In Pursuit of the Elusive Bond-Stretch Isomers by ab Initio Methods—Benzocyclobutene, Benzo[1,2:4,5]dicyclobutadiene, and Some Related Substituted Systems

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The problem of bond-stretch isomerism in benzocyclobutene (**1**) and benzo[1,2:4,5]- dicyclobutadiene is addressed by single-state (SS-CASSCF and SS-CASPT2) as well by two-state (TWS-CASSCF and TWS-CASPT2) theoretical formalisms. It is shown beyond reasonable doubt that benzocyclobutene **1** does not exhibit bond-stretch isomerism. The situation is more complex and interesting in the case of benzo[1,2:4,5]-dicyclobutadiene. The TWS-CASPT2$^{(\pi)+\sigma}$ approach, based on the TWS-CASSCF(10,10)$^{\pi}$ zeroth-order wave function, yields two bond-stretch isomers **2** and **3**. Their total energies, including the ZPVE contributions, indicate that the structure **3** is slightly favored. Because they are separated by an almost vanishing potential energy barrier (0.4−1.0 kcal/mol), it is concluded that **3** prevails and that bond-stretch isomerism probably does not occur in the case of benzo[1,2:4,5]dicyclobutadiene either. However, the final asnwer will be given only by high level multireference (MR) ab initio calculations. It is important to stress that **3** exhibits a pattern of 10π electrons fully delocalized over the CC bonds of the molecular perimeter and thus represents a planar pseudo-[10]annulene system par excellence. Finally, it is argued that strategic substitution of benzo[1,2:4,5]-dicyclobutadiene might lead to a discrimination of the isomers **2** and **3** and to the isolation of some judiciously selected derivatives in the laboratory. In particular, it is shown that a number of substituted pseudo-[10]annulene systems are possible.

1. Introduction

Aromaticity and antiaromaticity are fundamental concepts in organic chemistry, because they reflect two important, but antipodal patterns of molecular behaviour. It is, therefore, not surprising that the juxtapostion of aromatic [$4n + 2$] and antiaromatic [$4n$] π-electron fragments leads to a very interesting family of organic compunds, annulenoannulenes, which exhibit some unusual properties.[1] This is primarily because of the antagonistic competition between the two tendencies of [$4n + 2$] π and [$4n$] π rings: maximization of their aromatic and minimization of their antiaromatic characters, respectively. These two requirements are difficult to fulfill simultaneously, implying that only a compromise is possible. The fine-tuning of these two principles yields the wide variety of properties of the various annulenoannulenes.

For $n = 1$, one obtains a class of molecules named phenylenes. Their structures are characterized by a very strong angular strain—which, in turn, by an interplay with aromaticity and antiaromaticity gives rise to some interesting and unexpected features. For example, it appears that bent phenylenes are more stable than their linear counterparts, although the former possess a more pronounced π-electron bond localization.[2] These results were confirmed and extended to higher phenylenes by Schulman and Disch.[3] It is interesting to point out that these systems provide particularly illuminating examples of the Mills−Nixon effect.[4]

Because annulenoannulenes might play an important role in designing new materials with applications ranging from electric conductors to memory storage devices,[1] they are interesting per se. However, annulenoannulenes also exhibit highly remarkable electronic structure features, which makes continuation of their meticulous investigation worthwhile. A particularly intriguing problem is given by the elusive Kekulé isomerization of some simple[4]annuleno[6]annulenes involving cyclobutadiene (CBD) ring(s) fused to a benzene moiety. A pioneering study on this topic was performed by Schulman and Disch,[5] who examined the potential energy hypersurface (PEH) of benzocyclobutene and found that only a single true minimum existed, which corresponded to compound **1** (Scheme 1). The electron pair coupling modes **1a** and **1b** were found not to correspond to stable isomers. This result is intuitively expected in view of a diminished antiaromaticity of the CBD ring in **1**, in contrast to a strong antiaromatic destabilization implied in the resonance structures **1a** and **1b**.

On the other hand, geometric structures **2** and **3**, represented by their predominant spin-coupling patterns depicted in Scheme 2, offer much more promising candidates for Kekulé isomers of the benzo[1,2:4,5]dicyclobutadiene (BDCB) moiety according to Schulman and Disch.[5] However, their theoretical models (MP2(fc)/6-31G*//HF/6-31G* and GVB/STO-3G) applied were not quite adequate for studying Kekulé isomers of BDCB, because this problem requires a full account of the nondynamical part of the correlation energy, at least for π electrons. Hence multiconfiguration wave functions should have been employed.

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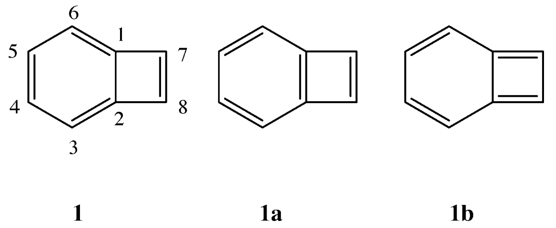
SCHEME 1



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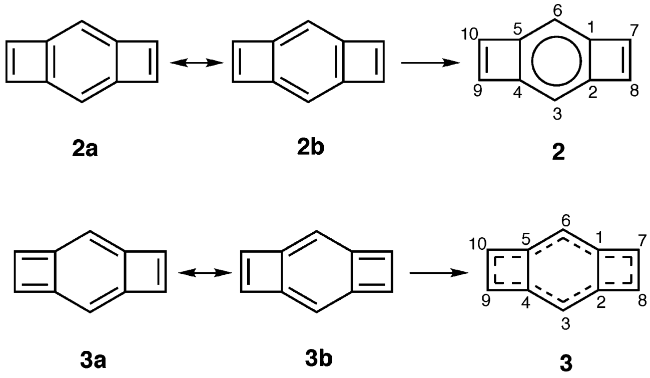


Second, the contribution of the dynamical correlation of both σ and π electrons should be explicitly included too. It will be shown in the present paper that: (a) the problem requires at least a two state (TWS) description of the PEH and (b) the dynamical correlation energy of both σ and π electrons plays an important role in description of isomerization of the planar π systems. Finally, it should be pointed out that only the valence bond structure **3a** and its equivalent mirror image counterpart **3b** were considered by Schulman and Disch,[5] and not a fascinating delocalized 10π structure **3**, which will be the main focus of the present work.

The structure **3** is particularly interesting, because it represents an alternative form of the elusive [10]annulene, which was predicted to be capable of existing only in a fused form realized by 5-fold exo-annelated three- or four-membered rings.[6] The electronic structure of **3** is a result of strong mixing of **3a** and **3b** resonance structures, implying an almost even distribution of the π-electron density around the molecular perimeter with minor π-bond orders along the fused bonds. This would imply that the annelated CC bonds are much longer than in free benzene or in **2** meaning that the twin structures **2** and **3** might represent a couple of very elusive bond-stretch isomers.

The notion of bond-stretch isomers has a long history and deserves a few brief comments. It was introduced by Chatt et al.[7] as the term “distortional isomerism” to characterize metallic complexes that differ only by the length of one or several bonds. The possibility of the existence of the renamed bond-stretch isomerism was theoretically studied by Hoffmann et al.[8,9] Since the early 1970s, this was the subject of a considerable controversy. A number of the experimental measurements were reinvestigated and revisited,[10] and it was concluded that some X-ray data had been misinterpreted because of serious disorder problems.[11] During this period, some researchers cast serious doubt onto the very existence of bond-stretch isomers.

The aim of the present paper is not to discuss the problem of bond-stretch isomerism in general but to focus on the specific case of possible isomerism of **2** and **3** instead. This study is a continuation of our interest in annulenoannulenes[2,4,12] being prompted by the experimental X-ray measurements of 3,6-di-tertbutyl-7,8,9,10-tetraphenyl- benzo[1,2:4,5]dicyclobutadiene derivative of **3**.[13] The observed bond distance for annelated (fused) CC bonds was 1.540(5) Å, thus being very large for two participarting sp^2 carbon atoms. An unsubstituted compound which would correspond either to **2** or **3** is not known. Consequently, the problem of bond-stretch isomerism in species **2** and **3**, free of substituent effects and crystal packing forces, deserves close scrutiny at a reliable theoretical level. It should be stressed that this implies not only establishing their existence in the form of the corresponding minima on the Born−Oppenheimer potential energy hypersurface (PEH) but also the appearance of transition state (TS) separating two true minima by a significatly high energy barrier. In the last part of this paper, various polysubstituted derivatives of BCBD will be considered in an attempt to allow for better discrimination between isomers **2** and **3**.

