm{nn}} + V^{\sigma\pi}_{\mathrm{nn}}$, where the self-repulsion within the same carbon nucleus is disregarded. By using the stockholder criterion one obtains

$$V^{\sigma\pi}_{\mathrm{nn}}(\mathrm{sigma}) = (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}} \text{ and } V^{\sigma\pi}_{\mathrm{nn}}(\mathrm{pi}) = (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}} \tag{19}$$

in full analogy with expression 18. Formulas 18 and 19 provide a basis for the stockholder partitioning scheme (S).

The second possibility is offered by fifty-fifty partitioning of the $V^{\sigma\pi}_{\mathrm{ee}}$ term implying that $V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{sigma}) = V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{pi}) = (1/2)V^{\sigma\pi}_{\mathrm{ee}}$. The nuclear term could be separated in the same way, but we would prefer to retain the stockholder principle for Coulomb repulsion between the nuclei, since it is much more realistic. This forms the second or the so-called equipartitioning scheme (eqp).

Finally, we shall examine the standard partitioning (st) as it was used in the early theories of the π-electronic structure of the planar molecules.[11] This means that the Coulomb repulsion $V^{\sigma\pi}_{\mathrm{ee}}$ is attached to the π-electrons and V_{nn} is completely associated to the σ framework.

It follows that, by using a specific partitioning scheme (ps), it is possible to write the total HF energy in a form

$$E(\mathrm{HF}) = E^{\sigma}_{\mathrm{HF}}(\mathrm{ps}) + E^{\pi}_{\mathrm{HF}}(\mathrm{ps}) \tag{20}$$

where

$$E^{\sigma}_{\mathrm{HF}} = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + V^{\sigma}_{\mathrm{ne}} + V^{\sigma\sigma}_{\mathrm{ee}} + V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{sigma}) + V^{\sigma\sigma}_{\mathrm{nn}} + V^{\sigma\pi}_{\mathrm{nn}}(\mathrm{sigma}) \tag{21}$$

and

$$E^{\pi}_{\mathrm{HF}} = E(\mathrm{T})^{\pi}_{\mathrm{HF}} + V^{\pi}_{\mathrm{ne}} + V^{\pi\pi}_{\mathrm{ee}} + V^{\sigma\pi}_{\mathrm{ee}}(\mathrm{pi}) + V^{\pi\pi}_{\mathrm{nn}} + V^{\sigma\pi}_{\mathrm{nn}}(\mathrm{pi}) \tag{22}$$

which holds for the stockholder and equipartition schemes. In the standard π-electron theory model, we have

$$E^{\sigma}_{\mathrm{HF}} = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + V^{\sigma}_{\mathrm{ne}} + V^{\sigma\sigma}_{\mathrm{ee}} + V_{\mathrm{nn}} \tag{23}$$

and

$$E^{\pi}_{\mathrm{HF}} = E(\mathrm{T})^{\pi}_{\mathrm{HF}} + V^{\pi}_{\mathrm{ne}} + V^{\pi\pi}_{\mathrm{ee}} + V^{\sigma\pi}_{\mathrm{ee}} \tag{24}$$

Another interesting possibility is given by the molecular orbital energies, which are mutually clearly distinguished by the σ and π symmetry. Unfortunately, the sum of MO energies is not equal to the total molecular energy

$$E(\mathrm{HF}) = 2\sum_{i=1}^{\mathrm{occ}}\epsilon_i - V_{\mathrm{ee}} + V_{\mathrm{nn}} \tag{25}$$

where i denotes MO and summation is extended over doubly occupied levels. Since we would like to work with scaled wave functions satisfying virial theorem, the corresponding expression reads

$$E(\mathrm{HF})_{\eta} = (2\sum_{i=1}^{\mathrm{occ}}\epsilon_i - E(\mathrm{T})_{\mathrm{HF}})\eta + (E(\mathrm{T})_{\mathrm{HF}})\eta^2 - V_{\mathrm{ee}}\eta + V_{\mathrm{nn}}\eta \tag{26}$$

After the proper scaling is performed, the V_{ee} and V_{nn} terms have to be broken down by stockholder, equipartition or standard

