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On the Correlation Energy of π-Electrons in Planar Hydrocarbons

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We considered the nondynamical $E(\mathrm{ND})^{\pi}$ and dynamical $E(\mathrm{D})^{\pi}$ correlation energies of π electrons in a wide variety of planar hydrocarbons. The former could be conveniently calculated within the CASSCF formalism by using modest basis sets. The dynamical part of the correlation energy was studied with the CASPT2 method. It appeared that $E(\mathrm{D})^{\pi}$ was sensitive to the basis set. It is also found that the ab initio $E(\mathrm{ND})^{\pi}$ and $E(\mathrm{D})^{\pi}$ values follow very simple additivity rules, which allow fairly good estimates of the nondynamical and dynamical correlation effects of π electrons simply by counting the carbon and hydrogen atoms. Small deviations from the additivity of $E(\mathrm{D})^{\pi}$ are found in benzene (2.1 kcal/mol), naphthalene (3.3 kcal/mol), and cyclobutadiene (−3.0 kcal/mol), indicating that some care has to be exercised in applying the additivity rules to (anti)aromatic molecules. Nondynamical correlation $E(\mathrm{ND})^{\pi}$ exhibits even more pronounced deviations from the additivity in the systems characterized by a π-electron delocalization larger than that in linear polyenes. A novel electrostatics + correlation interpretation of (anti)aromaticity is introduced which sheds new light on an old but central problem of chemistry. It is also suggested that endo- and exoaromaticity should be distinguished. An interesting result of the present calculations is that the Hartree−Fock electron−electron (V_{ee}) interactions and the nondynamical correlation are much more favorable in cyclobutadiene's (CBD's) transition structure (TS) than in its ground state (GS). It appears, however, that the overwhelming effect in the CBD(TS) is an increase in the nuclear repulsion (V_{nn}), which is higher by 86.8 kcal/mol than in the GS. Consequently, the propensity of CBD to assume a rectangular geometry in the GS occurs inter alia because of a dramatic relief in the nuclear repulsion. The opposite is the case in the GS of benzene, where the dominating V_{ne} in the regular hexagon prevails over an increase in V_{ee} and V_{nn} repulsions caused by the D_{6h} formation. Intriguing and counterintutitive results are obtained by comparing the $E(\mathrm{ND})^{\pi}$ of the CBD(GS) and benzene with those of corresponding linear polyenes. The $E(\mathrm{ND})^{\pi}$ of the CBD(GS) is higher by 8 kcal/mol than that of the 1,3-butadiene, whereas the $E(\mathrm{ND})^{\pi}$ of benzene is lower by 5.7 than that of hexatriene (in kcal/mol). The (anti)aromatic (de)stabilization of CBD and benzene relative to 1,3-butadiene is 40.7 and 28.4 kcal/mol, respectively. The V_{ne} attraction in both compounds is appreciably higher (i.e., less favorable) than that in the reference molecule, 1,3-butadiene. However, this is overcompensated in benzene by more advantageous V_{ee} and V_{nn} terms, but it is not the case for CBD. This difference makes benzene exoaromatic and CBD exoantiaromatic.

1. Introduction

The electron correlation energy of molecular systems was, and still is, one of the most serious bottlenecks to the chemical accuracy of computational quantum chemistry. Operationally, the correlation energy $E(\mathrm{corr})$ was defined by Löwdin as the difference between the exact nonrelativistic energy $E(\mathrm{exact})_{\mathrm{NR}}$ and Hartree−Fock (HF) energy $E(\mathrm{HF})_{\mathrm{L}}$ obtained through the complete basis set

$$E(\mathrm{corr}) = E(\mathrm{exact})_{\mathrm{NR}} - E(\mathrm{HF})_{\mathrm{L}} \qquad (1)$$

where index L denotes the basis set limit.[1]

There currently exists a variety of methods suitable for tackling the correlation problem, including configuration interaction (CI), multireference configuration interaction (MRCI), and the coupled-cluster (CC) procedures.[2] Although very good estimates of correlation energy are possible in small and medium size molecules, relatively little is known about its interpretation in simple chemical terms. An important step in this direction was the observation that correlation energy can be resolved into two contributions differing in nature: nondynamical $E(\mathrm{ND})$ and dynamical $E(\mathrm{D})$, as first put forward by Sinanoğlu.[3] The former occurs from the degeneracy or near-degeneracy of the SCF one-electron energy levels in the system under consideration. Since degeneracy is related to the symmetry, $E(\mathrm{ND})$ reflects the properties of the whole molecular system. It is, as a rule, a result of a strong mixing of the initial Hartree−Fock configuration with low-lying excited states. Concomitantly, it is expected that $E(\mathrm{ND})$ could be convergent within the first order of configuration interaction (CI). In contrast, dynamical correlation arises due to tight inner-shell electron pairs, localized covalent bonds, and other such factors, thus making dynamical correlation local in nature. However, there is not just one configuration or only a few configurations in the CI expansion to mix strongly with the initial HF wave function. Indeed, there are very many

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TABLE 1: Dependence of the Total Correlation Energy E(corr) (in kcal/mol) of Ethylene and Its Nondynamical and Dynamical Components E(ND) and E(D) on the Size of Basis Sets and the Selection of Active Space

	active space of π-electrons (2,2)			active space of σ-electrons (10,10)			active space of all $\sigma + \pi$ electrons (12,12)		
basis set	$E(\text{corr})^{\pi}$	$E(\text{ND})^{\pi}$	$E(\text{D})^{\pi}$	$E(\text{corr})^{\sigma}$	$E(\text{ND})^{\sigma}$	$E(\text{D})^{\sigma}$	$E(\text{corr})^{\sigma+\pi}$	$E(\text{ND})^{\sigma+\pi}$	$E(\text{D})^{\sigma+\pi}$
B1	21.2	17.7	3.5	109.8	53.6	56.2	178.9	88.1	90.8
B2	21.6	17.4	4.2	123.8	56.3	67.5	199.3	89.9	109.4
B3	22.3	17.3	5.0	140.2	56.8	83.4	223.2	90.2	133.0
B4	22.5	17.3	5.2	142.3	56.9	85.4	226.2	90.3	135.9

configurations, which in turn are weakly coupled, implying a very slow convergence.[4] The nondynamical correlation energy can be conveniently taken into account by using the multiconfigurational SCF(MCSCF) method employing a complete active space (CAS) in the configuration mixing procedure (CASSCF).[5,6] The dynamical part of the correlation energy E(D) can be approximately estimated with the second-order perturbation theory employing CASSCF wave function as a starting point (CASPT2).[7,8] The total electronic energy within the CASPT2 approximation can be decomposed into the HF energy, the nondynamical correlation energy E(ND), and the dynamical correlation energy E(D)

$$E(\text{CASPT2}) = E(\text{HF}) + E(\text{ND}) + E(\text{D}) \tag{2}$$

where

$$E(\text{ND}) = E(\text{CASSCF}) - E(\text{HF}) \tag{3}$$

and

$$E(\text{D}) = E(\text{CASPT2}) - E(\text{CASSCF}) \tag{4}$$

Consequently, the total electron correlation within the adopted framework is given by

$$E(\text{corr}) = E(\text{ND}) + E(\text{D}) \tag{5}$$

implying that it approaches the rigorous definition of the correlation energy according to eq 1 as long as E(CASPT2) offers a good approximation of the exact nonrelativistic energy $E(\text{exact})_{\text{NR}}$. We shall assume that the latter holds at least as a working hypothesis and then try to examine E(ND) and E(D) correlation energies in a number of widely differing planar hydrocarbons to find the rules governing their variation. Anticipating forthcoming results, we can say that both the dynamical and nondynamical correlation energies of π-electrons exhibit a simple additivity property in linear polyenes. The deviation from additivity in other planar π-electron hydrocarbons leads to some interesting conclusions. In particular, it will become clear that the nondynamical correlation energy shows some features which differ from common ideas about anti/aromaticity. Ultimately, we shall show that antiaromaticity and aromaticity have a common root. It will also become clear that an interplay of V_{ne}, V_{ee}, and V_{nn} interactions makes one compound aromatic and the other antiaromatic. Finally, we employed the 6-31G* basis set in the geometry optimization and a number of correlation-adapted atomic natural orbital (ANO) basis sets[9,10] in the final single-point CASSCF and CASPT2 calculations. It is important to stress that to better separate various contributions to the energy, we executed the CASPT2 calculations by keeping all the non-CAS active electrons frozen. MOLCAS,[11] GAUSSIAN,[12] and GAMESS[13] programs were utilized in this work.