2. Methodology

Preliminary searches of the PEHs were performed by the HF/6-31G* model, B3LYP/6-31G* density functional approach,[14,15] and perturbational MP2(fc)/6-31G* calculations.[16] Minima on the corresponding Born−Oppenheimer hypersurfaces were verified by vibrational analyses. However, it is important to realize that these methods formally belong to a single configuration theoretical framework. Thus, they cannot properly describe the nondynamical part of the electron correlation energy. An exception might be given by the MP2 procedure, which will be discussed later (vide infra). Consequently, these pilot calculations have to be supplemented by multiconfiguration methods, which can be accomplished by using a generalized valence bond (GVB) theory[17,18] or, more conveniently, by the complete active space self-consistent field (CASSCF) approach.[19,20] The latter describes very well the nondynamical correlation energy. The dynamical correlation energy is conveniently taken into account, albeit only approximately, by the CASPT2 perturbation calculations, where the CASSCF wave function is employed as the zeroth-order approximation.[21,22] Because the CASSCF wave function characterizing the ground state is utilized, this type of perturbational treatment is termed also as the single-state CASPT2 (SS-CASPT2) method. However, in situations where several electronic states of the same symmetry are strongly coupled, the multi-state CASPT2 (MS-CASPT2) approach is necessary.[23] In such a situation, the most proper choice of the zeroth order reference function is obtained by treating all the states of interest simultaneously in a MS-CASSCF approach. The corresponding solution is obtained by solving the generalized Bloch equation.[24] It will become clear that the two-state CASPT2 (TWS-CASPT2) is indispensable in considering the problem of bond-stretch isomerism in systems such as benzo[1,2:4,5]dicyclobutadiene (vide infra). Finally, one should point out that we shall use in the forthcomming discussion the correlation energy defined as positive for practical reasons, although it is an intrinsically negative quantity. More specifically, the total correlation energy E(corr) is given here by

$$E(\mathrm{corr}) = E(\mathrm{ND}) + E(\mathrm{D}) \tag{1}$$

where the nondynamical compenent is

$$E(\mathrm{ND}) = E(\mathrm{HF}) - E(\mathrm{CASSCF}) \tag{2}$$

and the dynamical PT2 correlation is determined as

$$E(\mathrm{D}) = E(\mathrm{CASSCF}) - E(\mathrm{CASPT2}) \tag{3}$$

In eqs 2 and 3, the Hartree−Fock, CASSCF, and CASPT2

TABLE 1: Bond Distances of Compounds 1−3 Calculated by MP2 and CASSCF Theories and Their Comparison with Available Experimental Data[a]

molecule	bond	MP2 (fc)	CASSCF	exptl.	BO (π)
1	C(1)−C(2)	1.420[b] (1.429)[c]	1.434[d]	1.416[g]	0.41[i]
	C(2)−C(3)	1.368 (1.378)	1.355	1.347	0.74
	C(3)−C(4)	1.429 (1.436)	1.446	1.435	0.43
	C(4)−C(5)	1.386 (1.396)	1.374	1.373	0.74
	C(1)−C(7)	1.521 (1.532)	1.509	1.531	0.19
	C(7)−C(8)	1.360 (1.372)	1.361	1.359	0.82
2	C(1)−C(2)	1.409[b] (1.419)[c]	1.421[e] (1.430)[f]		0.54
	C(2)−C(3)	1.394 (1.404)	1.394 (1.394)		0.60
	C(1)−C(7)	1.536 (1.547)	1.521 (1.513)		0.15
	C(7)−C(8)	1.355 (1.367)	1.361 (1.367)		0.82
3	C(1)−C(2)	1.555[b] (1.563)[c]	1.504[e] (1.554)[f]	1.540 (5)[h]	0.19
	C(2)−C(3)	1.390 (1.400)	1.393 (1.392)	1.416 (5)	0.19
	C(1)−C(7)	1.397 (1.409)	1.422 (1.415)	1.402 (5)	0.51
	C(7)−C(8)	1.439 (1.472)	1.439 (1.442)	1.471 (5)	0.48

[a] Bond orders describing π density along CC Bonds (BO(π)) are given for interpretive purposes. Bond distances are in angstroms. [b] MP2(fc)/6-31G*. [c] MP2(fc)/cc-pVDZ. [d] SS-CASSCF$(8,8)^{\pi}$/6-31G*. [e] SS-CASSCF$(10,10)^{\pi}$/6-31G*. [f] TWS-CASSCF$(10,10)^{\pi}$/6-31G*. [g] Winter, W.; Butters, T. *Acta Cryst. B* **1981**, *37*, 1524. [h] This structure refers to 3,6-di-*tert*-butyl-7,8,9,10-tetraphenylbenzo[1,2:4,5]dicyclobutadiene.[13] [i] Löwdin π-bond orders obtained by the SS-CASSCF$(8,8)^{\pi}$/6-31G* method for **1** and SS-CASSCF$(10,10)^{\pi}$/6-31G* calculations for isomers **2** and **3**.

energies are denoted by E(HF), E(CASSCF), and E(CASPT2), respectively.

All computations have been performed by utilizing Gaussian 94,[25] GAMESS,[26] and MOLCAS[27] programs.

3. Results and Discussion

3.1. Benzocyclobutene. The HF/6-31G*, B3LYP/6-31G*, and MP2(fc)/6-31G* preliminary calculations indicate that there are two minima on the PEH corresponding to **1** and **1b**. However, the latter appeared to be a false minimum as shown by the more appropriate CASSCF$(8,8)^{\pi}$/6-31G* method, which has led to a single structure **1** (Scheme 1). This illustrates the fact that results obtained by the single configuration models such as, e.g., HF, B3LYP, and MP2 should be taken with due caution. It should be pointed out, however, that despite of this shortcoming the HF/6-31G*, B3LYP/6-31G*, and MP2(fc)/6-31G* models correctly predict that **1** is the global minimum, which is more stable than the false critical point **1b** by 49.3, 46.7, and 49.0 kcal/mol, respectively. This is of importance, because, provided due caution is exercised, the B3LYP/6-31G* and MP2(fc)/6-31G* models can be employed in identifying the most stable isomers in large systems.

Our findings support the earlier conjecture of Schulman and Disch[5] that valence isomerization does not occur in benzocyclobutene. This is in disagreement with the interpretation of some NMR data in favor of the structure **1b**,[28] which seems to be erroneous. In fact, it was shown by Schulman et al.[29] that the proton chemical shifts, calculated at the HF/6-31G* GIAO level, are fully compatible with the structure **1**. The bond lengths of **1** calculated by the MP2(fc)/6-31G*, MP2(fc)/cc-pVDZ, and SS-CASSCF$(8,8)^{\pi}$/6-31G* models are compared with X-ray data in Table 1. Here, cc-pVDZ denotes the correlation consistent polarized valence shell basis set of the double-ζ quality.[30] One can say that theoretical bond distances are in good overall agreement with measured values, if it is taken into account that the experiment was carried out on a heavily substituted derivative in a molecular crystal.