TABLE 5: Scaled Values of the σ and π Contributions to the Total Hartree−Fock Energy of Ethylene, Butadiene, and Cyclobutadiene (in a.u.) and Their Participation in the Destabilization Energy $E(\mathrm{d})_{\mathrm{CBD}}$ (in kcal/mol)[a,b,c]

	cc-pVDZ			cc-pVTZ			$\Delta E(\mathrm{d})_{\mathrm{CBD}}$	
energy	ethylene	butadiene	CBD	ethylene	butadiene	CBD	cc-pVDZ	cc-pVTZ
$E(\mathrm{T})^{\sigma}_{\mathrm{HF}}$	76.10052	151.01005	149.51328	76.13541	151.06577	149.56455	−191.9	−185.8
$E(\mathrm{T})^{\pi}_{\mathrm{HF}}$	1.93969	3.92497	4.14314	1.92901	3.91303	4.13272	108.3	103.3
V^{σ}_{ne}	−232.87868	−526.02940	−512.84656	−233.36107	−527.17546	−513.94118	46092.9	46239.0
V^{π}_{ne}	−15.57667	−42.37382	−43.76151	−15.55955	−42.41022	−43.80953	6170.1	6207.1
$V^{\sigma\sigma}_{\mathrm{ee}}$	46.38920	119.31487	113.78523	46.60432	119.82970	114.27611	−20121.5	−20189.6
$V^{\pi\pi}_{\mathrm{ee}}$	0.44953	1.73034	1.96508	0.44651	1.72687	1.96211	−374.3	−375.6
$V^{\sigma\pi}_{\mathrm{ee}}$	11.98478	33.45378	34.18010	11.97669	33.49453	34.23045	−5495.6	−5525.3
$(n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{ee}}$	10.48668	28.99328	29.29723	10.47960	29.02859	29.34039	−4841.8	−4867.9
$(n_{\pi}/N)V^{\sigma\pi}_{\mathrm{ee}}$	1.49810	4.46050	4.88287	1.49709	4.46594	4.89006	−653.8	−657.4
$V^{\sigma\sigma}_{\mathrm{nn}}$	26.17994	78.48246	73.00959	26.34981	78.90042	73.40244	−19826.2	−19891.0
$V^{\pi\pi}_{\mathrm{nn}}$	0.40089	1.73119	1.99106	0.40273	1.73861	1.99982	−420.1	−421.6
$V^{\sigma\pi}_{\mathrm{nn}}$	6.97060	23.82057	24.36419	7.01172	23.93795	24.48525	−5858.2	−5877.9
$(n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}}$	6.09928	20.64449	20.88359	6.13526	20.74622	20.98736	−5149.8	−5167.2
$(n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}}$	0.87132	3.17608	3.48060	0.87647	3.19173	3.49789	−708.4	−710.7
V_{nn}	33.55143	104.03422	99.36483	33.76425	104.57698	99.88750	−26104.5	−26190.6
$E^{\sigma}_{\mathrm{orb}}$[b]	−52.01500	−102.93583	−101.58274	−52.04033	−102.95574	−101.59400	162.5	148.6
E^{π}_{orb}[b]	−0.75316	−1.53440	−1.50809	−0.76082	−1.54891	−1.52213	34.1	33.9
(1) $E^{\sigma}_{\mathrm{HF}}(\mathrm{S})$	−67.62306	−127.58424	−126.35764	−67.65667	−127.60476	−126.37033	−4038.1	−4062.5
(1) $E^{\pi}_{\mathrm{HF}}(\mathrm{S})$	−10.41713	−27.35074	−27.29876	−10.40774	−27.37404	−27.32693	4121.7	4145.1
(2) $E^{\sigma}_{\mathrm{HF}}(\mathrm{eqp})$	−72.11735	−139.85064	−138.56482	−72.14792	−139.88608	−138.59549	−1944.1	−1957.3
(2) $E^{\pi}_{\mathrm{HF}}(\mathrm{eqp})$	−5.92284	−15.08435	−15.09158	−5.91648	−15.09271	−15.10176	2027.7	2039.8
(3) $E^{\sigma}(\mathrm{st})$	−76.83755	−151.67026	−150.18322	−76.85709	−151.70299	−150.21302	−324.9	−327.0
(3) $E^{\pi}(\mathrm{st})$	−1.20269	−3.26474	−3.47319	−1.20733	−3.27578	−3.48425	408.5	409.5