2. Results and Discussion

2.1. Ethylene. We consider ethylene **1** as the smallest possible π-electron hydrocarbon in our examination of the sensitivity of the HF and correlation energies to the selection of complete active space and the quality of basis sets. For this purpose, we shall optimize the geometry at the CAS(2,2)/6-31G* level and perform a series of single-point calculations employing CAS$(2,2)^{\pi}$, CAS$(10,10)^{\sigma}$, and CAS$(12,12)^{\sigma+\pi}$ active spaces (superscripts refer to all π, all σ, and all σ+π MO valence levels, respectively). Several ANO basis sets of increasing intricacy and flexibility have been utilized. They are specified in a shorthand notation as follows: B1 = ANO (3s2p1d,2s1p), B2 = ANO (4s3p2d,3s2p), B3 = ANO (5s4p3d2f,3s2p1d), and B4 = ANO (7s6p4d3f,3s2p1d). An additional basis set is used in the case of CBD (vide infra). The results are summarized in Table 1 and depicted in Figure 1. The latter illustrates the dependence of HF energy on the quality of the basis set. The depicted curve indicates that the ANO (7s6p4d3f,3s2p1d) set is close to the HF limit. The data in Table 1 offer some interesting conclusions. It appears that for CAS$(2,2)^{\pi}$/Bn (n = 1−4) formalism, both SCF and PT2 calculations, encompassing only π-MOs in the active space, recover just a small fraction of the total correlation energy. The numerical values of the correlation energy are given as positive numbers for the sake of convenience. It appears that $E(\text{ND})^{\pi}$ is highly insensitive to the applied basis set. In contrast, the $E(\text{D})^{\pi}$ calculated within the CASPT2 formalism does depend quite strongly on the quality of the employed set. The same holds for the total correlation energy $E(\text{corr})^{\pi}$. The inclusion of σ-electrons and disregard of π-electrons in the correlation calculations of CAS$(10,10)^{\sigma}$/Bn yield a dramatic increase in the correlation energy, since five "localized" σ-bonds are now explicitly taken into account. Interestingly, $E(\text{D})^{\sigma}$ becomes larger than $E(\text{ND})^{\sigma}$. Furthermore, $E(\text{D})^{\sigma}$ is strongly dependent on the basis set. It is

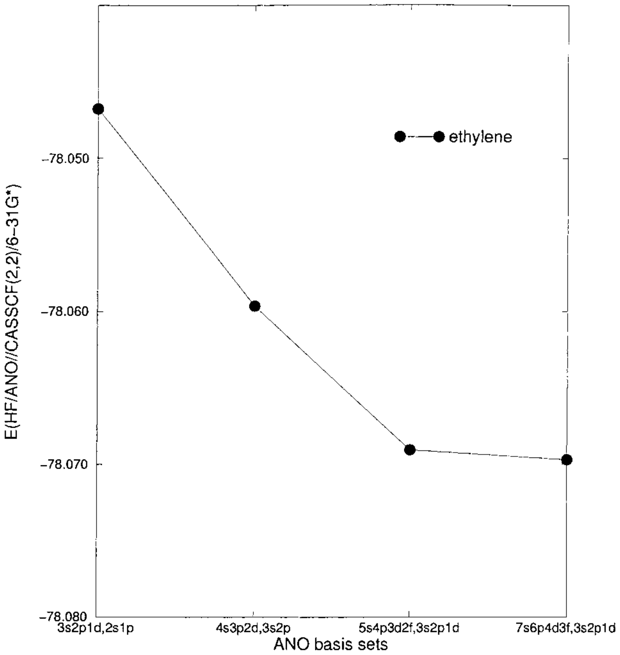


Figure 1. Dependence of the HF energy of ethylene on the quality of basis sets.

TABLE 2: Dependence of the Energy (in kcal/mol) of the Correlated Motion between σ- and π-electrons in Ethylene on the Choice of the Basis Set[a]

basis set	$\Delta E(\mathrm{corr})^{\sigma*\pi}$	$\Delta E(\mathrm{ND})^{\sigma*\pi}$	$\Delta E(\mathrm{D})^{\sigma*\pi}$	$\delta E(\mathrm{HF})$
B1	47.9	16.8	31.1	0
B2	53.9	16.2	37.7	−8.1
B3	60.7	16.1	44.6	−14.0
B4	61.4	16.1	45.3	−14.4

[a] $\delta E(\mathrm{HF})$ is change in HF energy upon an increase in the basis set flexibility: $\delta E(\mathrm{HF}) = E(\mathrm{B}n)_{\mathrm{HF}} - E(\mathrm{B1})_{\mathrm{HF}}$, $n = 2-4$.

reasonable to expect, however, that the B4 basis set offers a reliable dynamical correlation energy $E(\mathrm{D})^{\sigma}$ at the CASPT2 level. One should also point out that $E(\mathrm{ND})^{\sigma}$ is again fairly insensitive to the basis sets, which holds for CAS$(12,12)^{\sigma+\pi}$ calculations of the nondynamical correlation, too. It is interesting to compare the nondynamical energy obtained at the CAS$(12,12)^{\sigma+\pi}$ level with the results of the summation of CAS$(2,2)^{\pi}$ and CAS$(10,10)^{\sigma}$ nondynamical energies, where σ- and π-electrons are separately treated. Namely, the difference in nondynamical energy $\Delta E(\mathrm{ND})^{\pi*\sigma}$

$$\Delta E(\mathrm{ND})^{\pi*\sigma} = E[\mathrm{CAS}(12,12)^{\sigma+\pi}] - E[\mathrm{CAS}(2,2)^{\pi}] - E[\mathrm{CAS}(10,10)^{\sigma}] \quad (6)$$

gives an estimate of the nondynamical correlation energy between σ- and π-electrons. Analogous expressions hold for $\Delta E(\mathrm{corr})^{\pi*\sigma}$ and $\Delta E(\mathrm{D})^{\pi*\sigma}$. The corresponding information is displayed in Table 2 for basis sets Bn ($n = 1-4$). Once again, the nondynamical correlation energy is practically independent of the chosen basis set. This is not unexpected due to the insensitivity of the CASSCFF$(2,2)^{\pi}$, CASSCF$(10,10)^{\sigma}$, and CASSCF$(12,12)^{\sigma+\pi}$ contributions to the ND$^{\sigma*\pi}$ correlation energy.

The nondynamical correlation between σ- and π-electrons is almost equal to that of π-electrons only (Tables 1 and 2), which is, of course, fortuitous. The dynamical correlation $\Delta E(\mathrm{D})^{\pi*\sigma}$ and, concomitantly, the $\Delta E(\mathrm{corr})^{\pi*\sigma}$ energy depend rather strongly on the basis sets, as expected. The results suggest that the B4 set is close to convergence in the correlation calculations, as was the case in the HF model (Table 2).

To summarize this case study, we can say that both $E(\mathrm{ND})$ and $E(\mathrm{D})$ depend naturally on the choice of the active space. However, once the active space is selected, $E(\mathrm{ND})$ can be retrieved within the CASSCF formalism even with a modest basis set. On the contrary, $E(\mathrm{D})$ is sensitive to the flexibility of the basis set, particularly if σ-electrons are explicitly taken into account. $E(\mathrm{D})$ is estimated only at the second-order perturbation CASPT2 level of theory, implying that a portion of dynamical correlation energy remains unrecovered. Although the B4 basis set should be preferred, it seems that reasonable results can also be obtained through a more economical B3 basis set with a relatively small sacrifice in accuracy. More work in this respect would be necessary before the final conclusion could be reached.