The variation in bond distances is consistent with the Mills−Nixon effect, which implies shortening of exo-[C(2)−C(3)] bond distances and lengthening of the fused C(1)−C(2) bond relative to a free benzene value.[4] It is interesting to note that the SS-CASSCF$(8,8)^{\pi}$/6-31G* picture amplifies this distortion. Indeed, the Mills−Nixon effect in **1** has two contributions: (a) rehybridization of the carbon junction atoms in the molecular plane and (b) the π-electron density distribution above and below the molecular plane. The latter tries to diminish the interaction between the six-π-electron moiety and the peripheral π-double bond. This is nicely illustrated by the π-bond orders, which assume a low 0.19 value in C(1)/C(2)−C(7)/C(8) bonds and high values (0.74−0.82) in C(2)−C(3), C(4)−C(5), and C(7)−C(8) bonds. The meta [C(3)−C(4) and C(5)−C(6)] bonds possess an intermediate 0.43 value. It follows that the fusion of the cyclobutene ring induces considerable π-bond localization in the aromatic benzene fragment in addition to the in-plane rehybridization effect.

It is interesting to note that benzocyclobutene cannot possibly have a bond-stretched isomer corresponding to the pseudo-cyclic 8π-electron pattern. This was carefully checked by a search involving an artifical stretching of the annelated CC bond to very large bond distances in a parametrical way. By keeping the annelated CC bond distance fixed at a particular value, the rest of the independent structural parameters were optimized at the SS-CASSCF$^{\pi}$/6-31G* level. Subsequently, the single-point HF, SS-CASSCF$(8,8)^{\pi}$, SS-CASPT2$^{\pi}$, and SS-CASPT2$^{(\pi)+\sigma}$ calculations have been executed employing Dunning's correlation consistent cc-pVDZ basis set.[30] The most important result of this is that stretching of the annelated CC bond does not lead to an another isomer and that the same electron configuration remains persistently dominant in the process of a stepwise lengthening of the C(1)−C(2) bond.

The correlation energies, $E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$, and $E(\mathrm{D})^{(\pi)+\sigma}$, of **1** assume 66.9, 24.7, and 581.3 kcal/mol, respectively, as obtained by the cc-pVDZ basis set. Additional cc-pVTZ calculations enable the extrapolation of the estimated correlation energies to their corresponding infinite basis set (IB) values, as described in our earlier paper.[31] This extrapolation yields correlation energies of 66.3, 37.9, and 808.5 kcal/mol, correspondingly. It is noteworthy that the nondynamical π-electron correlation energy is insensitive to the quality of the basis set as observed earlier.[31] In contrast, the dynamical correlation energy is highly sensitive to the flexibility of the basis set as exemplified by $E(\mathrm{D})^{\pi}$ of **1**, which assumes 24.7, 31.5, and 37.9 kcal/mol for cc-pVDZ, cc-pVTZ, and IB sets, respectively. Changes upon the increased quality of the basis sets are even more dramatic for the dynamical correlation energy of all valence electrons within the CASPT2 formalism as evidenced by 581.2, 717.2, and 808.5 kcal/mol, respectively. This finding underlines the importance of extrapolation of the dynamical correlation energy to the complete basis set limit.

It is noteworthy that the correlation energies at the infinite basis set $E(\mathrm{ND})^{\pi}_{\mathrm{add}}$, $E(\mathrm{D})^{\pi}_{\mathrm{add}}$, and $E(D)^{(\pi)+\sigma}_{\mathrm{add}}$ obtained by additivity formulas[31] yield 65.6, 37.1, and 808.9 kcal/mol, respectively. These results are in very good accordance with results of actual ab initio calculations (66.3, 37.9, and 808.5 kcal/mol, above). Particularly interesting is a good agreement obtained for the nondynamical correlation π-electron energy. We have shown previously[12] that the $E(\mathrm{ND})^{\pi}$ correlation energy serves as a qualitative but useful diagnostic tool in examining the anti/aromatic character of planar π systems. In particular, we found, counterintuitively as it is, that $E(\mathrm{ND})^{\pi}_{\mathrm{add}}$ was larger in antiaromatic molecules and smaller in aromatic systems compared to the corresponding open chain π-electron zigzag systems (for a more detailed analysis of this finding, see ref 32). It would

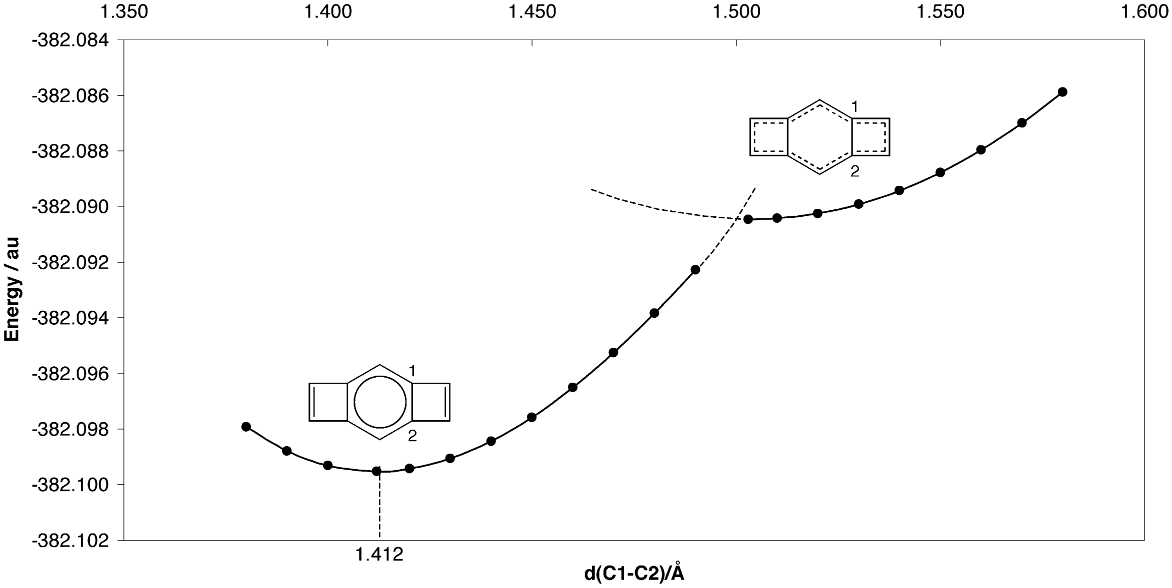
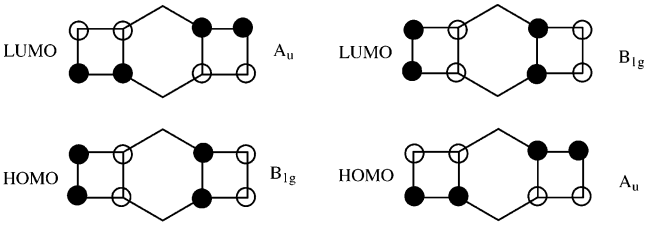


Figure 1. Dependence of the SS-CASSCF(10,10)$^{\pi}$/6-31G* electronic energy of isomers **2** and **3** on the C(1)−C(2) distance.

SCHEME 3



2 **3**

appear, consequently, that benzocyclobutene **1** should be a nonaromatic compound. A qualitative support to this conjecture is offered by the NICS (nucleus independent chemical shift) criterion.[33−36] Employing a simple GIAO-HF/6-31G*//SS-CASSCF(8,8)$^{\pi}$/6-31G* model one obtains that NICS(1) values calculated 1 Å above the centers of six- and four-membered rings are −4.6 and 12.5 ppm, respectively. Because the corresponding values in free benzene and cyclobutadiene are −12.8 and +24.0 ppm, correspondingly, it follows that both fragments retain a portion of their aromatic and antiaromatic character in **1**, respectively. One is tempted to conclude that the antagonistic interplay of stabilizing and destabilizing interactions in this fused bicyclic system should roughly cancel out according to the $E(\mathrm{ND})^{\pi}$ and NICS(1) indices of anti/aromaticity.

3.2. Benzo[1,2:4,5]dicyclobutadiene. This compound is distinctly different from **1** considered so far. The reason behind this is that the two potential bond-stretch isomers **2** and **3** have interconverted HOMO and LUMO orbitals (Scheme 3).