[a] The sigma and pi contributions are obtained by using the following recipes: (1) $E^{\sigma}_{\mathrm{HF}}(\mathrm{S}) = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + V^{\sigma}_{\mathrm{ne}} + V^{\sigma\sigma}_{\mathrm{ee}} + (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{ee}} + V^{\sigma\sigma}_{\mathrm{nn}} + (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}} = E^{\sigma}_{\mathrm{orb}} - V^{\sigma\sigma}_{\mathrm{ee}} - (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{ee}} + V^{\sigma\sigma}_{\mathrm{nn}} + (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}}$; $E^{\pi}_{\mathrm{HF}}(\mathrm{S}) = E(\mathrm{T})^{\pi}_{\mathrm{HF}} + V^{\pi}_{\mathrm{ne}} + V^{\pi\pi}_{\mathrm{ee}} + (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{ee}} + V^{\pi\pi}_{\mathrm{nn}} + (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}} = E^{\pi}_{\mathrm{orb}} - V^{\pi\pi}_{\mathrm{ee}} - (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{ee}} + V^{\pi\pi}_{\mathrm{nn}} + (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}}$. (2) $E^{\sigma}_{\mathrm{HF}}(\mathrm{eqp}) = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + V^{\sigma}_{\mathrm{ne}} + V^{\sigma\sigma}_{\mathrm{ee}} + (1/2)(V^{\sigma\pi}_{\mathrm{ee}}) + V^{\sigma\sigma}_{\mathrm{nn}} + (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}} = E^{\sigma}_{\mathrm{orb}} - V^{\sigma\sigma}_{\mathrm{ee}} - (1/2)V^{\sigma\pi}_{\mathrm{ee}} + V^{\sigma\sigma}_{\mathrm{nn}} + (n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{nn}}$; $E^{\pi}_{\mathrm{HF}}(\mathrm{eqp}) = E(\mathrm{T})^{\pi}_{\mathrm{HF}} + V^{\pi}_{\mathrm{ne}} + V^{\pi\pi}_{\mathrm{ee}} + (1/2)(V^{\sigma\pi}_{\mathrm{ee}}) + V^{\pi\pi}_{\mathrm{nn}} + (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}} = E^{\pi}_{\mathrm{orb}} - V^{\pi\pi}_{\mathrm{ee}} - (1/2)V^{\sigma\pi}_{\mathrm{ee}} + V^{\pi\pi}_{\mathrm{nn}} + (n_{\pi}/N)V^{\sigma\pi}_{\mathrm{nn}}$. (3) $E^{\sigma}_{\mathrm{HF}}(\mathrm{st}) = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + V^{\sigma}_{\mathrm{ne}} + V^{\sigma\sigma}_{\mathrm{ee}} + V_{\mathrm{nn}} = E^{\sigma}_{\mathrm{orb}} - V^{\sigma\sigma}_{\mathrm{ee}} - V^{\sigma\pi}_{\mathrm{ee}} + V_{\mathrm{nn}}$; $E^{\pi}_{\mathrm{HF}}(\mathrm{st}) = E(\mathrm{T})^{\pi}_{\mathrm{HF}} + V^{\pi}_{\mathrm{ne}} + V^{\pi\pi}_{\mathrm{ee}} + V^{\sigma\pi}_{\mathrm{ee}} = E^{\pi}_{\mathrm{orb}} - V^{\pi\pi}_{\mathrm{ee}}$. [b] $E^{\sigma}_{\mathrm{orb}}$ and E^{π}_{orb} stand for sums of the energies of occupied MO, where $E^{\sigma}_{\mathrm{orb}} = 2\sum_{i=1}^{\mathrm{occ}(\sigma)}\epsilon_i$, and $E^{\pi}_{\mathrm{orb}} = 2\sum_{i=1}^{\mathrm{occ}(\pi)}\epsilon_i$. [c] A contribution of the particular energy component to the destabilization energy of CBD is given under heading $\Delta E(\mathrm{d})_{\mathrm{CBD}}$.