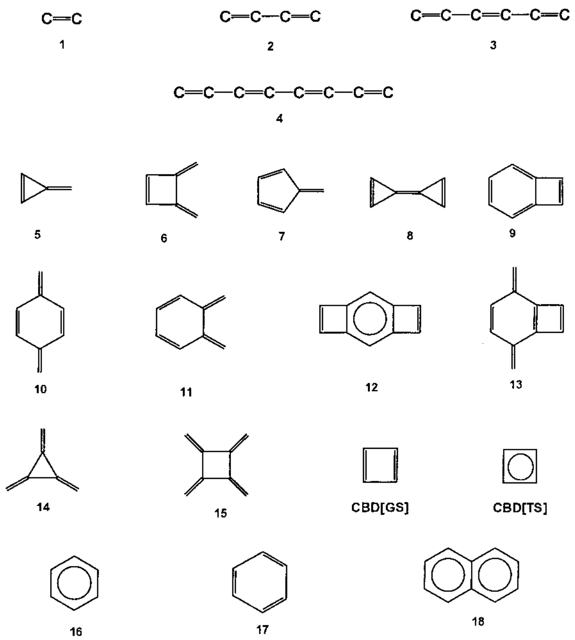


Figure 2. Schematic representation of the planar π-systems studied in this paper.

2.2. π-Electron Correlation Energy in Polyenes and Some Related Planar Hydrocarbons. In this section, we discuss extended π-systems encompassing linear polyenes as well as some cyclic and polycyclic planar hydrocarbons. We shall consider first the correlation energy of polyenes. It would be desirable to perform CASSCF and CASPT2 calculations by selecting very large active spaces and employing the B4 (or at least the B3) basis set. Unfortunately, this is precluded in sizable systems for practical reasons. Consequently, we have to confine our active space to π-MOs and π-electrons, utilizing only the modest B1 basis set. Although our calculated correlation energies thus correspond only to a rather small fraction of the total correlation energy, some interesting conclusions pertinent to π-electrons will emerge. The examined π-systems are depicted in Figure 2. They are all identified as true minima on the potential energy hypersurfaces (PEHs) computed within the adopted CAS scheme encompassing the $(n/2)$ highest-occupied and $(n/2)$ lowest-unoccupied π-MOs populated by all (n) π-electrons (CASSCF$(n,n)^{\pi}$ formalism). The 6-31G* basis set was utilized in all geometry optimizations. The ANO (3s2p1d,2s1p) basis set (B1) was used in the final CASSCF and CASPT2 single-point calculations. The results are displayed in Table 3. We focus first on the nondynamical correlation of linear polyenes. We can easily check that the $E(\mathrm{ND})^{\pi}$ of linear polyenes **1**−**4** is linearly related to the number of carbon and hydrogen atoms

$$E(\mathrm{ND})^{\pi}_{\mathrm{add}} = 8.09n_{\mathrm{C}} + 0.38n_{\mathrm{H}}\ (\mathrm{kcal/mol}) \quad (7)$$

This linear least-squares fit equation perfectly reproduces $E(\mathrm{ND})^{\pi}$ with a correlation coefficient $R = 0.99\dot{9}$. It is interesting to note that the additive constant is zero. The influence of the hydrogen atoms, arising from the 1p polarization function, is significantly smaller than that of carbons. Equation 7 will be used to estimate $E(\mathrm{ND})^{\pi}$ in other planar systems which, in most cases, possess well-localized π-bonds (Table 3). Deviations of the calculated nondynamical correlation energies from the additivity indicate a departure from the electronic structure pattern given by linear polyenes. In particular, it is possible to interpret $E(\mathrm{ND})^{\pi}$ as corresponding to the electronic resonance interaction in a broad sense, and thus, dramatic differences could be expected in benzene, naphthalene, and the transition structure (TS) of cyclobutadiene (GS). The results show that systems with perpendicular arrangement of endo and exo bonds in **5** and **8** have nondynamical energies lower than those of their linear counterparts. This agrees with the finding of Radom et al.[14] that these two molecules are destabilized by π-interactions. The regular behavior of **6** and **7** shows that they exhibit features of “classical” polyenes. Radialenes **14** and **15** also possess $E(\mathrm{ND})^{\pi}$ values close to those of linear polyenes **3** and **4**, respectively. More specifically, these compounds are slightly more stable than predicted by eq 7. It is interesting to note that the π-bonds in **9**

TABLE 3: Partitioning of the Correlation Energy $E(\mathrm{corr})^\pi$ (in kcal/mol) of π-electrons in Polyenes and Some Related Planar Hydrocarbons into $E(\mathrm{ND})^\pi$ and $E(\mathrm{D})^\pi$ Components[a]

molecule	$E(\mathrm{ND})^\pi$	$E(\mathrm{D})^\pi$	$E(\mathrm{corr})^\pi$	$E(\mathrm{ND})^\pi_{\mathrm{add}}$	$E(\mathrm{D})^\pi_{\mathrm{add}}$	$E(\mathrm{corr})^\pi_{\mathrm{add}}$	$\delta E(\mathrm{ND})^\pi$	$\delta E(\mathrm{D})^\pi$
1	17.7	3.5	21.2	17.7	3.4	21.1	0.0	0.1
2	34.6	9.1	43.7	34.6	9.2	43.8	0.0	−0.1
3	51.5	14.9	66.4	51.5	15.0	66.5	0.0	−0.1
4	68.5	20.8	89.3	68.5	20.7	89.2	0.0	0.1
5	28.8	10.7	39.5	33.9	11.5	45.4	−5.1	−0.8
6	51.1	16.2	67.3	50.8	17.3	68.1	0.3	−1.1
7	51.5	16.8	68.3	50.8	17.3	68.1	0.7	−0.5
8	46.0	17.2	63.2	50.1	19.6	69.7	−4.1	−2.4
9	67.0	25.0	92.0	67.0	25.4	92.4	0.0	−0.4
10	69.3	23.0	92.3	67.8	23.0	90.8	1.5	0.0
11	70.9	22.6	93.5	67.8	23.0	90.8	3.1	−0.4
12	92.0	31.7	123.7	83.2	33.5	116.7	8.8	−1.8
13	95.6	29.4	125.0	83.9	31.2	115.1	11.7	−1.8
14	52.9	15.8	68.7	50.8	17.3	68.1	2.1	−1.5
15	71.2	21.1	92.3	67.8	23.0	90.8	3.4	−1.9
16	45.6	19.4	65.0	50.8	17.3	68.1	−5.2	2.1
17	45.4	18.6	64.0	50.8	17.3	68.1	−5.4	1.3
18	77.2	34.5	111.7	83.9	31.2	115.1	−6.7	3.3
CBD(GS)	42.8	8.5	51.3	33.9	11.5	45.4	8.9	−3.0
CBD(TS)	64.8	8.2	73.0	33.9	11.5	45.4	30.9	−3.3

[a] As obtained by CASSCF(n,n)/B1 and CASPT2(n,n)/B1 single-point calculations utilizing CASSCF(n,n)/6-31G* optimized geometries. They are compared to the corresponding values provided by the additivity formulas eqs 7−9. Here, (n,n) denotes numbers of active π-electrons and π-orbitals, respectively. A difference in the correlation energies obtained by ab initio calculation and additivity formula is signified by δ.