Their corresponding π-electron ground-state configurations are $(B_{3u})^2$ $(B_{3u})^2$ $(B_{2g})^2$ $(A_u)^2$ $(B_{1g})^2$ and $(B_{3u})^2$ $(B_{3u})^2$ $(B_{2g})^2$ $(B_{1g})^2$ $(A_u)^2$, respectively. It appears then that the ground state π-electron configuration of **2** is the first excited state of **3** and vice versa. Apparently, an avoided crossing should occur in the interconversion process. Consequently, one should employ at least the two-state TWS-CASSCF procedure with the subsequent TWS-CASPT2 perturbation calculations. It is instructive, however, to commence with the SS-CASSCF formalism and proceed with a series of stepwise computations involving a parametrically increased C(1)−C(2) bond distance (similar to those performed for **1**), which leads from the structure **2** to its valence isomer **3** (Figure 1). The SS-CASSCF(10,10)$^{\pi}$/6-31G* method suggests that **2** is more stable than **3** by some 5 kcal/mol. The functional dependence of E[SS-CASSCF(10,10)$^{\pi}$/6-31G*] on the C(1)−C(2) bond distance reveals that structure **3** smoothly slides along the curve ending up in the more stable structure **2** without barrier.

TABLE 2: Total Electronic Energies, Involving the Nuclear Repulsion Term (in a.u.), of Molecules 1−3 as well as of the TS for the Interconversion Process 2 → 3 Obtained by Various Theoretical Models[a]

	molecule			
energy	**1**	**2**	TS	**3**
HF/6-31G*	−306.33569	−381.95391		
B3LYP/6-31G*	−308.36034	−384.46237		−384.46618
B3LYP/cc-pVDZ	−308.37945	−384.48651		−384.49062
MP2(fc)/6-31G*	−307.34133	−383.21922		−383.22509
MP2(fc)/cc-pVDZ	−307.39270	−383.27351		−383.28155
SS-CASSCF$(n,n)^{\pi}$/6-31G*	−306.44297	−382.09953		−382.09046
SS-CASPT2$(n,n)^{\pi}$/cc-pVDZ//M_1[b]	−306.50482	−382.17693		−382.17096
SS-CASPT2$^{(\pi)+\sigma}$/cc-pVDZ//M_1[b]	−307.39178	−383.21498		−383.21832
TWS-CASSCF-$(n,n)^{\pi}$/6-31G*	−306.43987	−382.09598	−382.08994[c]	−382.08691
SS-CASPT2$^{\pi}$/cc-pVDZ//M_2[b]	−306.50412	−382.17541	−382.16823[c]	−382.16897
SS-CASPT2$^{(\pi)+\sigma}$/cc-pVDZ//M_2[b]	−307.39369	−383.21721	−383.21380[c]	−382.21979
TWS-CASPT2$^{\pi}$/cc-pVDZ//M_2[b]	−306.50413	−382.17563	−382.16823[c]	−382.16951
TWS-CASPT2$^{(\pi)+\sigma}$/cc-pVDZ//M_2[b]	−307.39370	−383.21927	−383.21380[c]	−383.22425

[a] The number of active π electrons and active orbitals in the CASSCF procedure (n,n) is (8,8) for **1** and for the rest of the systems considered. [b] M_1 = SS-CASSCF$(n,n)^{\pi}$/6-31G*, M_2 = TWS-CASSCF$(n,n)^{\pi}$/6-31G*. [c] C(1)−C(2) = 1.496 Å.

Employing the more appropriate TWS-CASSCF(10,10)$^{\pi}$/6-31G* calculations (Table 2 and Figure 2), however, does not reveal an avoided crossing either. It should be mentioned than in applying the TWS procedure both states are taken into account by equal weight. It is also noteworthy that the structure **2** is still more stable by 5.7 kcal/mol. Particularly important is to emphasize that inclusion of the dynamical correlation of only π electrons does not change the relative stability. More specifically, the TWS-CASSPT2(10,10)$^{\pi}$/cc-pVDZ calculations yield −382.17563 and −382.16951 (in a.u.) for **2** and **3**,

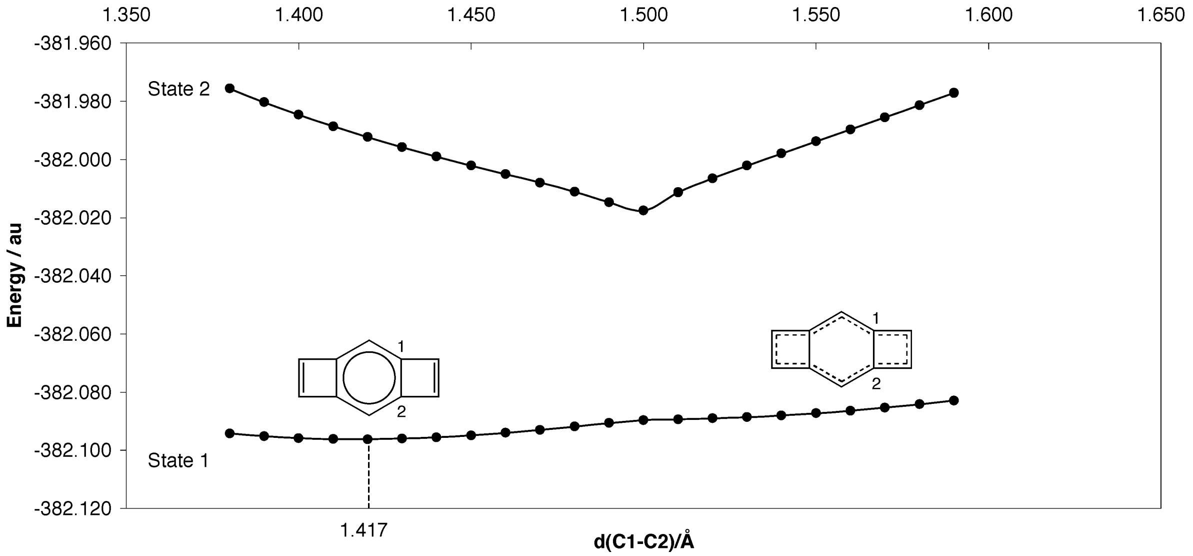


Figure 2. Dependence of the TWS-CASSCF(10,10))$^{\pi}$/6-31G* electronic energy of isomers **2** and **3** on the C(1)−C(2) distance. The energy profile for state **2** indicates interconversion of electron configurations in **2** and **3**.

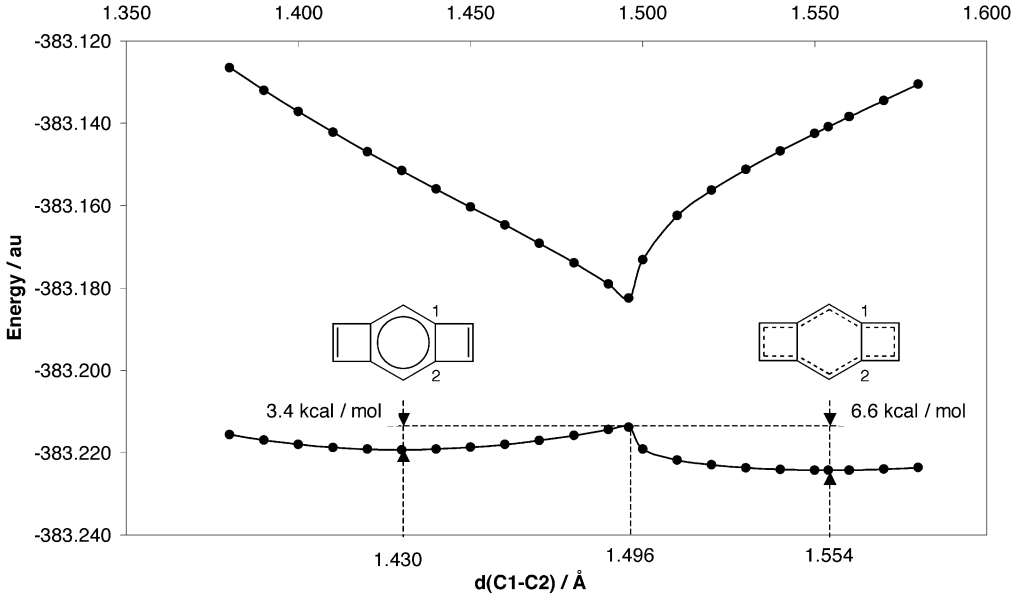


Figure 3. Dependence of the TWS-CASPT2/cc-pVDZ$^{(\pi)+\sigma}$//TWS-CASSCF(10,10)$^{\pi}$/6-31G* electronic energy of isomers **2** and **3** on the C(1)−C(2) distance.