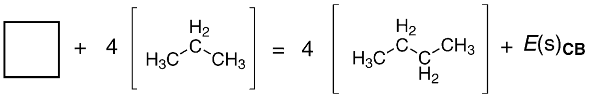
scheme as defined above. It is apparent that the E(HF) total energy given by the formula 25 becomes identical to expression 20, if the same partitioning scheme is employed.

Results obtained by described analysis are summarized in Table 5. Perusal of data presented in Table 5 offers a number of interesting conclusions. First, it is obvious that the final $E(\mathrm{d})_{\mathrm{CBD}}$ values defined by eq 1 do not depend on the adopted partitioning recipe. They assume 83.6 and 82.5 kcal/mol for cc-pVDZ and cc-pVTZ HF calculations, respectively. It should be mentioned that the resulting destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ is a difference of several very large numbers. For example, it turns out that the electron repulsion is a very strong stabilizing factor in CBD as evidenced by −20121.5, −4841.8, and −2747.8 kcal/mol values for $V^{\sigma\sigma}_{\mathrm{ee}}$, $(n_{\sigma}/N)V^{\sigma\pi}_{\mathrm{ee}}$, and $(1/2)V^{\sigma\pi}_{\mathrm{ee}}$ terms, respectively, as obtained by the HF/cc-pVDZ model. Coulomb repulsion between the π-electrons is much smaller in its absolute value $V^{\pi\pi}_{\mathrm{ee}} = -374.3$ kcal/mol. Nevertheless, it appreciably stabilizes CBD too. The same holds for the $(n_{\pi}/N)V^{\sigma\pi}_{\mathrm{ee}}$ which assumes a value −653.8 kcal/mol. Therefore, a claim of some researchers that antiaromaticity of CBD is caused by the "overlap repulsion" between two localized vis-á-vis π bonds in rectangular cyclobutadiene is unjustified. It is also important to notice that the nuclear repulsion V_{nn} is highly favorable in CBD relative to open chain polyene. The Coulomb attraction V_{ne} between the nuclei and electrons is on the other hand the main reason behind a considerably decreased stability of CBD as illustrated by $V^{\sigma}_{\mathrm{ne}} = 46092.9$ and $V^{\pi}_{\mathrm{ne}} = 6170.1$ (in kcal/mol) with an additional positive contribution of the kinetic energy of π-electrons (108.3 kcal/mol). A very high V_{ne} contribution to $E(\mathrm{d})_{\mathrm{CBD}}$ is partly a consequence of long C−C bonds and considerable bending of the σ-electron density around the ring perimeter, which decreases the overlap charge between the bonded nuclei. It is useful to notice that the total kinetic energy $E(\mathrm{T})_{\mathrm{HF}} = E(\mathrm{T})^{\sigma}_{\mathrm{HF}} + E(\mathrm{T})^{\pi}_{\mathrm{HF}}$ has a stabilizing effect due to the predominating influence of the σ-electrons. However, a conclusion based solely on the virial theorem and the corresponding kinetic energies $E(\mathrm{HF}) = -E(\mathrm{T})^{\sigma}_{\mathrm{HF}} - E(\mathrm{T})^{\pi}_{\mathrm{HF}}$ that the σ-framework is responsible for destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ would be completely wrong (vide infra).