behave as if they were localized in the manner indicated in Figure 2. Also, **11** has a $E(\mathrm{ND})^\pi$ higher by 1.6 kcal/mol than that of its ortho isomer, **10**. The additivity rule, however, cannot distinguish such a fine difference when predicting the ND correlation energy (67.8 kcal/mol). Many more systems need to be examined before a refinement of formula 7 is attempted, which could discriminate closely related isomers. The most striking finding, however, is that the $E(\mathrm{ND})^\pi$ in cyclobutadiene CBD(GS) is significantly higher (by 8 kcal/mol) than that in 1,3-butadiene, **2**. The deviation from the additivity rule of the former is 9 kcal/mol. This is astonishing at first sight, given the Hückel theory arguments and the fact that CBD(GS) is a very unstable and reactive compound. Hence, we could intuitively expect $E(\mathrm{ND})^\pi$, on the basis of its correspondence to the electronic resonance interaction in a broad sense, to be lower in CBD(GS) than in its open-chain counterpart. Apparently, this is not the case. There is no perfect localization of electrons, and the so-called highly localized π-bonds in CBD(GS) do interact indeed in a strong stabilizing fashion. Some authors have already expressed their doubts that 4π electrons within the four-membered ring are in fact an intrinsic destabilizing factor per se. Rather, it was argued that CBD is less stable than the sum of its acyclic fragments.[15,16] We shall address this question later. For the time being, we note that CBD(TS) in its lowest $^1B_{1g}$ state has 4π fully delocalized electrons and D_{4h} symmetry possessing substantially increased $E(\mathrm{ND})^\pi$ relative to the ground-state CBD(TS) (by 22 kcal/mol). This is compatible with the fact that CBD(TS) cannot be successfully described with a single configuration.[17,18] Moreover, Voter and Goddard[18] have shown by using the generalized resonating valence bond (GRVB) method that CBD(TS) has a delocalization energy of 21.8 kcal/mol relative to that of a single valence bond structure, thus agreeing with our present result. The fact that Voter and Goddard used somewhat different basis sets is of no significance because $E(\mathrm{ND})$ is insensitive to the quality of basis sets (vide supra). Obviously, scepticism regarding an intrinsic instability of 4π electrons is vindicated, since their cyclic delocalization leads to a substantial gain in (nondynamical correlation) energy. The reason behind such a large increase in $E(\mathrm{ND})$ is a consequance of the very definition of the correlation energy as a deviation from the HF energy. The HF approximation is not even qualitatively correct for CBD(TS). More specifically, the HF wave function has broken C_s symmetry. Another counterintuitive result is obtained for benzene **16** and its hypothetical D_{3h} localized structure **17**. In constructing the structurally frozen 1,3,5-cyclohexatriene skeleton **17**, we employed CC distances of the pure sp^2-sp^2 single bond in cyclooctatetraene and the double bond in ethylene, which assume values of 1.460 Å and 1.339 Å, respectively.[19] An intriguing point is that the open-chain polyene **3** has a $E(\mathrm{ND})^\pi$ higher than those of both **16** and **17** by some 6 kcal/mol. The “localized” structure of **17** has practically the same $E(\mathrm{ND})^\pi$ as that of fully relaxed benzene, indicating that the geometrically “localized” π-bonds are heavily mixed and correlated, like those in CBD(GS) considered earlier. It follows as a corollary that bond distances cannot be used as a measure of the localization of π-bonds, implying their complete isolation. In other words, even if the π-electron density were more concentrated in some CC bonds than in interpolated bonds, their interaction would be quite substantial.

Whereas $E(\mathrm{ND})^\pi$ is well-reproduced by the modest B1 basis set, the dynamical part of $E(\mathrm{D})^\pi$ requires larger and more flexible basis sets. Nevertheless, we shall employ the same B1 set in CASPT2 perturbation calculations within the same active space to obtain a broad picture of the variation of $E(\mathrm{D})^\pi$ and, ultimately, of the total π-electron correlation in planar hydrocarbons. The dynamical correlation energies of π-electrons in Table 3 are linear functions of the number of carbon and hydrogen atoms. The least-squares fit method for linear polyenes yields

$$E(\mathrm{D})^\pi_{\mathrm{add}} = 4.06\, n_{\mathrm{C}} - 1.18\, n_{\mathrm{H}} \text{ (kcal/mol)} \tag{8}$$

where n_{C} and n_{H} denote the numbers of carbon and hydrogen atoms, respectively. A high correlativity of the numbers of C and H atoms with $E(\mathrm{D})^\pi$ values is reflected in a large correlation coefficient, $k = 0.999$, and a low average absolute deviation, $\Delta E(\mathrm{D})^\pi_{av} = 0.1$ kcal/mol. The performance of the simple additivity rule is surprisingly good. It could be further improved by enlarging the set of gauge molecules in the linear fitting procedure, since deviations from the ab initio values are systematically of the same sign with very few exceptions. This is not attempted, however, because our focus will be exactly

TABLE 4: Energies of CBD(GS) and CBD(TS) (in kcal/mol)[a]

basis set	state	HF	δ(HF)	CASSCF	δ(CASSCF)	CASPT2	δ(CASPT2)	$E(\mathrm{ND})^\pi$	$\delta E(\mathrm{ND})^\pi$	$E(\mathrm{D})^\pi$	$\delta E(\mathrm{D})^\pi$
B1	GS	−153.66530	–	−153.73353	–	−153.74704	–	42.8	–	8.5	–
	TS	−153.61961	28.7	−153.72285	6.7	−153.73592	7.0	64.8	22.0	8.2	−0.3
B2	GS	−153.68315	–	−153.75106	–	−153.76725	–	42.6	–	10.2	–
	TS	−153.63661	29.2	−153.73945	7.3	−153.75482	7.8	64.5	21.9	9.7	−0.5
B5	GS	−153.68646	–	−153.75428	–	−153.77125	–	42.6	–	10.6	–
	TS	−153.63970	29.3	−153.74242	7.4	−153.75850	8.0	64.5	21.9	10.1	−0.5

[a] As obtained by single-point calculations employing the HF model and CASSCF(4,4) and CASPT2(4,4) methods utilizing the B1, B2, and B5 basis sets. Structural parameters were obtained by CASSCF(4,4)/6−31G* optimization. Total energies in au. Differences δ relative to GS for various basis sets are given in kcal/mol. It should be kept in mind that $E(\mathrm{D})^\pi$ is defined as a positive entity, i.e., it is multiplied by −1.

on these differences. They are negligible for linear polyenes and other well-localized systems such as **7**, **10**, and **11**. In contrast, significant deviations are observed for CBD, benzene, and naphthalene (±2−3 kcal/mol). These deviations are much smaller, however, than might be intuitively expected. Remarkably, the additivity formula predicts larger a $E(\mathrm{D})^\pi$ for CBD than with the more reliable CASPT2 method, which is compatible with the traditional concept of antiaromatic destabilization. Since $E(\mathrm{D})^\pi$ significantly increases with the flexibility of the basis sets, this feature should be carefully examined with more advanced calculations in the future. Clearly, the dynamical correlation behaves in a manner diametrically opposite to the nondynamical correlation. We note in passing, however, that CBD(GS) and CBD(TS) have practically the same dynamical correlation energies of π-electrons, contrary to their nondynamical correlation $E(\mathrm{ND})^\pi$. This is not surprising because unlike the HF model, both the CASSCF and CASPT2 methods treat the GS and TS of CBD equally. Apparently, $E(\mathrm{D})^\pi$ conforms to the additivity rule to a much greater extent. Similarly, the actual ab initio result for $E(\mathrm{D})^\pi$ in benzene is larger by 2 kcal/mol than the value offered by the additivity rule. This agrees with a pronounced stability of this aromatic molecule par excellence. We conclude that $E(\mathrm{D})^\pi$ is compatible with the anti/aromatic de/stabilization in $4n\pi/(4n+2)\pi$ electron systems, whereas $E(\mathrm{ND})^\pi$ is antagonistic in this respect. Finally, it is noteworthy that the $E(\mathrm{D})^\pi$ in naphthalene **18** from the CASPT2 estimate is larger by 3.3 kcal/mol than that from the simple additivity estimate, which is somewhat less than twice the deviation in benzene. This is compatible with a well-known finding that the aromatic stabilization of naphthalene is smaller than that of two free benzenes. We would like to reiterate that the $E(\mathrm{D})$ should be re-examined later by using larger B3 and B4 basis sets, calculations which are currently hampered by practical reasons.

In view of the additivity of $E(\mathrm{ND})^\pi$ and $E(\mathrm{D})^\pi$ correlation energies in linear polyenes, it follows as a corollary that they should behave as if their π-bonds were perfectly localized exactly as predicted by Dewar some forty years ago.[20] Combining eqs 7 and 8, we obtain the additivity formula for the correlation energy of π-electrons in linear polyenes

$$E(\mathrm{corr})^\pi = 12.15n_\mathrm{C} - 0.8n_\mathrm{H}\ (\mathrm{kcal/mol}) \qquad (9)$$

The estimated total π-correlation energies are given in Table 3, and their deviations from CASPT2 results speak for themselves.

2.3. Cyclobutadiene and Benzene. We shall discus the problem of (anti)aromaticity at some length because it is topical to chemistry. Since CBD and benzene are archetypal antiaromatic and aromatic molecules, respectively, it is of interest to consider their striking features in some more detail. Their antipodal behavior is reflected in the symmetries of their GS and TS structures. The most stable geometry of benzene has the highest possible symmetry (D_{6h}), whereas structure **17**, possessing D_{3h} symmetry, mimicks an "aromaticity-free" reference system. The opposite is the case for CBD: the most symmetric D_{4h} geometry is that of the transition state for the automerization process, which interconverts two equivelent D_{2h} structures. We shall focus on the problem of antiaromaticity first.