respectively, meaning that **2** is more stable by 3.8 kcal/mol. Hence, the difference is diminished by some 2 kcal/mol. A more reliable answer is obtained, however, by taking into account the dynamical correlation of all valence electrons. Namely, the relative stability is reversed, if the dynamical correlation of σ electrons is included in the total energy (Figure 3). The delocalized structure **3** is then more stable by 3.2 kcal/mol as estimated by TWS-CASPT2(10,10)$^{(\pi)+\sigma}$/cc-pVDZ//TWS-CASSCF(10,10)$^{\pi}$/6-31G* calculations. Obviously, the dynamical correlation energy of σ electrons plays a very important role in phenylenes. The barrier hight relative to **2** and **3** is 3.4 and 6.6 kcal/mol, respectively (Table 2). The C(1)−C(2) distances corresponding to energy minima characterizing isomers **2** and **3** are 1.430 and 1.554 Å, respectively, the latter being extremly large for two carbon atoms in the sp^2 hybridization state. The transition state (TS) should occur around the distance d[C(1)−C(2)] = 1.496 Å (Figure 3). It should be pointed out that TS cannot be accurately identified, because critical points on the energy hypersurfaces cannot currently be calculated by the CASPT2 method. It should be mentioned that the C(1)−C(2) bond distance is strongly coupled with the changes in other bond distances of the molecular perimeter. Consequently, we shall call the point corresponding to d[C(1)−C(2)] = 1.496 Å the transition state only conditionally for the sake of the simplicity. It turns out that the cross section of the PEH exhibits an unphysical cusp in the vicinity of TS. Hence, we tried to improve it by altering the extent of participation of the lower and upper states in the two state calculations. However, the general picture did not change. For example, by giving a weight of 40% to the lower state and 60% to the upper state one obtains that the delocalized isomer **3** is more stable by 2.9 kcal/mol. The TS is higher by 3.6 and 6.5 kcal/mol than isomers **2** and **3**, respectively. The difference between the upper and lower curve at the TS is 19.9 kcal/mol. Similar results are obtained by assuming that the ratio in contributions of the lower and upper state are 60%:40%. It appears that the delocalized **3** is more stable than **2** by 3.4 kcal/mol. The TS is higher than **3** and **2** by 6.8 and 3.4 kcal/mol, respectively, and the difference between the upper and lower states at the TS is 19.7 kcal/mol. Obviously, all of these changes are negligible implying that the unphysical

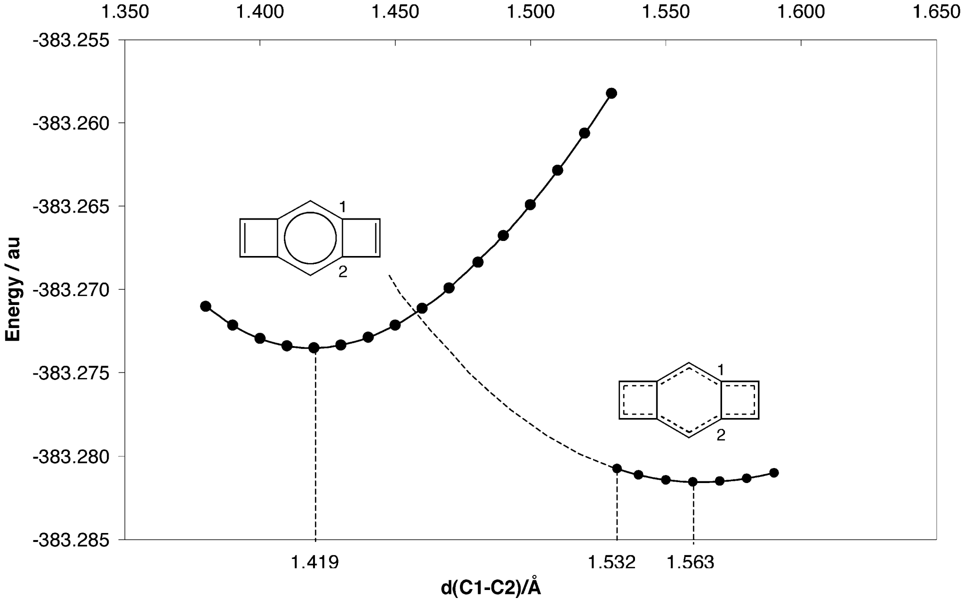


Figure 4. Dependence of the MP2(fc)/cc-pVDZ electronic energy of isomers **2** and **3** on the C(1)−C(2) distance.

TABLE 3: HOMO and LUMO Occupation Numbers along the Bond-Stretch Pathway Characterized by the *d*[C(1)−C(2)] Distance, which Is Parametrically Changed in the Isomerization Process[a]

distance (in Å)	1.430	1.494	1.496	1.498	1.4985	1.499	1.500	1.554
A_u	0.36	0.74	0.79	0.90	1.14	1.18	1.22	1.54
B_{1g}	1.64	1.26	1.21	1.10	0.86	0.82	0.78	0.45
critical points	**2**		TS					**3**

[a] The occupation numbers are obtained by the TWS-CASSCF(10,10)$^{\pi}$/cc-pVDZ//TWS-CASSCF(10,10)$^{\pi}$/6-31G* method.

behavior around the TS is inherent in the TWS-CASPT2 wave functions implying that all conclusions regarding the bond-stretch isomerism should be taken cum grano salis. Undoubtedly, a complete treatment of this problem requires calculations of the high level multireference wave functions.

It is interesting to examine the occupation numbers of natural orbitals obtained by the TWS-CASSCF(10,10)$^{\pi}$/cc-pVDZ//TWS-CASSCF(10,10)$^{\pi}$/6-31G* method. They are given for HOMO and LUMO orbitals, which change the most during the bond-stretch isomerization (Table 3). Perusal of the data reveals that in both isomers a significant admixture of the LUMO orbital occurs. It appears also that the natural populations strongly depend on the C(1)−C(2) distance particularly in the vicinity of the turnover point. At the estimated TS for d[C(1)−C(2)] = 1.496 Å, the population of A_u is still lower than that of B_{1g} (0.79 vs 1.21). The turnover point should take place at the d[C(1)−C(2)] distance slightly lower than 1.4985 Å. The A_u and B_{1g} populations at the latter distance are 1.14 and 0.86, respectively. An approximately equal participation of B_{1g} and A_u orbitals in the TS shows why the single-configuration methods are condemned to fail in describing the bond-stretch isomerization process and in the pursuit of the corresponding isomers, unless an extreme care is exercised.