One of the most striking conclusions is that all three partitioning schemes (stockholder, equipartition and standard) show that destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ occurs because of the π-electron framework. The σ-framework stabilizes CBD but to a lesser extent by some 84 kcal/mol. Hence, the π-electron framework prevails, which results in a low stability of this extremely interesting molecule. Furthermore, it turns out that the one-electron MO picture is misleading for at least two reasons. Both $E^{\sigma}_{\mathrm{orb}}$ and E^{π}_{orb} contribute to the destabilization energy of CBD, the σ-share being almost 5 times larger. Their sum $E^{\sigma}_{\mathrm{orb}} + E^{\pi}_{\mathrm{orb}} = 196.6$ kcal/mol grossly overestimates $E(\mathrm{d})_{\mathrm{CBD}}$ implying that simple orbital schemes such as HMO and EHT methods or standard π-MO theories cannot perform better. Therefore, it should be kept in mind that if the one-particle MO schemes give good results, they are for the wrong reasons. It is also noteworthy that a difference between $E^{\pi}_{\mathrm{orb}}(\mathrm{CBD}) - 2E^{\pi}_{\mathrm{orb}}(\mathrm{ethylene}) = -1.1$ kcal/mol meaning that

CBD would be more stable than the two isolated π-bonds in ethylene by 1 kcal/mol as far as π-MOs are concerned.

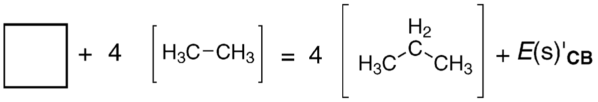
To estimate the antiaromatic destabilization energy $E(\mathrm{ean})_{\mathrm{CBD}}$ one has to have at hand a good assessment of the angular strain in CBD. For this purpose we carried out the HF/cc-pVDZ calculation for homodesmotic reaction which yields $E(\mathrm{s})_{\mathrm{CB}} =$


(27)

26.8 kcal/mol as the angular strain energy of cyclobutane. It is of interest to dissect $E(\mathrm{s})_{\mathrm{CB}}$ into separate contributions of the kinetic and potential energies

$$E(\mathrm{s})_{\mathrm{CB}} = \Delta E(\mathrm{T}) + \Delta V \tag{28}$$

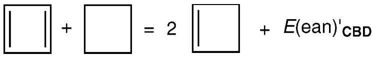
It appears that the total kinetic energy stabilizes cyclobutane (CB) just as in the case of CBD (Table 5), because $\Delta E(\mathrm{T}) = -26.5$ kcal/mol, whereas $\Delta V = 53.3$ kcal/mol shows that it is the potential energy, which determines the strain yielding $E(\mathrm{s})_{\mathbf{CB}} = 26.8$ kcal/mol. Resolution of ΔV into three components $\Delta V_{\mathrm{ee}} + \Delta V_{\mathrm{nn}} + \Delta V_{\mathrm{ne}}$ clearly shows that the strain energy of CB arises due to the unfavorable nucleus-electron attraction ΔV_{ne}, since $\Delta V_{\mathrm{ee}} = -40839.1$, $\Delta V_{\mathrm{nn}} = -40824.0$, and $\Delta V_{\mathrm{ne}} = 81716.4$ kcal/mol. This is analogous to the conclusion obtained earlier for the total destabilization energy of CBD, since a highly unfavorable V_{ne} term was the main reason for destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ (vide supra). It should be mentioned in this respect that the origin of the angular strain energy in other small rings is also a decreased nuclear-electron attraction implying that it is a general feature.[40] A related homodesmotic reaction


(29)

gives almost the same result $E(\mathrm{s})'_{\mathrm{CB}} = 26.8$ kcal/mol with $\Delta T = -26.5$ and $\Delta V = 53.3$ kcal/mol. This finding is encouraging, because it shows that the angular strain energy is not dependent on the choice of the homodesmotic reaction.

