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Retro [2 + 2 + 2] Ring Opening in Tricyclobutabenzene Derivatives. Thermochemistry and Reaction Barriers. A Theoretical Hybrid Density Functional Study

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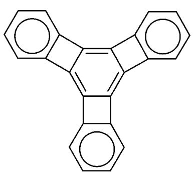
The starting materials, transition states, and products of the concerted retro [2 + 2 + 2] ring-opening reactions of several tricyclobutabenzene derivatives substituted by double-bonded substituents were calculated at the B3LYP/6-31G* theoretical level. It was found that the geometries of the products (cyclododecatriyne derivatives) are governed by the electronegativity of the substituents and hyperconjugation effects. The transition-state geometries of all the derivatives are similar. It was found that the retro [2 + 2 + 2] ring-opening reactions are endothermic (ca. 30−85 kcal mol^{-1}, depending on the substituents) with high barriers, ranging between ca. 95 and 115 kcal mol^{-1}. It is predicted that the tricyclobutabenzene derivatives under study will be stable when prepared and that they can be made by [2 + 2 + 2] intramolecular ring closure of the respective cyclododecatriyne derivative, especially with the use of transition metals as mediators or catalysts.

Introduction

Strained aromatic compounds have been a subject of basic research for more than 70 years. The idea of two basic phenomena in organic chemistry—strain and aromaticity—being present in one compound has triggered the research, aiming to understand the two concepts and their mutual interplay. In the mid-1980s, this topic experienced revival, triggered mainly by two findings. One was that of Shaik et al. that suggested that the symmetric structure of benzene is an outcome of the σ frame preference, whereas the π frame is more stable when localized.[1] The second was the synthesis of the "star"-phenylene (**1**) by Vollhardt and co-workers.[2] This system showed for the first time a cyclohexatriene moiety. The field has experienced a large number of theoretical and experimental studies[3] that were aimed to understand the factors controlling the structure and reactivity of strained aromatic compounds, including our own theoretical[4] and experimental[5] contributions.



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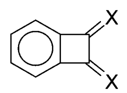
Recently, we have studied the geometries of **2**−**4** in order to understand how exocyclic double-bonded substituents affect the geometries of the central six-membered rings in tricyclobutabenzene derivatives.[4c] The availability of an efficient synthetic method for **5**[5b]



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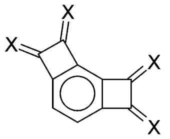

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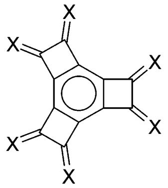

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a: X=BH; **b**: X=CH$_2$; **c**: C=NH; **d**: X=O

principally allows the synthesis of **4b** and **4d**. Indeed, we have recently shown that **2b** and **2d** can be prepared

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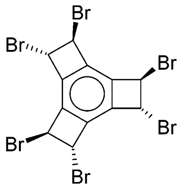
from **6**.[6] The question that triggered the study presented in this paper is how stable these compounds are. It has been shown that **2d** can photochemically open to the bisketene **7**,[7] but it is thermally stable. Our own experience with cyclobutabenzenes and tricyclobutabenzenes suggests that these compounds are relatively stable, and theoretical calculations suggest that the activation energy for isomerization of tricyclobutabenzene into hexaradialene is similar to that of the cyclobutabenzene−*o*-quinodimethane isomerization.[8] There is, however, one process that is specific to the tris-annulated system (to yield a cyclic compound), which is the retro [2 + 2 + 2] ring opening to the respective cyclododecatriyne.[9] It has been shown that **1** (as well as its hexahydro derivative)[10] undergoes this process although the activation barrier is high (judging by the reaction conditions).[2] In this paper, we study the reaction barriers and thermochemistry of the reactions described in eq 1.For comparison, we also present the process described in eq 2 that was demonstrated experimentally.[2]



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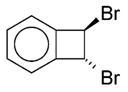

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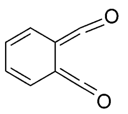

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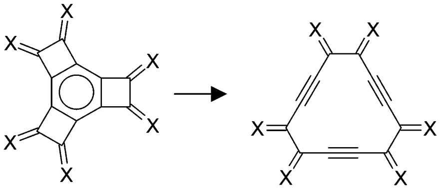
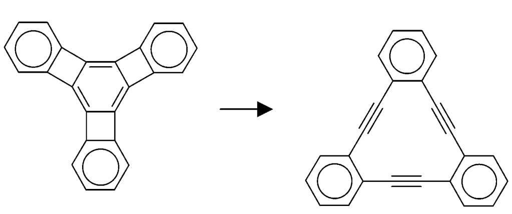