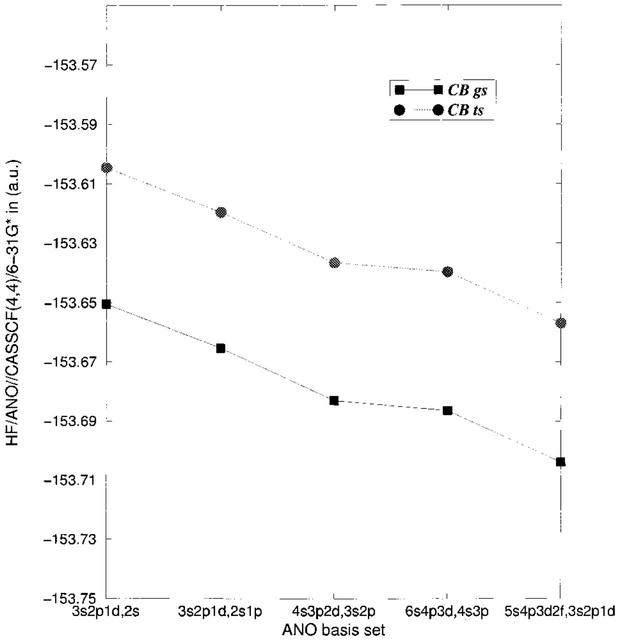


Figure 3. Dependence of the HF energy of CBD(GS) and CBD(TS) on the quality of basis sets.

2.3.1. Cyclobutadiene. To provide some more insight into the nature of automerization of CBD, we performed a series of calculations on its GS and TS structures by using several basis sets. The latter encompasses B1, B2, and a ANO (6s4p3d,4s3p) set denoted as B5. The results are given in Table 4. It follows that $\delta(\mathrm{ND})^\pi$ and $\delta(\mathrm{D})^\pi$, representing changes in the nondynamical and dynamical correlation energies, respectively, in going from GS to TS, are quite insensitive to the chosen basis set, assuming values ∼22.0 and ∼0.5 in kcal/mol, respectively. Although HF energies change substantially as the quality of the employed basis set increases, the barrier height estimated by the HF model varies by only 0.6 kcal/mol (between 28.7 and 29.3 kcal/mol). This is pictorially illustrated by Figure 3, where it is evident that the barrier height is practically constant. It is grossly exaggerated, however, as expected in view of the genuine and quintessential inadequacy of the single-configuration wave function in describing CBD(TS). The best available theoretical result for $\delta(\mathrm{E})$TS is 6.4 kcal/mol, obtained by Balkova and Bartlett[21] via the coupled cluster CCSDT method. Therefore, all our δ(CASSCF) and δ(CASPT2) results obtained through different basis sets are quite acceptable (Table 4). Consequently, we shall use the results obtained by the simplest

B1 basis set. In interpreting the facets of anti/aromaticity, we shall make use of an electrostatic + correlation analysis based on the resolution of the HF energy into V_{ne}, V_{ee}, and V_{nn} components according to the virial theorem. The difference in energy δ(E)TS between TS and GS of cyclobutadiene can be expressed in the following manner:

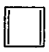
$$\delta(\mathrm{E})\mathrm{TS} = \delta(\mathrm{HF})\mathrm{TS} - \delta E(\mathrm{ND})^{\pi}_{\mathrm{TS}} - \delta E(\mathrm{D})^{\pi}_{\mathrm{TS}} \qquad (10)$$

Here, changes in the nondynamical and dynamical π-electron correlation energies denoted as $\delta E(\mathrm{ND})^{\pi}_{\mathrm{TS}}$ and $\delta E(\mathrm{D})^{\pi}_{\mathrm{TS}}$, respectively, are taken with the opposite sign because the numerical values of the correlation energies are conventionally given as positive numbers for convenience. The increase in HF energy at the TS structure, δ(HF)TS, relative to the rectangular GS geometry can be broken down into three contributions with the virial theorem

$$\delta(\mathrm{HF})\mathrm{TS} = {}^{1}/_{2}\delta(V_{ne})\mathrm{TS} + {}^{1}/_{2}\delta(V_{ee})\mathrm{TS} + {}^{1}/_{2}\delta(V_{nn})\mathrm{TS} \qquad (11)$$

where V_{ne}, V_{ee}, and V_{nn} denote the Coulomb attraction between nuclei and electrons, the repulsion among electrons, and the repulsion among nuclei, respectively. Employing the B1 basis set and CASSCF(4,4)/6-31G* optimized geometric structures, we obtain ${}^{1}/_{2}\delta(V_{ne})\mathrm{TS} = 1.7$ kcal/mol, ${}^{1}/_{2}\delta(V_{ee})\mathrm{TS} = -16.4$ kcal/mol, and ${}^{1}/_{2}\delta(V_{nn})\mathrm{TS} = 43.4$ kcal/mol, which, combined, give $\delta(\mathrm{HF})\mathrm{TS} = 28.7$ kcal/mol. It follows that the Coulomb repulsion among electrons is more favorable in the CBD(TS) than in its CBD(GS) counterpart, whereas attraction between the nuclei and electrons is only slightly diminished in its absolute value. The barrier height is determined by the dominating nuclear Coulomb repulsion contribution to the change in the total energy $\delta(E)$TS of 43.4 kcal/mol, diminished by substantially lower electron−electron repulsions and the increased nondynamical electron correlation in the TS of cyclobutadiene, the latter being as high as 22 kcal/mol, as shown earlier. By adding up all contributions to $\delta(E)$TS, we find the barrier of CBD automerization to be as low as 3.8 kcal/mol. Here, a difference in the zero-point vibration energy of 2.6 kcal/mol is also taken into account since one vibration along the reaction path is not activated.[21] This result coincides with the outcome of the best theoretical calculation obtained so far by Balkova and Bartlett, who used the CCSDT method,[21] as pointed out earlier. Such good agreement is somewhat fortuitous. Nevertheless, it shows that our adopted simple model provides meaningful results. The limited inclusion of σ-electrons in the active space involving 10 electrons and 10 MOs (5 highest OMOs and 5 lowest UMOs, where OMO and UMO stand for occupied and unoccupied molecular orbitals, respectively) increased the barrier by 0.8 kcal/mol, leading to $\delta(E)\mathrm{TS} = 4.6$ kcal/mol.[22] All these results are in very good accordance with the experimental enthalpy of activation ΔH^{*}(TS) of 5.3 kcal/mol obtained for a CBD derivative tri-*t*-butyl-(isopropoxydimethylsilyl)cyclobutadiene.[23] Other experimental estimates lie within the range of 1.6−10 kcal/mol.[24] It follows that the barriers of automerization for CBD are relatively low, which is significant in view of the important role of the four-membered ring π-system pattern in the rationalization of some thermally forbidden pericyclic chemical reactions involving antiaromatic TS.[25,26] It is interesting to compare our results with those of earlier theoretical works. Bernardi et al.[26] employed the effective Hamiltonian to perform CASSCF(4,4)/4-31G calculations on CBD and transform the computed wave functions into all-neutral covalent valence bond (VB) determinants. Their diagonalization has led to Coulomb and exchange energy components, which were subsequently used in interpreting the energetic features of the automerization process. It was found that the delocalization energy in CBD-(TS) is 14.5 kcal/mol, which qualitatively compared with our $\delta(\mathrm{ND})^{\pi}_{\mathrm{TS}}$ of 22 kcal/mol. Moreover, their estimate of the delocalization energy for the supra−supra $[2\pi_s + 2\pi_s]$ transition state in the ethylene dimerization reaction was 20.5 kcal/mol. Although the π-electron delocalization energy and $\delta(\mathrm{ND})^{\pi}_{\mathrm{TS}}$ differ by definition, their variation should be similar in a broad sense. This is gratifying because the analysis of the antiaromaticity in the present paper apparently holds for thermally forbidden pericyclic reactions, too. In particular, the influence of the V_{nn} term in considering antiaromaticity in the transition states should be taken into account, which is sometimes overlooked.[27,28] An interesting hypothesis has recently been put forward by Hiberty et al.,[29] who define the π-electron bonding energies by selecting the reference nonbonding level as the π-quasiclassical state. In this way, it seems that the problem of the $\sigma-\pi$ separation is circumvented, whereas the influence of the nuclear repulsion vanishes by the very definition. Employing the concept of the quasiclassical π-state, Hiberty et al.[29] discussed the stability of some aromatic and antiaromatic systems utilizing a rather modest CISD π-approximation in treating the electron correlation problem. Our calculations show, however, that the correlated motion of σ- and π-electrons might be an important factor in determining the properties of planar molecular systems, as evidenced by the relatively large values of the corresponding correlation energy components $\Delta E(\mathrm{ND})^{\sigma*\pi}$ and $\Delta E(\mathrm{D})^{\sigma*\pi}$ in ethylene (Table 2). Hence, the role of the $\sigma-\pi$ coupling might increase as the theoretical model becomes intricate and more realistic. Additionally, the nuclear repulsion obviously undergoes changes in molecular transformations, as exemplified here by the automerization of CBD. Consequently, it seems that the analysis in terms of HF energies decomposed by using the virial theorem and explicit consideration of the correlation energy is more promising in this respect. It is based on the physical entities being free of any ad hoc assumptions. Much more work, however, is necessary before the final conclusion is reached. The cyclic delocalization of antiaromatic 4π electrons is not disadvantageous as some people think. On the contrary, their full delocalization in CBD(TS) lowers the total energy leading to a softer barrier for the internal conversion.