A good illustration of this failure is provided by the MP2(fc)/cc-pVDZ calculation of the total electronic energy profile E(tot) against the C(1)−C(2) bond-stretch parameter (Figure 4). This model correctly predicts that **3** is a more stable isomer (5.1 kcal/mol) than **2**. However, both isomers are described by separate curves, which should in principle intersect somewhere, or better to say, form an avoided crossing. However, this does not occur within the MP2(fc)/cc-pVDZ formalism. Instead, there is a discontinuous jump from the upper curve to the lower one at d[C(1)−C(2)] = 1.532 Å, implying that the two configurations are abruptly interchanged at this distance. The difference in the total electronic energy between the upper curve (at 1.531 Å) and the lower curve (at 1.532 Å) is 14.3 kcal/mol. For the sake of curiosity, we carried out calculation for d[C(1)−C(2)] = 1.5315 Å, which has shown that this point was already on the lower curve as evidenced by the corresponding total energy −383.28074 au, meaning that it is very close in energy to that obtained for d[C(1)−C(2)] = 1.532 Å (−383.28076 au). It follows that the MP2(fc)/cc-pVDZ model correctly describes both isomers at their equilibrium geometries in a qualitative sense but completely fails in reproducing the transition structure. A good performance of the MP2 model near equilibrium structures stems from the fact that double excitations inherent in the MP2 calculations mimic the multiconfigurational character of the wave functions to an appreciable extent. We have shown earlier, namely, that the correlation energy of valence electrons calculated at the MP2 level ($E(\text{corr})_{\text{MP2}}$) in planar molecules in their ground states and equilibrium geometries is approximately, but very closely, equal to the sum of nondynamical correlation energy of π electrons $E(\text{ND})^{\pi}$ and the dynamical correlation energy of all valence electrons $E(\text{D})^{(\pi)+\sigma}$ obtained by the corresponding CASPT2$^{(\pi)+\sigma}$ calculations.[31] It should be pointed out that the MP2 model is successful in describing the ground states of isomers **2** and **3** because their multiconfigurational character is moderate. This is evidenced by the electron populations of A_u (B_{1g}) MOs, which assume values 0.36 (1.64) and 1.54 (0.45) in **2** and **3**, respectively. A complete breakdown of the MP2 model occurs at the TS, where both A_u and B_{1g} are of almost equal importance (Table 3). Despite that, it is interesting to point out that both B3LYP/cc-pVDZ and MP2(fc)/cc-pVDZ models correctly predict that **3** is more stable than **2**. Moreover, the corresponding difference in stability is 2.6 and 5.0 kcal/mol, respectively, (Table 2) which is in surprisingly good accordance with the TWS-CASPT2$^{(\pi)+\sigma}$//cc-pVDZ//CASSCF(10,10)$^{\pi}$/6-31G* estimate of 3.2 kcal/mol. We note in passing that $E(\mathbf{2}) - E(\mathbf{3})$ is 3.7 kcal/mol by the MP2(fc)/6-31G* calculations.

Let us consider now a very important problem of the isomerization barrier in some more detail. Inspection of Figure

3 reveals that parts of the energy curve around true minima **2** and **3** are very flat implying that their accurate location is not easy to achieve. Moreover, to obtain the correct energy profile for isomerization of the bond-stretch isomers **2** and **3** in spe one has to take into account zero-point vibrational energies (ZPVEs). Intuitively, one would not expect a significant difference in ZPVEs between the ground-state structures of **2** and **3** in view of their additivity property. It was shown by Schulman and Disch et al. that the ZPVE is a multilinear function of the number of participating atoms of each element only.[37,38] Therefore, the ZPVEs of isomers **2** and **3** should be roughly equal. However, because the difference in the total electronic energies between **2** and **3** is very small, we need a more accurate estimate of the ZPVEs. The problem is that it is computationally impossible to optimize molecular geometries and estimate vibrational frequences by the TWS-CASPT2 method. On the other hand, the TWS-CASSCF and MP2 methods, which enable optimization of the molecular structures, do not yield a transition state at all. Some idea about the influence of the ZPVE on the relative stability of isomers **2** and **3** could be derived from the MP2(fc)/cc-pVDZ calculations. One obtains, by employing a customary scaling factor of 0.94, ZPVE(**2**) = 69.6 kcal/mol and ZPVE(**3**) = 71.9 kcal/mol meaning that the zero-point vibrations diminish the energy difference between **2** and **3** to only 2.3 kcal/mol. More importantly, the barrier hight should be lowered too, because the bond-stretch vibration involving C(1)−C(2) bonds would not contribute to the ZPVE due to its imaginary vibration frequency. It is useful to recall in this respect that the ZPVE lowered the barrier height for isomerization of cyclobutadiene and cyclobutadieno-*p*-benzoquinone (**4**) by 2.6 and 2.4 kcal/mol, respectively.[39] Hence, it is plausible to assume that approximately the same would take place in the bond-stretch isomerism **2** → **3**. A decrease in the barrier by 2.5−3.0 kcal/mol due to the ZPVE, would imply a height of only 0.4−1.0 kcal/mol, which would be practically negligible. Therefore, we can draw a tentative conclusion that isomers **2** and **3** are almost degenerate in energy, the latter slightly prevailing in stability. Further, systems **2** and **3** are separated by an almost vanishingly small barrier. Taking into account the approximate nature of all applied theoretical methods employed including TWS-CASPT2$^{(\pi)+\sigma}$ and a well-known fact that a better description of the electron correlation would diminish the transition state energy even further, one is tempted to resolve the bond-stretch dilemma in the case of benzo[1,2:4,5]dicyclobutadiene by stating that this system exists in a form of the fully delocalized 10π electrons system, which represents the pseudo-[10]annulene structure par excellence. This conjecture is consistent with some experimetnal evidence,[13] which will be discussed later. It should be strongly pointed out that all of these conclusions are tentative and that a not quite satisfactory behavior of the TWS-CASPT2$^{(\pi)+\sigma}$ energy in the TS region provides a caveat emptor, which should be kept in mind.

It is quite conceivable, however, that a deliberate choice of various substituents, placed at strategic positions on the molecular perimeter, might significantly stabilize one isomer over the other, thus making it amenable to laboratory preparation. Hence, a deliberate choice of substitutents could lead to two different types of benzo[1,2:4,5]dicyclobuta-diene derivatives. This aspect will be discussed in some more detail in section 3.3.

Before concluding this section, the structural and electronic features of systems **2** and **3** should be briefly discussed. An examination of bond distances in **2** and **3** shows that the Mills−Nixon effect is less pronounced than in **1**, apparently due to the higher symmetry of the benzo[1,2:4,5]dicyclobutadiene system. Consequently, the benzene ring is preserved to a high degree, which is reflected in the corresponding π-bond orders (Table 1). The peripheral four-membered ring π bonds participate very little in the overall conjugation in **2**. In contrast, π-electron density is almost evenly distributed over the perimeter CC bonds in **3**, thus forming a pseudo-[10]annulene system. The π-electron propagation over fused C(1)−C(2) and C(4)−C(5) bonds is weak as evidenced by the rather small π-bond order 0.19. Formation of a cyclic 10π delocalized pattern leads to unusually long C(1)−C(2) and C(7)−C(8) bonds (Table 1). Moreover, the existence of relatively little perturbed 6π and 10π electron cyclic patterns in **2** and **3**, respectively, underlines importance of the much debated Hückel aromaticity rule.[40−42] There is no doubt that π electrons prefer to form an aromatic ribbon around the molecular perimeter and try to avoid the antiaromatic pattern in [4]annuleno[6]annulenes at the same time. However, it is important to keep in mind that the correct electronic structure of **2** and **3** is obtained only by explicitly taking into account the dynamic correlation energy of σ electrons in the TWS-CASPT2$^{(\pi)+\sigma}$ calculations (vide supra). This finding underlines the crucial role of σ electrons in determining the structure and properties of anti/aromatic compounds.

3.3. Substituted Benzo[1,2:4,5]dicyclobutadienes. In this section, we shall discuss some substituted benzo[1,2:4,5]-dicyclobutadienes with particular emphasis on 3,6-di-*tert*-butyl-7,8,9,10-tetraphenylbenzo[1,2:4,5]dicyclobutadi-ene, because it was synthesized by Toda and Ohi[43] and examined by X-ray structural measurements by Boese et al.[13] Model compounds for possible bond-stretch isomers of BDCB will be denoted by **2*x*** and **3*x***, respectively, where $\boldsymbol{x} = \alpha, \beta, \gamma$, and ϵ. Here, the *t*-Bu groups were replaced by the CH_3 groups in our calculations for the sake of simplicity. Such a simplification is expected to have a very minor effect on the structure (except on the C(3)−*t*-Bu bond distance) and relative stability of the isomers. In addition, 4,5,9,10-tetraethenyl derivatives **2*β*** and **3*β*** and several other benzo[1,2:4,5]dicyclobutadiene substituted by a variety of donor and/or acceptor groups will be considered (Figure 5). They are studied by the MP2(fc)/cc-pVDZ and B3LYP/cc-pVDZ models, because more sophisticated theoretical methods are not feasible in the complex systems **2α**−**2ϵ** and **3α**−**3ϵ**. Although the MP2 and B3LYP single-determinant formalisms cannot satisfactorily describe the isomerization process, it is expected that the relative stability of the potential bond-stretch isomers is correctly reproduced in a semiquantitative sense. The energy difference between the parent compounds **2** and **3** obtained at the same theoretical level will serve as a useful hint in this respect. The characteristic structural results are collected in Table 4.