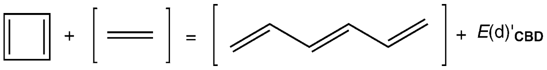
The problem is that the strain energy in unsaturated CBD is larger than that in saturated cyclobutane because the bond bending in the former molecule is larger.[41] To get an idea about it, let us consider the heats of hydrogenation of cyclohexene and cyclobutene. The experimental estimates are -28.3 and -30.7 kcal/mol the difference being 2.5 kcal/mol, which corresponds to a strain energy release in going from cyclobutene to cyclobutane.[42] One concludes that the strain energy in CBD is approximately higher than that in CB by some 5 kcal/mol. This gives for $E(\mathrm{s})_{\mathrm{CBD}}$ about 31.8 kcal/mol. This estimate is in excellent agreement with the experimental result 32 ± 2 kcal/mol as reported by Deniz et al.[43] Taking $E(\mathrm{s})_{\mathrm{CBD}}$ energy into account one obtains for extrinsic antiaromatic destabilization $E(\mathrm{ean})_{\mathrm{CBD}} = 51.8$ kcal/mol in accordance with the experimental study of Deniz et al.,[43] which gave 55 ± 11 kcal/mol, which unfortunately has a large error margin. It should be mentioned that this estimate of antiaromaticity is derived by assuming that the delocalization energy of π-electrons in *trans*-1,3-butadiene is negligible. This is not the case as shown by Carreira[44] by determining experimentally the torsional potential of *trans*-1,3-butadiene. It is 7 kcal/mol implying that the extrinsic aromaticity of cyclobutadiene is 38 kcal/mol. This result is in good accordance with the earlier G2 calculations of Glukhovtsev et al.,[45] which gave $E(\mathrm{ean})_{\mathrm{CBD}} = 40.6$ kcal/mol by using localized C=C bonds as a reference level. It is, therefore, safe to conclude that the antiaromaticity is larger than the angular strain in CBD.

It is worth noting that the present estimate of the antiaromatic destabilization $E(\mathrm{ean})_{\mathrm{CBD}}$ is obtained indirectly by calculating the strain energy first. One could try to determine $E(\mathrm{ean})_{\mathrm{CBD}}$ directly by utilizing homodesmotic reaction 30 It is obvious


(30)

that reaction 30 is very well strain balanced implying that $E(\mathrm{ean})'_{\mathrm{CBD}}$ should reproduce antiaromaticity of CBD rather closely. This is indeed the case since $E(\mathrm{ean})'_{\mathrm{CBD}} = 38.1$ kcal/mol as calculated by HF/cc-pVDZ model, which is in harmony with the estimate given above. It should be kept in mind, however, that both lines of thought rest on an assumption that the angular strain in CBD is twice that in cyclobutene.

As a final remark we would like to mention that alternative homodesmotic reaction for CBD involving a larger open chain all trans polyene gives $E(\mathrm{d})'_{\mathrm{CBD}} = 84.0$ kcal/mol for the HF/


(31)

cc-pVDZ model calculations thus proving the point that the choice of a homodesmotic reaction based on zigzag polyenes is not crucial and that it does not affect the final conclusions. This is not surprising in view of the additivity of the HF energies of linear polyenes. Namely, both homodesmotic reactions 1 and 31 can be reduced to

$$E(\mathrm{HF})_{\mathrm{CBD}} + 4(k^{\sigma}_{\mathrm{C}} + k^{\pi}_{\mathrm{C(inn)}} + k^{\sigma}_{\mathrm{H}}) = E(\mathrm{d})_{\mathrm{CBD}} \tag{32}$$

The HF energies for CBD obtained by cc-pVDZ and cc-pVTZ basis sets are -153.65641 and -153.69727 (in a.u.), respectively. Substitution of the weighting factors taken from the Table 1 gives for $E(\mathrm{d})_{\mathrm{CBD}}$ 84.6 and 83.3 kcal/mol for cc-pVDZ and cc-pVTZ basis sets, respectively. This is in good agreement with full HF calculations of $E(\mathrm{d})_{\mathrm{CBD}}$ for eqs 1 and 31, being 83.6 and 84.0 kcal/mol, respectively.

A relatively large strain energy contribution to $E(\mathrm{d})_{\mathrm{CBD}}$ is seemingly in contradiction with earlier conclusion that the total destabilization energy in CBD is a consequence of the π-electron framework. In fact, if the strain energy $E(\mathrm{s})_{\mathrm{CBD}}$ were absent, then the contribution of the V^{σ}_{ne} term to $E(\mathrm{d})_{\mathrm{CBD}}$ would be lower by that amount, since it is the unfavorable V_{ne} attraction, which makes small rings angularly strained (viz. eqs 27 and 28). As a consequence, E^{σ}_{HF} component would be more negative by that amount and the total destabilization energy $E(\mathrm{d})_{\mathrm{CBD}}$ would be reduced to $E(\mathrm{ean})_{\mathrm{CBD}}$ term only. It is important to bear in mind that both components of the total destabilization energy $E(\mathrm{s})_{\mathrm{CBD}}$ and $E(\mathrm{ean})_{\mathrm{CBD}}$ are consequence of the highly unfavorable V_{ne} term.