It is interesting estimate the amount of energetic destabilization $E(\mathrm{CBD})_d$ of cyclic CBD relative to linear polyene (1,3-trans-butadiene). For that purpose we shall make use of the homodesmic reaction concept.[30] It is generally believed that the



$$+ 2(\mathrm{CH_2{=}CH_2}) \rightarrow 2(\mathrm{CH_2{=}CH{-}CH{=}CH_2}) + E(\mathbf{CBD})_d \qquad (12)$$

influence of the correlation effect can be neglected in homodesmic reactions since they preserve the numbers of closely similar atoms, bonds, lone-pairs, etc. This supposition is true as a rule, but CBD is an apparent exception because $E(\mathrm{ND})^{\pi}$ is higher in CBD than in the corresponding open-chain polyene (Table 3). We shall determine $E(\mathrm{CBD})_d$ at the Hartree−Fock level and then introduce the electronic correlation energy correction. The HF model calculations have been carried out at the CASSCF-(*n*,*n*)/6-31G* optimized geometries employing the B1 basis set, where $n = 2$ and 4 for ethylene and butadiene (and CBD), respectively, yielding $E(\mathrm{CBD})^{\mathrm{HF}}_{d} = 84.9$ kcal/mol. Since this energy is a measure of the propensity of CBD to take part in ring-opening reactions, we shall call it exoantiaromaticity. Analysis performed with the virial theorem revealed that the contributions to $E(\mathrm{CBD})^{\mathrm{HF}}_{d}$ were 41.24923, −20.53749, and −20.57638 au for the ${}^{1}/_{2}V_{ne}$, ${}^{1}/_{2}V_{ee}$, and ${}^{1}/_{2}V_{nn}$ potential energy components, respectively. In other words, the origin of the CBD(GS) destabilization (as measured by $E(\mathrm{CBD})_\mathrm{d}$) can be assigned to a considerably less favorable nuclear−electron attraction interactions than that in the correspoding molecular fragments (i.e., in 1,3-butadiene). In contrast, V_ee and V_nn repulsions are weaker in the CBD(GS). Taking into account that $E(\mathrm{ND})^\pi$ decreases $E(\mathrm{CBD})_\mathrm{d}$ by 9 kcal/mol whereas $E(\mathrm{D})^\pi$ increases it by 2.7 kcal/mol (Table 3), we finally obtain the destabilization energy of CBD, 78.6 kcal/mol. It is a sum of the angular strain $E(\mathrm{CBD})_\mathrm{s}$ and the conventional antiaromatic destabilization energy $E(\mathrm{CBD})_\mathrm{ad}$ gauged by an open-chain polyene. The former was recently estimated empirically to be 32 ± 2 kcal/mol.[32] Adopting this value, we obtain the antiaromatic destabilization $E(\mathrm{CBD})_\mathrm{ad}$ of 46.6 ± 2 kcal/mol. This value compares with the experimental work of Deniz et al., which gave $E(\mathrm{CBD})_\mathrm{ad} = 55 \pm 11$ kcal/mol "relative to conjugated π-bond reference".[31] The previous theoretical estimate at the MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p)+ZPE(HF/6-31G(d)) level yielded $E(\mathrm{CBD})_\mathrm{ad} = 41.6$ kcal/mol.[32] An even earlier G2 study gave $E(\mathrm{CBD})_\mathrm{ad} = 40.6$ kcal/mol.[33] It is safe to conclude that $E(\mathrm{CBD})_\mathrm{ad}$ is significantly higher than the angular strain energy $E(\mathrm{CBD})_\mathrm{s}$. This conclusion disagrees with the assertion of Mo et al.[34] that the energetic destabilization of CBD is a direct outcome of the σ frame's ring strain. All these estimates of $E(\mathrm{CBD})_\mathrm{ad}$ are defined relative to the open-chain butadiene via eq 12. The latter reference compound has the π-electron delocalization energy of 3.0−3.3 kcal/mol, as experimentally estimated from spectroscopic measurements comparing the ground state of 1,3-butadiene with its orthogonal form, where π-electron conjugation energy is strictly precluded.[35,36] Consequently, our final estimate of $E(\mathrm{CBD})_\mathrm{ad}$ as the genuine exoantiaromaticity would be 40 ± 2 kcal/mol relative to two isolated π-double bonds.

2.3.2. Benzene. In benzene, the same type of analysis leads to the following results. The largest contribution to the stability of D_{6h} benzene **16** originates from the lower HF energy compared to that of the lower-symmetry frozen structure **17** (difference, 5.6 kcal/mol). This is in striking disparity with the highly symmetric delocalized D_{4h} TS of CBD, where the HF energy is considerably increased relative to that of the distorted D_{2h} CBD(GS). The correlation energy components $E(\mathrm{ND})^\pi$ and $E(\mathrm{D})^\pi$ in benzene are increased, albeit by only 0.2 and 0.8 kcal/mol, respectively. Hence, analysis of the difference between the energies of **16** and **17** $\delta E(\mathrm{HF})_{\mathbf{16}}$ is of particular importance. We consider the difference of **16**−**17** instead of **17**−**16** to reflect the change from low symmetry to high symmetry, as in CBD. It appears that the changes to $^1/_2\delta(V_\mathrm{ne})_{\mathbf{16}}$, $^1/_2\delta(V_\mathrm{ee})_{\mathbf{16}}$, and $^1/_2\delta(V_\mathrm{nn})_{\mathbf{16}}$ are −168.7, +78.7, and +84.4 kcal/mol, respectively. Once again, the perfectly symmetric D_{6h} structure has a nuclear repulsion higher than that of the artificially deformed D_{3h} structure, like with CBD(TS) vs CBD(GS). Indeed, the nuclear repulsion is always maximum for a symmetric arrangment of the nuclei on a circle with a fixed radius. The difference between benzene and CBD is that the nuclear-electron attraction in the regular six-membered ring prevails over substantial increases in V_ee and V_nn repulsions. It is this interplay of the effects that results in the ideal benzene structure. Another notable difference is given by the repulsion among electrons, which is highly unfavorable in benzene relative to that in the localized D_{3h} structure, in stark contrast to the analogous quantities in CBD(TS). Apparently, the topology and geometry of four- and six-membered rings framing CBD and benzene, respectively, make these two paradigmatic organic molecules very different. The stability of benzene is further enhanced by the total correlation effect, which contributes an additional 1.0 kcal/mol within the adopted theoretical framework. The $E(\mathrm{corr})^\pi$ of benzene is lower by 3 kcal/mol than an estimate from the additivity formula, implying that the open-chain polyene structure would be advantageous as far as the π-electron correlation is concerned. This is in line with the arguments put forward by Shaik et al.[27,28] that the D_{6h} structure of benzene is a consequence of σ-interactions. Additional study based on the π-electron quasiclassical reference state has led to the conclusion that benzene possesses a unique delocalized π-component which has a dual nature; in any geometry with the C_6H_6 structure, the π-electrons are strongly stabilized by the quantum mechanical resonance energy, and at the same time, they possess a global distortive tendency toward a D_{3h} structure.[29] Indeed, this deformation costs only 5.6 kcal/mol, according to present calculations. Jug and Köster[37] reached the same conclusion by allowing for the change in the nuclear repulsion energy. Neither of these studies, however, offered a physical explanation of the distortive tendency of 6π electrons. Before the final conclusion is drawn, the behaviors of $E(\mathrm{corr})^\sigma$ and $\Delta E(\mathrm{corr})^{\sigma*\pi}$ correlation energies in benzene should be examined like they were for ethylene (section 3.1). Unfortunately, such an analysis is precluded for technical reasons at present.