We shall commence discussion with the structural parameters of 3,6-di-*tert*-buthyl-7,8,9,10-tetraphenylbenzo[1,2:4,5]dicyclobutadiene denoted by **2α** and **3α** in Figure 5. Comparison with the measured X-ray data[13] undoubtedly shows that they belong to the structure **3α**. Our results are essentially in agreement with that of Boese et al.[13] obtained by the B3LYP/6-31G* calculations. It follows also that accordance between B3LYP/cc-pVDZ C−C bond distances and the measured values is reasonably good. A notable exception is given by the C(6)−*t*-Bu bond, which is considerably longer in the real molecule due to a larger repulsion of the bulky *t*-Bu group with the molecular backbone. Also, the bond distance between the C(7) atom and the phenyl group is experimentally lower by 0.029 ± 0.005 Å. Whether this is a consequence of the crystal packing forces not taken

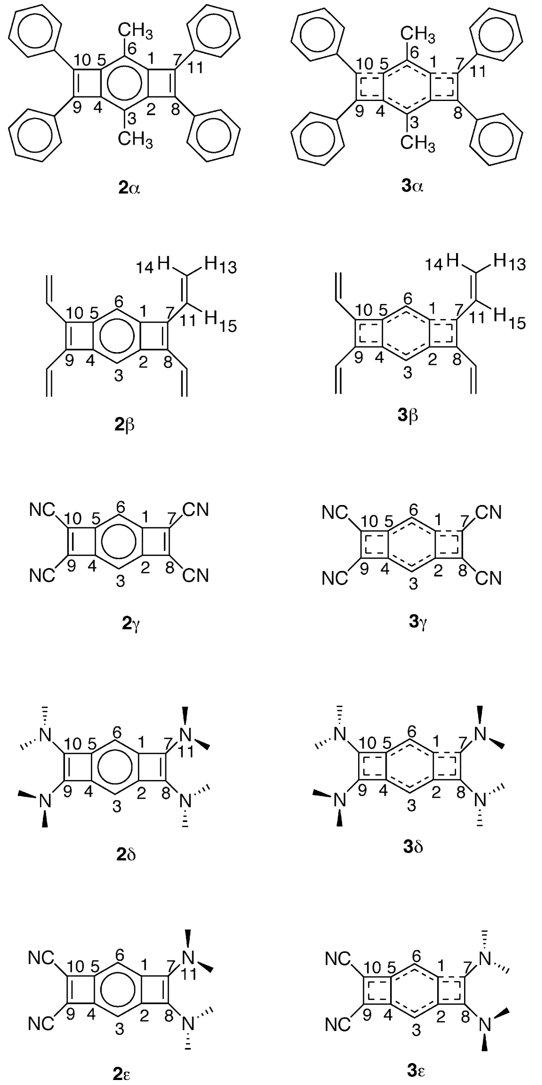
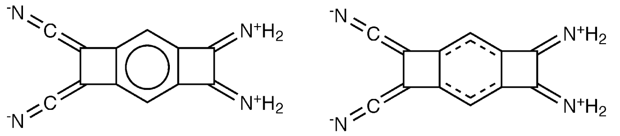


Figure 5. Schematic representation of some polysubstituted potential bond-stretch isomers.

into account in the calculations remains an open question. It is noteworthy that the repulsion between the phenyl rings contributes to the preference of the **3α** pattern over **2α** electronic structure (vide infra). Geometries obtained by the MP2(fc)/6-31G* calculations are in good accordance with B3LYP/cc-pVDZ results and the measured value of **3α** (Table 4).

A very interesting system is given by 7,8,9,10-tetraethenyl derivatives **2*β*** and **3*β***, which was selected by Boese at al[13] as a model compound for the synthesized compound **3α**. Our B3LYP/cc-pVDZ results compare favorably with the bond distances of **3*β*** calculated by the B3LYP/6-31G* model.[13] However, the problem is that 7,8,9,10-tetraethenyl is the wrong model, because our computations show that **2*β*** is more stable than **3*β*** (vide infra). Moreover, the present B3LYP/cc-pVDZ calculations indicate that the π-electron conjugation effect between the vinyl fragment and the main molecular framework is much more pronounced than for the phenyl moiety in **3α** (or **2α**) as evidenced by the rather short C(7)−C(11) distance (1.438 Å) in **3*β***. The reason behind this is the fact that phenyl groups attached to the same double bond (C(7)=C(8)) in **2α** and **3α** are paralelly rotated around C(7)−C(11) and C(8)−C(17) bonds by 32°. This amount of nonplanarity is certainly responsible for a significant reduction in the conjugation interaction. In contrast, the vinyl groups in **2*β*** and **3*β*** are coplanar, enabling optimal π conjugation.

SCHEME 4



2ε' **3ε'**

A comparison of tetrasubstituted molecules involving π-electron withdrawing and donating CN and NH_2 groups, respectively, reveals that the only difference in the bond distances along the series **2α**−**2*δ*** is found in the C(7)−C(8) bond, which decreases along the series. Apparently, there is a strong resonance with the cyano-groups and the formation of $=C=N^-$ fragments and back-donation of π electrons by the NH_2 groups, which introduces a double bond character in the $=N^+H_2$ moieties despite pyramidal nitrogen atoms. The latter is conveniently calculated according to a formula:[44]

$$(DP)\% = [360 - \sum_{i=1}^{3}\alpha_i]/0.9 \qquad (4)$$

where DP stands for a degree of pyramidalization (in %) and the summation is extended over the three sharp bond angles α_i of the apical nitrogen. It appears that the degree of pyramidalization in **2*δ*** and **3*δ*** is 30% and 27%, respectively. The most interesting system is provided by a combination of CN and NH_2 groups, as in **2*ε*** and **3*ε*** (Figure 5). Their structural parameters are consistent with a strong charge-transfer donor−acceptor interaction illustrated by Scheme 4, where both **2*ε*′** and **3*ε*′** represent a collection of two principal donor−acceptor resonance structures. This interaction is reflected in the diminished degree of pyramidalization of nitrogens, which assume 26% and 13.3% in **2*ε*** and **3*ε***, respectively.

The relative stabilities of the potential isomers $\Delta E(\mathbf{2x} - \mathbf{3x})$, where $\mathbf{x}$ stands for α, β, γ, and ϵ, are of particular interest. They are given in Table 5. Perusal of the results shows that the fully delocalized structures **3*x*** are always more stable with one notable exception: the 7,8,9,10-tetraethenyl derivative is the only compound where the more localized structure **2*β*** has a lower energy than the fully delocalized structure **3*β***. A particularly striking difference in stability is found in a donor−acceptor derivative ϵ, where **3*ε*** is more stable by 16−17 kcal/mol than **2*ε***. It is also noteworthy that the MP2(fc)/6-31G* method predicts much larger difference in stability $E(\mathbf{2\alpha}) - E(\mathbf{3\alpha}) = 11$ kcal/mol than the B3LYP/cc-pVDZ approach. To summarize, it would be of great interest to synthesize some of these compounds and submit them to X-ray examinations.