4. Concluding Remarks

We have conclusively shown that the extrinsic antiaromatic destabilization of CBD could be conveniently retrieved by homodesmotic reaction(s) relating the target cyclobutadiene system to the open chain zigzag polyene(s). The $E(\mathrm{d})_{\mathrm{CBD}}$ destabilization energy can be calculated at the HF/cc-pVDZ level, since the contribution of the correlation energy and *ZPVE* are relatively small and of the opposite sign. Hence, they can be disregarded in the first approximation. It is shown that $E(\mathrm{d})_{\mathrm{CBD}}$, its strain energy component $E(\mathrm{s})_{\mathrm{CBD}}$ and extrinsic antiaromaticity $E(\mathrm{ean})_{\mathrm{CBD}}$ do not depend on the choice of the homodesmotic reactions based on zigzag polyenes or by using strain-balanced reaction such as (30). Further, although σ- and π-electron interactions cannot be unambiguously separated into σ and π contributions, there are several partitioning schemes which include the stockholder, equipartition and standard π-electron theory criteria, enabling dissection of the total molecular energy into σ and π components. The stockholder principle seems to be the most acceptable one. All three of them, however, strongly indicate that extrinsic antiaromaticity of CBD arises because of the features of its π-electron framework. Our best estimate of the antiaromaticity per π electron is close to 10 kcal/mol. It is also important to point out that antiaromaticity of CBD is larger than its angular strain energy.

It is of interest to compare our findings with results of Shaik et al.,[46] who considered intrinsic antiaromaticity of CBD. According to their analysis CBD in its square TS structure is π distortive, whereas the opposite holds for the σ framework. In principle, this is not contradictory with the present results, because extrinsic and instrinsic antiaromaticity have completely different origin.[15] Another point of interest is given by the fact that extrinsic aromaticity of archetypal benzene is a consequence of its σ framework as shown recently.[20]

Finally, it is found that the one-electron MO picture cannot offer a satisfactory description of antiaromaticity, since both the σ-MOs and π-MOs energies contribute to $E(\mathrm{d})_{\mathrm{CBD}}$ with an overwhelming influence of the σ electrons. The total destabilization energy is grossly exaggerated if the MO one-electron picture is not rectified with the $-V_{\mathrm{ee}} + V_{\mathrm{nn}}$ terms. The π electron only MO approximation significantly underestimates $E(\mathrm{d})_{\mathrm{CBD}}$ energy yielding 34.1 and 33.9 kcal/mol by the HF model employing cc-pVDZ and cc-pVTZ basis set, respectively. In addition, the π-electron picture is unsatisfactory, because it cannot describe the angular strain of the σ framework.

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References and Notes

(1) Breslow, R. *Chem. Eng. News* **1965**, 43.

(2) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(3) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131.

(4) Masamune, S.; Nakamura, N.; Suda, M.; Ona, A. *J. Am. Chem. Soc.* **1973**, *95*, 8481.

(5) Gommper, R.; Holsboer, F.; Schmidt, W.; Seybold, G. *J. Am. Chem. Soc.* **1973**, *95*, 8479.

(6) Kipling, H.; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932.

(7) Toda, F.; Ohi, M. *J. Chem. Soc. Chem. Commun.* **1975**, 506. Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153.

(8) Gleiter, R.; Kratz, D. *Acc. Chem. Res.* **1993**, *26*, 311 and references therein.

(9) Eckert-Maksić, M.; Maksić, Z. B. In *The Chemistry of Cyclobutanes*; Rappoport, Z., Liebman, J. F., Eds.; John Wilay & Sons, Ltd.: Chicester, in print.