The aromatic stabilization of benzene is usually determined relative to 1,3-butadiene via the corresponding homodesmic reaction (the subscript "as" stands for the aromatic stabilization,

$$+ 3(\mathrm{CH_2{=}CH_2}) \rightarrow 3(\mathrm{H_2C{=}CH{-}CH{=}CH_2}) - E(\mathrm{benz})_\mathrm{as} \quad (13)$$

defined as a positive entity). It reflects the resistance of the benzene moiety to the ring-opening reaction. Consequently, it could be named exoaromaticity. Calculations at the HF/ANO-(3s2p1d,2s1p)//CASSCF(n,n)/6-31G* level give $E(\mathrm{benz})_\mathrm{as}^\mathrm{HF} = 21.9$ kcal/mol. Taking into account the correlation energies (Table 3), we find the energy of aromatic stabilization to be 19.4 kcal/mol. This is in good agreement with other theoretical ab initio MO estimates, assuming values of 23.6 (HF/6-311G**),[38] 24.3 (MP4/6-31G*),[39] and 21.35 kcal/mol (MP4/6-31G*).[40] The second and third results were obtained at the MP4 level of theory with the basis set superposition error correction. A more recent calculation at the MP4SDTQ/6-31G-(d,p)//MP2/6-31G(d,p)+ZPVE(6-31G(d)) level provided an aromatic stabilization of 25.4 kcal/mol.[32] Cooper et al.[41] found that the resonance energy in benzene is 20 kcal/mol, as obtained from the difference between the full spin-coupled wave function and the VB function, corresponding to a Kekulé structure. An experimental estimate based on the homodesmic reaction (eq 13) and measured enthalpies of formation gave 21.3 ± 0.2 kcal/mol.[30,42] Since 1,3-butadiene has an intrinsic delocalization energy of 3 kcal/mol (vide supra), our final estimate of corrected $E(\mathrm{benz})_\mathrm{as}^\mathrm{HF}$ relative to isolated double bonds is 28.4 ± 1.0 kcal/mol. It follows that CBD(GS) antiaromatic destabilization is higher by 12 kcal/mol than the aromatic stabilization in benzene. This finding is important to understanding fused systems involving benzene and cyclobutadiene rings.[43] The partitioning of $E(\mathrm{benz})_\mathrm{as}^\mathrm{HF}$ into $^1/_2\delta(V_\mathrm{ne})$, $^1/_2\delta(V_\mathrm{ee})$, and $^1/_2\delta(V_\mathrm{nn})$ contributions yields −6.86871, 3.43876, and 3.46483 au, respectively. In other words, the nuclear−electron attraction in benzene in less favorable than in alternating single and double bonds, represented by weakly coupled π-bonds in 1,3-butadiene. In contrast, V_ee and V_nn repulsions are more advantageous in benzene, leading to a net stabilization of 21.9 kcal/mol. This picture is completely different than that obtained with the respect to the frozen structure **17** (vide supra), where V_ee and V_nn were

TABLE 5: Energy Components (in kcal/mol) Per >CH Structural Unit in Benzene, CBD(GS), and CBD(TS)[a]

energy	benzene	CBD(GS)	CBD(TS)
E(HF)/n (>CH)	−38.45602	−38.41633	−38.40490
$^1/_2V_{ne}/n$ (>CH)	−78.66267	−69.49522	−69.49453
$^1/_2V_{ee}/n$ (>CH)	23.24646	18.68523	18.67869
$^1/_2V_{nn}/n$ (>CH)	16.96019	12.39366	12.41094
E(ND)/n (>CH)	7.6	10.7	16.2
E(D)/n (>CH)	3.2	2.1	2.1

[a] As obtained by adopted HF, CASSCF, and CASPT2 models employing the ANO (3s2p1d,2s1p) basis set and CASSCF/6-31G* geometries. Hartree−Fock entities in au and correlation energies in kcal/mol.

smaller and V_{ne} was greater, favoring **16** over **17**. The additional stabilization of the D_{6h} structure and its resistance to deformations, which lead to alternate CC bond distances but preserve the ring closure, could be termed as endoaromaticity. It should be stressed that exoaromaticity is entirely analogous in nature to the origin of the antiaromatic destabilization in CBD(GS) when compared to the same linear zigzag polyene. The notable difference in benzene, however, is that favorable V_{ee} and V_{nn} repulsions overcompensate the unfavorable V_{ne} attraction as compared to 1,3-butadiene, whereas the opposite is the case for CBD. Consequently, both exoaromaticity and exoantiaromaticity can be described in a unified way employing a simple physical picture. Both types the aromaticity predict an additional stabilization of benzene, albeit to a different extent. The first definition (endoaromaticity) based on the frozen cyclohexatriene **17** as the gauge structure predicts a relatively small gain by the aromatization of the planar six-membered ring. Indeed, deformations of the ideal benzene structure easily occur in Mills−Nixon and reversed Mills−Nixon compounds involving aromatic fragments annelated to small rings, which has some important chemical consequences.[44] By the same token, distortions from the perfect benzene structure and the accompanying changes in energy are frequently used as criteria for the aromaticity defect[45,46] or, in our terminology, the endoaromatic defect.

Finally, we compare energy components per >CH structural subunit in Table 5. It appears that the E(HF)/n(>CH) of benzene is lower than its counterpart in CBD(GS) and CBD(TS) by 24.9 and 32.1 kcal/mol, respectively, where n (>CH) is the number of the structural fragments. Their decomposition in terms of V_{ne}, V_{ee}, and V_{nn} potential energy components is easily deduced from the numbers given in Table 5. It turns out that both V_{ee} and V_{nn} are higher in benzene than in CBD if partitioned to a single >CH fragment. In contrast, however, V_{ne} is considerably lower than in CBD, thus overcoming unfavorable repulsion and providing a fundamental difference between aromaticity and antiaromaticity. Taking into account E(ND) and E(D) correlation energies, we calculate the above-mentioned numbers to be 22.9 and 24.8 kcal/mol for the GS and TS of cyclobutadiene, respectively. The nondynamical correlation energy of the fully delocalized CBD(TS) is larger by 8.6 kcal/mol per >CH building block than that of the GS of benzene. This is a consequence of the fact that the single state HF model provides an artificial reference level for measuring the nondynamical correlation energy in CBD(TS).