4 **8** (1)

a: X=BH; **b**: X=CH$_2$; **c**: C=NH; **d**: X=O



1 **9**

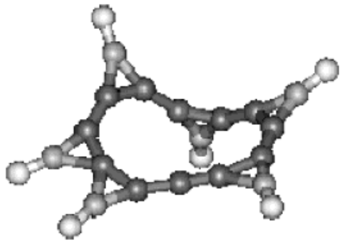
TABLE 1. Energy Differences (kcal mol^{-1}) between Fully Optimized and D_{3h} Symmetry of 8 (Numbers are E(FO) − E(D_{3h})

	$\Delta E_{\mathrm{elect}}$	$\Delta(E_{\mathrm{elect}} + \mathrm{ZPE}^{a})$	ΔH^{b}	ΔG^{b}
8b	3.4	2.6	1.2	6.4
8c	0.4	0.4	−1.3	5.5
8d	0.4	0.4	−1.3	5.6

[a] Electronic energy corrected for zero point energy. [b] Uncorrected at 25 °C,

Methods

All the calculation were carried out with the Gaussian 98[11] package of programs. The B3LYP/6-31G* hybrid density functional theoretical level was used. This level has been shown to accurately describe energies and geometries of systems such as those under study. All the systems (starting materials, products, and transition states) underwent geometry optimization within D_{3h} symmetry. Next, analytical frequencies were calculated for all the minima and transition states. All the derivatives of **4** and their transition states for the retro [2 + 2 + 2] reaction described in eq 1 were found to be real minima and transition states (i.e., $N_{\mathrm{imag}} = 0$ and 1, respectively). None of the D_{3h} **8** are minima on the potential surface.Compound **8a** has four imaginary frequencies, and **8b**−**d** have three imaginary frequencies each. These systems were therefore optimized again without symmetry restrictions. Compound **8a** is not a minimum on the potential surface and isomerizes to **10**, which is 163.5 kcal mol^{-1} more stable than **8a**. However, the energy differences between D_{3h} and C_1 symmetries in **8b**−**d** are small (Table 1), and therefore, all the discussion below will be based on the D_{3h} symmetric systems. In eq 2, **1**, **9**, and the transition state between the two are of D_{3h} symmetry.



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Geometries. The geometries of **1**, **4**, and **9** were discussed previously.[4,12] We will therefore limit the discussion to the geometries of **8** and the transition-state structures of eq 1 (**8TS**).

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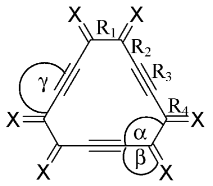
TABLE 2. Main Geometrical Parameters (Å and deg) of 8



	R_1	R_2	R_3	R_4	α	β	γ
8a	1.4827	1.4279	1.2235	1.4027	120.0	106.7	180.0
8b	1.5037	1.4285	1.2152	1.3502	117.7	118.9	177.7
8c	1.5181	1.4393	1.2157	1.2816	117.2	124.0	177.2
8d	1.5525	1.4542	1.2146	1.2102	117.6	122.7	177.6

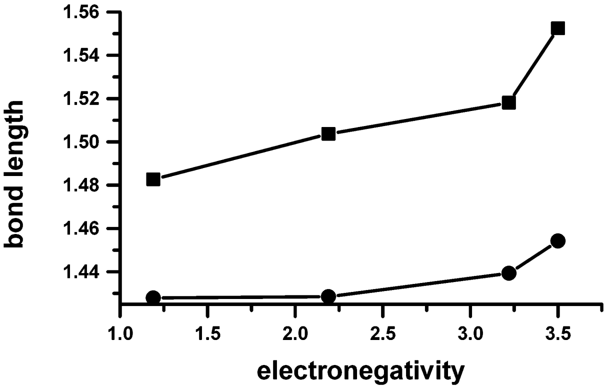


FIGURE 1. R_1 (■) and R_2 (●) in **8** as a function of electronegativity of =X. Electronegativity values taken from reference.