(10) Heilbronner, E.; Bock, H. *Das HMO—Modell und seine Anwendung*, 2 Auflage; Verlag Chemie: Weinheim, Germany, 1978.

(11) Parr, R. G. *Quantum Theory of Molecular Electronic Structure*; W. A. Benjamin Inc.: New York, 1963.

(12) Murray, J. S.; Seminario, J. M.; Politzer, P. *Int. J. Quantum Chem.* **1994**, *49*, 575.

(13) Bauld, N. L.; Welsher, T. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920.

(14) Voter, A. F.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 2830.

(15) Maksić, Z. B.; Barić, D.; Petanjek, I. *J. Phys. Chem. A* **2000**, *104*, 10873.

(16) Meier, G.; Wolf, R.; Kalinowski, H. O. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 738.

(17) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473. Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

(18) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 137.

(19) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. *Tetrahedron* **1976**, *32*, 313; *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222. George, P.; Trachtman, M.; Brett, A.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. George, P.; Bock, C. W.; Trachtman, M. *J. Chem. Educ.* **1984**, *61*, 225.

(20) Kovačević, B.; Barić, D.; Maksić, Z. B.; Müller, Th. *ChemPhysChem*, in print.

(21) Schleyer, P. v. R., Guest Editor; *Chem. Rev.* **2001**, *101*, No. 5, pp. 1115−1566.

(22) Fock, V. *Z. Physik*. **1930**, *63*, 855. Slater, J. C. *J. Chem. Phys.* **1933**, *1*, 687.

(23) Löwdin, P. O. *J. Mol. Spectry.* **1959**, *3*, 46.

(24) Ruedenberg, K.; Cheung, L. M.; Elbert, S. T. *Int. J. Quantum Chem.* **1979**, *16*, 1069.

(25) Roos, B. O. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 175.

(26) Andersson, K.; Malmquist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(27) Andersson, K.; Malmquist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(28) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**,*90*, 1007.

(29) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45. Feas, P. L.; Sánches, M. L.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *111*, 2921.

(30) Smith, D. M.; Barić, D.; Maksić, Z. B. *J. Chem. Phys.* **2001**, *115*, 3474. Barić D.; Maksić, Z. B. *J. Phys. Chem. A* **2002**, *106*, 1612.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(32) *MOLCAS*, version 4; Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmquist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O.; Lund University: Sweden, 1997.

(33) *MOLPRO*, version 2000.1; Werner, H.-J.; Knowles, P. J.; Lindh, R.; Ryu, U.; Liu, B. *J. Chem. Phys.* **1991** *95* 5889. Schütz, M.; Lindh, R.; Werner, H.-J. *Mol. Phys.* **1999**, *96*, 719. Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985** *115*, 259. Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645.

(34) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 692.

(35) Maksić, Z. B.; Smith, D. M.; Barić, D. *Chem. Phys.* **2001**, *269*, 11.

(36) Schulman J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

(37) Ibrahim, M. R.; Fataftah, Z. A. *Chem. Phys. Lett.* **1986**, *125*, 149.

(38) Barić, D.; Maksić, Z. B.; Vianello, R. *J. Mol. Struct. (THEOCHEM)* **2003**, *672*, 201.

(39) Hirschfeld, F. L. *Theor. Chim. Acta* **1997**, *44*, 129.

(40) Barić, D.; Maksić, Z. B. *Theor. Chem. Acc.*, in print.

(41) Maksić, Z. B.; Kovačević, K.; Eckert-Maksić, M. *Tetr. Lett.* **1975**, 101.

(42) Slayden, S. W.; Liebman, J. F. *Chem. Rev.* **2001**, *101*, 1541.

(43) Deniz, A. A.; Peters K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119.

(44) Carreira, L. A. *J. Chem. Phys.* **1975**, *62*, 3851.

(45) Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1995**, *99*, 6828.

(46) Shaik, S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. A. Chem. Soc.* **1987**, *109*, 363. Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501. Hiberty, P. C.; Ohanessian, G.; Shaik, S.; Flament, J. P. *Pure and Appl. Chem.* **1993**, *65*, 35.