2.4. Concluding Remarks. We have conclusively shown that the nondynamical correlation energy of π-electrons in planar hydrocarbons can be quite accurately calculated within the CASSCF formalism by employing a rather modest basis set. In contrast, the CASPT2 description of the dynamical π-electron correlation requires involved and flexible basis sets. Both types of correlation energies follow very simple additivity rules as linear functions of the number of C and H atoms. The additivity holds strictly for linear polyenes. Deviations from the additivity provide interesting information about systems localized to a lesser extent than polyenes, as exemplified by paradigmatic benzene and CBD(TS). The origins of (anti)aromaticity are of some interest. These concepts are analyzed by applying an electrostatics + correlation analysis, which provides a vivid and transparent interpretation of these two basic facets of both organic and inorganic chemistry. The electrostatic part of the analysis is based on the decomposition of the total HF energy into the V_{ne}, V_{ee}, and V_{nn} contributions according to the virial theorem. It is important to realize that there are two distinctly different definitions of aromaticity if the energetic (thermodynamic) criterion is adopted. The latter is, in our opinion, the most fundamental of all possible indices designed for probing aromaticity. The first definition is given by selecting the artificial "aromatic-free" system **17**, possessing three double and single bonds in an alternating pattern. Since this gauge structure is obtained by keeping the ring perimeter practically constant, the corresponding stabilization of the D_{6h} geometry is called the intrinsic, inherent, or endoaromaticity. It measures resistance of benzene toward the D_{3h} deformation. The second definition of aromaticity is given by the homodesmic reaction (eq 13). It is termed the extrinsic, external, or exoaromaticity because it characterizes the reluctance of benzene to undergo ring-cleavage reactions. Both definitions have their merits. The former is able inter alia to rationalize the ease of deformation of the benzene nucleus upon the annelation of small ring(s) (Mills−Nixon and reversed Mills−Nixon effects), whereas the latter helps in understanding some aspects of the reactivity of aromatic compounds. By analogy, we can define the exoantiaromaticity of CBD by the homodesmic reaction (eq 12), which, in turn, measures its susceptibility to some ring-opening reactions. Analysis of the HF energies shows that both benzene and CBD have an increased V_{ne} term (the nuclear−electron attraction has a negative sign) and decreased V_{ee} and V_{nn} repulsion terms relative to those of the same reference linear polyene (1,3-butadiene). There is, however, a fundamental difference between these two molecules. In benzene, the decrease in ($V_{ee} + V_{nn}$) overrides the increase in the V_{ne}, yielding exoaromaticity. In contrast, the opposite occurs in CBD, resulting in exoantiaromaticity. Consequently, exoaromaticity and exoantiaromaticity have common roots and can be reduced to the same underlying mechanism involving a simple physical picture—an interplay of the electrostatic V_{ne}, V_{ee}, and V_{nn} interactions. As to the endoaromaticity, its driving force is a dramatic decrease in V_{ne} in going from the D_{3h} deformed structure to the perfectly symmetric D_{6h} structure. This decrease in V_{ne} overcomes the increase in ($V_{ee} + V_{nn}$) repulsions. The correlation energy of π-electrons adds to the stability of benzene (GS) a very small amount of only 1.0 kcal/mol. Another interesting distinction between the aromatic benzene and antiaromatic CBD can be made by comparing their total energies, reduced (normalized) to the energy of a constituent >CH fragment. It appears that the normalized energy per >CH fragment is higher in CBD by 22.9 kcal/mol than that in benzene, implying that CBD is 91.6 kcal/mol less stable than the hypothetical four-membered ring constructed by four >CH building blocks of benzene. This is a good measure of endoantiaromaticity. It is compatible with the semantic meaning of the word antiaromaticity as something related to and measured by aromaticity but exibiting quite opposite (antipodal) features. The estimate of endoantiaromaticity qualitatively compares with the 101 kcal/mol obtained by adding exoaromatic stabilization of benzene (28.4 kcal/mol), the angular strain of CBD (32 kcal/mol), and the exoantiaromatic destabilization of CBD (40.7 kcal/mol). Better accordance was not expected because these data refer to exo(anti)aromatic entities. It is also important that 4π electrons are not necessarrily a destabilizing factor per se. The easiest way of conceiving this is to consider a mixing of π-levels within the CASSCF$^{\pi}$ formalism as the generalized delocalization interaction. Since the E(ND)$^{\pi}$ energy of CBD is higher than that in 1,3-butadiene or an energy provided by the additivity rule, 4π electrons are in fact aromatic, in contrast to the old definition. Obviously, a proper treatment of the electron correlation is a prerequisite for tackling the (anti)aromaticity problem. This is exactly the point, where the Hückel theory leaves much to be desired. A serious stumbling block for all π-electron-only theories and interpretations of the (anti)aromaticity is given by the problem of σ-π separability. It is clear that the latter cannot rigorously hold for two reasons. The first is the nuclear repulsion term V_{nn}. It does not (explicitly) depend on electrons, and consequently, it cannot be assigned to σ- and π-electrons either. The one-to-one correspondence between electrons and protons is plausible but still somewhat arbitrary. The same holds for the partitioning of Jug and Köster.[37] The second obstacle is the $\sigma-\pi$ correlation energy given by eq 6, which is hopelessly complex and cannot be disentangled into σ and π contribution. Therefore, we believe that the theoretical analysis in the present work offers a promising alternative, particularly if the complete active space is extended to encompass σ-electrons and σ-MOs. These studies are under way. In conclusion, it should be mentioned that similar additivity formulas governing the variation of E(ND) and E(D) correlation energies are operative in planar heteroatomic systems too.[47] Hopefully, this type of approach will provide rationale for Benson's bond and group additivity values.[48]

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References and Notes

(1) Löwdin, P. O. *Adv. Chem. Phys.* **1959**, *2*, 207.

(2) Yarkony, D. R. *Modern Electronic Structure Theory*; World Scientific: Singapore, 1995; parts 1 and 2.

(3) Sinanoğlu, O. *Adv. Chem. Phys.* **1964**, *3*, 358.

(4) Mok, D. K. W.; Neumann, R.; Handy, N. C. *J. Phys. Chem.* **1996**, *100*, 6225.

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

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

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

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

(9) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *96*, 4070.

(10) Widmark, P.-O.; Malmquist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(11) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, 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. *MOLCAS*, Version 4; Lund University, Sweden, 1997.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. W. M.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Otiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *GAUSSIAN 94*, Revision D.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(14) Scott, A. P.; Agranat, I.; Biedermann, P. U.; Riggs, N. V.; Radom, L. *J. Org. Chem.* **1997**, *62*, 2026.

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

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

(17) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.

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

(19) Kovaček, D.; Maksić, Z. B.; Novak, I. *J. Phys. Chem.* **1997**, *101*, 1147.

(20) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; p 173.

(21) Balkova, A.; Bartlett, R. *J. Chem. Phys.* **1994**, *101*, 8972.

(22) Maksić, Z. B.; Petanjek, I.; Eckert-Maksić, M.; Novak, I. *J. Phys. Chem. A* **1998**, *102*, 10710.

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

(24) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700. Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

(25) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

(26) Bernardi, F.; Celani, P.; Olivucci, M.; Robb, M. A.; Suzzi-Valli, G. *J. Am. Chem. Soc.* **1995**, *117*, 10531.

(27) Shaik, S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363.

(28) Hiberty, P. C.; Ohanessian, G.; Shaik, S.; Flament J. P. *Pure Appl. Chem.* **1993**, *65*, 35.

(29) Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 7760.

(30) George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 313; *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

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

(32) Glukhovtsev, M. N.; Bach, R. D.; Laiter, S. *J. Mol. Struct. (THEOCHEM)* **1997**, *417*, 123.

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

(34) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048.

(35) Hollas, J. M. *Chem. Phys. Lett.* **1980**, *75*, 94.

(36) Caminati, W. *J. Mol. Spectrosc.* **1988**, *128*, 384.

(37) Jug, K.; Köster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

(38) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1988**, *152*, 402.

(39) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289.

(40) Tao, F.-M.; Pan, Y.-K. *Theor. Chim. Acta* **1992**, *83*, 377.

(41) Cooper, D. L.; Gerratt, J.; Raimondi, M. In *Pauling's Legacy: Modern Modelling of the Chemical Bond*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, 1999; p 503.

(42) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organomettalic Compounds*; Academic Press: New York, 1970.

(43) Maksić, Z. B.; Kovaček, D.; Eckert-Maksić, M.; Böckmann, M.; Klessinger, M. *J. Phys. Chem* **1995**, *99*, 6410.

(44) Maksić, Z. B.; Eckert-Maksić, M.; Mó, O.; Yañez, M. *The Mills−Nixon Effect: Fallacies, Facts and Chemical Relevance, in Pauling's Legacy − Modern Modelling of the Chemical Bond*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, 1999; p 47.

(45) Cyrański, M. K.; Krygowski, T. M. *Tetrahedron* **1998**, *54*, 14919.

(46) Krygowski, T. M.; Cyrański, M. K. In *Theoretical Organic Chemistry*; Párkanyi, C., Ed.; Elsevier: Amsterdam, 1998; p 53.

(47) Maksić, Z. B.; Smith, D. M.; Barić, D. Manuscript in preparation.

(48) Cohen, N.; Benson S. W. *Chem. Rev.* **1993**, *93*, 2419.