Table 2 lists the main geometrical parameters of **8**. It can be observed that on going along the first row of the periodic table (i.e., BH → O) there is a continuous change in some of the parameters. For example, R_1 (the bond between the two C(=X) moieties) lengthens on going from **8a** to **8d** by 0.073 Å, and the adjacent bond (R_2) lengthens by 0.0263 Å. This cannot be due to cyclic conjugation (aromaticity) effects. Thus, **8** can be viewed as a [12]-annulene derivative, all carbon atoms in sp^2 hybridization, and therefore conjugated. As the p_π orbital of the C(=X) carbons become less populated, the system should have become more aromatic and less antiaromatic. As a result, shorter single bonds (i.e., R_1 and R_2) and longer triple bonds (R_3) should have been found on going from the most electronegatively substituted system (**8d**) to the least electronigatively substituted system (**8a**). Indeed, the p_π populations of the C(=X) atoms behave as expected and are 1.09, 0.98, 0.92, and 0.81 electrons in **8a**, **8b**, **8c**, and **8c**, respectively. However, the bond lengths behave exactly the opposite from what is expected on the basis of this argument. The question is therefore what controls the geometries of **8**.

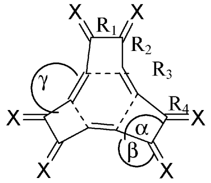
Figure 1 shows R_1 and R_2 as a function of the electronegativity of X. Clearly, as X becomes more electronegative R_1 and R_2 lengthen. The π overlap does not follow the bond length trend. Thus, the π populations in R_1 are 0.035, 0.161, 0.113, and 0.013 electrons in **8a**, **8b**, **8c**, and **8d**, respectively, and 0.214, 0.236, 0.219, and 0.210 electrons, respectively, in R_2. Thus, the R_1 and R_2 lengthening when going from **8a** to **8d** results simply from the fact that electronegative substituents leave less bonding electrons, i.e., a pure σ effect. Note, however, that there must be an additional effect, as R_1 in **8d** is longer than expected from the monotonic lengthening and so are R_2 in **8c** and **8d**. This comes from hyperconjugation. Table 3 lists the NBO interaction size between the lone pairs and X−H bonds and R_1 and R_2 in **8b**−**d** (**8a** has no such interaction). Clearly, the hyperconjugation between the oxygen substituents and R_1 is by far the largest, causing an additional (to the electronegativity effect) elongation of this bond. For R_2, an efficient hyperconjugation is found between the oxygen (in **8d**) and the nitrogen (in **8c**) lone pairs and R_2 in the respective systems, causing R_2 in these molecules to be longer than it should have been by the electronegativity effect alone. In conclusion, the geometries of systems **8** are determined mainly by σ and hyperconjugative effects, although it is a conjugated annulenic system.

TABLE 3. Hypercongugatoin Magnitudes (NBO) in 8

system	donor	acceptor	interaction[a]
8b	C−H	R_1	6.4
8c	LP[b](N)	R_1	1.9
8c	N−H	R_1	0.7
8d	LP[b](O)	R_1	23.5
8b	C−H	R_2	5.5
8c	LP[b](N)	R_2	13.2
8c	N−H	R_2	9.2
8d	LP[b](O)	R_2	21.9

[a] In kcal mol^{-1}. [b] Lone pair.

TABLE 4. Main Geometrical Parameters (Å and deg) of 8TS



	R_1	R_2	R_3	R_4	α	β	γ
8aTS	1.4721	1.4561	1.2579	1.4044	101.3	119.7	161.3
8bTS	1.4826	1.4499	1.2534	1.3431	101.5	127.6	161.5
8cTS	1.4992	1.4666	1.2528	1.2720	101.4	131.4	161.4
8dTS	1.5402	1.4850	1.2476	1.2011	101.7	128.3	161.7

TABLE 5. Energies of Reaction and of Activation for Eq 2

	ΔE_{elec}	ΔE_{elec} + ZPE[a]	ΔH^b	ΔG^b
ΔE^c	−12.6	−14.4	−13.1	−16.0
$\Delta E^{\ddagger c}$	60.3	57.2	58.0	56.4

[a] Zero point energy corrected electronic energy. [b] At 25 °C. [c] In kcal mol^{-1}.

The transition-state structures of the retro [2 + 2 + 2] process described in eq 1 are given in Table 4. The structures indicate that all the transition states are at about the same location along the reaction coordinates; namely, the substituents do not cause earlier or later transition states. Thus, for example, the bonds that are triple in **8** are all approximately the same lengths in the transition states, and so are the (X=)C−C≡C and the (X=)C−C(=X)−C(≡) bond angles. The structures are more similar to **8** than to **4**, as can be expected from highly endothermic reactions (see below).

Energies. Since **1** has been previously prepared, reaction 2 was experimentally carried out,[2] and some derivatives of **4** are principally synthetic feasible, it is important to discuss the enthalpy and free energy of activation as well as the thermochemistry of reactions 1. To calibrate our results, we have studied reaction 2 (that was studied experimentally) at the B3LYP/6-31G* theoretical level. The energies are given in Table 5.