The HOMO−LUMO gaps between two different structures (“isomers”) provide some information about the existence of a barrier in the isomerization process. For this purpose, we give in Table 5 $\Delta[E(\mathrm{LUMO}(\mathbf{2x}))-E(\mathrm{HOMO}(\mathbf{3x}))]$ values and vice versa, which all possess the same symmetry labels necessary for their mixing−that is to say B_{1g} for HOMO and A_u for LUMO in partially localized derivatives of **2** and the opposite in the fully delocalized derivatives of **3**. The orbital energy differences given indicate that the largest barrier can be expected for the parent systems **2** and **3**. However, calculations described in section 3 show that the barrier height is practically negligible. Extending this argument to other systems depicted in Figure 5, one can say that the barrier for isomerization is not expected implying that fully delocalized molecules **3*x*** ($\mathbf{x} = \alpha, \gamma, \delta$, and ϵ) should be prone to chemical synthesis. The only system exhibiting a partially localized structure, which could be perhaps amenable to preparation is **2*β***. It should be mentioned that all

TABLE 4: Characteristic Bond Distances in Substituted Benzo[1,2:4,5]dicyclobutadienes as Obtained by MP2(fc)/cc-pVDZ and B3LYP/cc-pVDZ Models (in [Å])[a]

molecule	C(1)−C(2)	C(2)−C(3)	C(1)−C(7)	C(7)−C(8)	C(6)−X[c]	C(7)−Y[c]
2α						
B3LYP	1.404	1.404	1.545	1.376	1.458	1.509
MP2	1.409	1.400	1.533	1.380	1.504	1.451
2β						
B3LYP	1.409	1.398	1.531	1.383	1.091	1.431
MP2	1.423	1.406	1.534	1.397	1.094	1.436
2γ						
B3LYP	1.404	1.395	1.539	1.370	1.090	1.409
MP2	1.418	1.403	1.540	1.386	1.094	1.417
2δ						
B3LYP	1.404	1.400	1.535	1.366	1.092	1.396
MP2	1.417	1.406	1.536	1.379	1.095	1.403
2ϵ						
B3LYP	1.420	1.388	1.519	1.373	1.090	−
MP2	1.426	1.400	1.525	1.385	1.094	−
3α						
B3LYP	1.534	1.399	1.409	1.489	1.457	1.508
MP2	1.523	1.396	1.411	1.484	1.504	1.449
	(1.540(5))[b]	(1.407(5))[b]	(1.412(5))[b]	(1.471(5))[b]	(1.524(5))[b]	(1.479(5))[b]
3β						
B3LYP	1.531	1.394	1.410	1.487	1.091	1.438
MP2	1.530	1.402	1.423	1.494	1.096	1.444
3γ						
B3LYP	1.538	1.392	1.403	1.482	1.091	1.410
MP2	1.537	1.399	1.418	1.489	1.095	1.418
3δ						
B3LYP	1.588	1.395	1.396	1.470	1.094	1.390
MP2	1.560	1.401	1.408	1.475	1.097	1.397
3ϵ						
B3LYP	1.523	1.381	1.420	1.449	1.091	
MP2	1.551	1.413	1.400	1.497	1.096	

[a] Additional structural parameters for asymmetrically substituted systems **2ϵ** are as follows: *d*[C(3)−C(4)] = 1.409 (1.410), *d*[C(4)−C(5)] = 1.389 (1.409), *d*[C(4)−C(9)] = 1.545 (1.545), *d*[C(9)−C(10)] = 1.369 (1.386), *d*[C(7)−N] = 1.387 (1.395), and *d*[C(9)−N] = 1.408 (1.417) in Å, where MP2 results are given within parentheses. The corresponding values in **3ϵ** are 1.406 (1.386), 1.541 (1.540), 1.388 (1.429), 1.522 (1.468), 1.362 (1.347), and 1.407 (1.420) in Å, respectively. Optimizations of the **2α** and **3α** at the MP2 level are carried out by using 6-31G* basis set. [b] Experimental X-ray bond distances.[13] [c] Substituents X and Y are defined in Figure 5.

of these predictions should be taken with a due caution in view of the extreme simplicity of the HOMO−LUMO argument and approximate nature of the B3LYP/cc-pVDZ method. However, a close agreement between B3LYP/cc-pVDZ and MP2(fc)/cc-pVDZ results with the TWS-CASPT2(10,10)$^{(\pi)+\sigma}$/cc-pVDZ//TWS-CASSCF(10,10)$^{\pi}$/6-31G* estimate of the difference in stability of **2** and **3** (vide supra) is both gratifying and encouraging.

4. Concluding Remarks

The present calculations illustrate the fact that the bond-stretch isomerism is a very elusive phenomenon, if it exists at all.[11] It definitely does not occur in benzocyclobutene (**1**). Benzo[1,2:4,5]dicyclobutadiene is a much better candidate, but unsubstituted isomers **2** and **3** seem to have almost the same total energy including the ZPVE contribution, being separated by an approximately vanishing potential energy barrier. Because **3** is energetically slightly more favorable, we are inclined to conclude that benzo[1,2:4,5]dicyclobutadiene exists in a form of fully delocalized 10π electrons extended over the CC perimeter bonds. Consequently, **3** represents a pseudo-[10]-annulene system par excellence, because the π-electron conjugation over fused CC bonds is weak, as evidenced by a rather small π-bond order 0.19. Despite the fact that **2** and **3** tend to form 6π and 10π electron delocalized patterns within the benzo[1,2:4,5]dicyclobutadiene framework, it should be stressed that their correct electronic structure is obtained only after explicit account of the dynamical correlation energy of σ electrons within the TWS-CASPT2$^{(\pi)+\sigma}$ formalism. This finding emphasizes the importance of σ electrons in determining the structure and properties of anti/aromatic molecules. It should be strongly

TABLE 5: Total Electronic Energies (a.u.), HOMO, LUMO Energies (a.u.), and Relative Stabilities of Potential Bond-Stretch Isomers (in kcal/mol)[a]

method	total electronic energies		Δ(**2*x***−**3*x***)	Δ(LUMO(**2*x***)−HOMO(**3*x***)) Δ(LUMO(**3*x***)−HOMO(**2*x***))
	E(**2**)	*E*(**3**)		
B3LYP	−384.48651	−384.49062	2.6	
MP2	−383.27351	−383.28155	5.0	
HOMO	−0.16370	−0.16689		58.3
LUMO	−0.07397	−0.07194		57.6
	E(**2**α)	*E*(**3**α)		
B3LYP	−1387.43351	−1387.43873	3.3	
MP2	−1382.84264	−1382.86036	11.1	
HOMO	−0.15233	−0.15543		43.7
LUMO	−0.08572	−0.08167		44.3
	E(**2**β)	*E*(**3**β)		
B3LYP	−694.15240	−694.14121	−7.0	
MP2	−691.93024	−691.92776	−1.6	
HOMO	−0.15997	−0.15556		40.1
LUMO	−0.09163	−0.09639		39.9
	E(**2**γ)	*E*(**3**γ)		
B3LYP	−753.48667	−753.49233	3.6	
MP2	−751.31312	−751.32712	8.8	
HOMO	−0.23784	−0.24291		46.8
LUMO	−0.16833	−0.16507		45.7
	E(**2**δ)	*E*(**3**δ)		
B3LYP	−605.93762	−605.95251	9.3	
MP2	−604.10875	−604.13024	13.5	
HOMO	−0.10820	−0.10923		50.0
LUMO	−0.02950	−0.01611		57.8
	E(**2**ϵ)	*E*(**3**ϵ)		
B3LYP	−679.72094	−679.74662	16.1	
MP2	−677.71784	−677.74462	16.8	
HOMO	−0.16226	−0.17650		34.7
LUMO	−0.12118	−0.09183		44.2

[a] The HOMO−LUMO gaps of MOs active in the isomerization process are also given (in kcal/mol). HOMO and LUMO energies are calculated by the B3LYP/cc-pVDZ method. ***x*** stands for α, β, γ, and ϵ.

pointed out that TWS-CASPT2$^{(\pi)+\sigma}$ formalism does not offer a quite satisfactory picture around the transition state region for the bond-stretch isomerization process. Hence, the final word on the existence of the bond-stretch isomers **2** and **3** should be given by the high level multireference calculations.

Finally, B3LYP and MP2 calculations indicate that elusive substituted pseudo-[10]annulenes might be prone to laboratory preparation in the form of a number of judiciously selected derivatives. In contrast to all other compounds considered herein, only tetravinyl substitution should facilitate isolation of the localized **2*β*** form. Particularly strong π delocalization over the molecular perimeter and concomitant stabilization is expected in the donor−acceptor derivative **3ϵ**, where the[10]annulene π-electron pattern should be pronounced the most.

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