The calculation seems to fit the qualitative experimental data. Thus, the reaction that is calculated to be exothermic occurs experimentally, but **1** is stable in neat solution at 400 °C (half-life about 10 min) and has to undergo flash pyrolysis at 700 °C in order to be converted to **9**, a result that is coherent

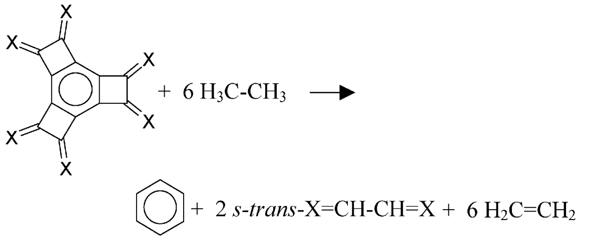
TABLE 6. Energies of Reaction and Activation (kcal mol^{-1}) for Eq 1

	X = BH	X = CH$_2$	X = NH	X = O
ΔE_{elec}	34.6	47.4	64.5	85.6
ΔE_{elec} + ZPE^a	30.3	45.1	62.7	82.6
ΔH^b	30.5	44.8	62.3	82.8
ΔG^b	29.6	46.0	63.6	83.4
$\Delta E^{\ddagger}_{\mathrm{elec}}$	100.4	97.2	105.2	116.8
$\Delta E^{\ddagger}_{\mathrm{elec}}$ + ZPE^a	96.1	93.4	101.8	112.4
$\Delta H^{\ddagger b}$	97.4	94.2	102.6	113.5
$\Delta G^{\ddagger b}$	94.2	92.2	100.4	110.3

^{a} Zero point energy corrected electonic energy. ^{b} At 25 °C.

with an activation energy of ca. 60 kcal mol^{-1} calculated for eq 2.[13]

Table 6 lists the reaction energies and activation energies for eq 1. In contrast to the analogous ring opening of "star"-phenylene (eq 2), the reactions are highly endothermic, ranging from ca. 30 kcal mol^{-1} for X = BH to more than 80 kcal mol^{-1} in X = O derivative (eq 1, Table 6). The differences between the derivatives may be caused by the reactants becoming more stable when going from **4a** to **4d** or the products that become less stable on going from **8a** to **8d**. Equation 3 measures the stability of **4** relative to the free X=CH−CH=X fragment.



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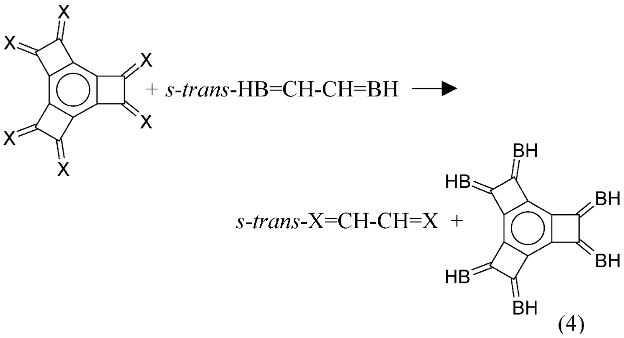


(4)

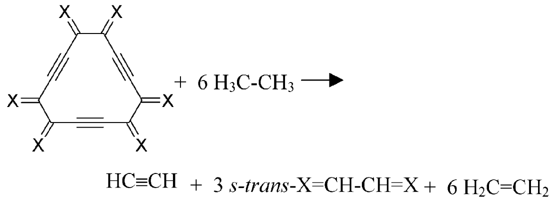
Since this is not an isodesmic reaction, the results may be erroneous, but the difference between two such reactions (eq 4) should yield dependable numbers. All reactions 3 are highly exothermic (Table 7), but the exothermicity drops on going from X = BH to X = O. Thus, the more electronegative X is, the more stable is the tricyclobutabenzene derivative **4**. But this is not the entire reason for the results of eq 1 (Table 6). Equations 5 and 6 (Table 8) measure the relative stability of **8** vs the free X=CH−CH=X fragment and vs **8a**, respectively. Here again, all the reactions are exothermic, but the stability order changes now, **8a** being the most stable. Thus, it may be concluded that the trend observed in eq 2 results from both the increased stability of the starting material and the decreased stability of the product on X becoming more electronegative.

TABLE 7. Energies (in kcal mol^{-1}) for Eqs 3 and 4

	X = BH	X = CH$_2$	X = NH	X = O
ΔE_{elec} (eq 3)	−281.7	−280.5	−272.2	−248.4
ΔE_{elec} (eq 4)	0.0	1.2	9.5	33.3

TABLE 8. Energies (in kcal mol^{-1}) for Eqs 5 an 6

	X = BH	X = CH$_2$	X = NH	X = O
ΔE_{elec} (eq 5)	−145.7	−157.5	−166.2	−163.5
ΔE_{elec} (eq 6)	0.0	−11.8	−20.5	−17.8



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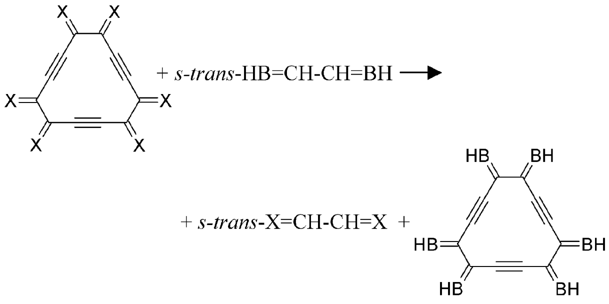

(6)

All reactions 2 have high barriers that range from ca. 90 to ca. 110 kcal mol^{-1}. This suggests that the transition states, being at about the same location along the reaction coordinate (see above), manifest the increasing stability of the starting material and decreasing stability of the products on going from X = BH to X = O. In any event, the activation barriers are too high for a reaction to occur under normal conditions, and are certainly higher than the alternative reaction of **4**, namely, the isomerization to the respective hexaradialene derivatives.[14]

Conclusions

The retro [2 + 2 + 2] ring opening reactions of the different derivatives of **4** to give the respective **8** are all highly endothermic and have high activation barriers. Thus, the calculations predict that **4**, when experimentally prepared, will be stable toward this isomerization. However, the calculations suggest that a feasible synthetic approach for preparing **4** is by the intramolecular [2 + 2 + 2] ring closure of **8**. The reaction barriers for

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(13) The activation ZPE corrected electronic energy for the analogous process benzene → three acetylene molecules is 189.8 kcal mol^{-1} at B3LYP/6-311+G** and 188.4 kcal mol^{-1} at MP4/6-311G*//MP2/6-31G*, which is considerably larger than the processes studied here. Also, the endothermicity of the process is much lager (ca. 139.5 kcal mol^{-1}). See Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655. This may be regarded as a perfect example for the Hammond postulate, and the differences between benzene and the systems studied here are probably a result of difference in strain release and entropy of activation and of reaction.

(14) The activation barrier for cyclobutabenzene → *o*-quinodimethane isomerization is 40.0 kcal mol^{-1} (Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741) but the product is less stable by 13.1 kcal mol^{-1} (thermochemical data taken from *NIST Standard Reference Database No. 69*, February 2000 Release. http://webbook.nist.gov/chemistry). (b) Our calculations (that reproduces the activations energy and the thermochemistry mentioned above within 0.2 kcal mol^{-1}) show that the barrier for the tricyclobutabenzene → hexaradialene isomerization is similar (see footnote).

such an intramolecular cyclization are not small (for example, 46−50 kcal mol^{-1} for the CH_2 derivative and 27−31 kcal mol^{-1} for the oxo derivative), but probably could be overcome by the use of transition metals as mediatos or catalysts.[15]

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Supporting Information Available: All the geometries in the form of z-matrix or Cartesian coordinates and total energies of **1**, **4**, **8**(D_{3h}), **8**(C_1), **9**, **10**, **8TS**, **9TS**, benzene, *s-trans*-X=CH−CH=X (X = BH, CH_2, NH, O), ethylene, ethane, and acetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Several complexes of **9** with metals are known. With Ni (Ferrara, J. D.; Tanaka, A. A.; Fierro, C.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2089. Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719) that even serves as a CO detector (Chemical colorimetric sensor for detection of carbon monoxide in air. Youngs, W. J.; Tessier, C. A.; Kinder, J. D. U.S. Pat. Application US 91-701039 19910516, 1992). With Cu^I (Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1987**, *6*, 676) and with Co (Djebli, A.; Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1988**, 548). As **9** is more stable than **1**, these are stable complexes. However, it is possible that these metals will catalyze the reaction **8** → **4** because **4** is far more stable than **8**. Alternatively, a transition metal fragment that is bound to an aromatic moiety stronger than to three alkyne units (such as $Cr(CO)_3$) may mediate this reaction.