J. Am. Chem. Soc. **2001,** *123,* 10322−10328

Butalene and Related Compounds: Aromatic or Antiaromatic?

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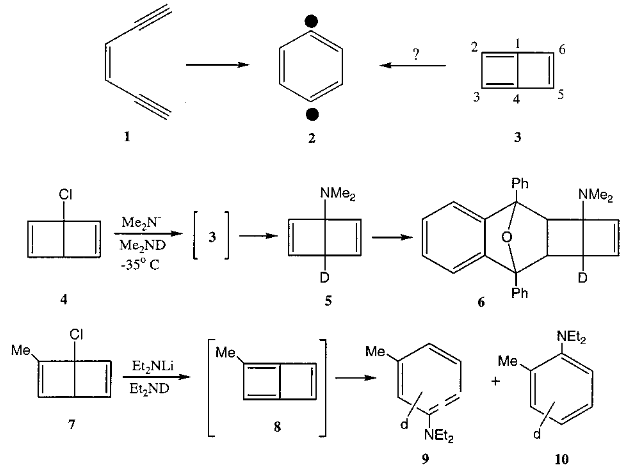
Received May 7, 2001

Abstract: Density functional theory (DFT) has been used to study the first three members of the condensed cyclobutadienoid series, butalene (**3**), bicyclobutadienylene (**12**), and dicyclobutenobutalene (**20**). The first is planar and is judged “aromatic” by comparisons with suitable models using both energetic and magnetic criteria. The second is nonplanar, and not aromatic, but not so antiaromatic as cyclobutadiene (**11**). The third is slightly more antiaromatic and best viewed as a butalene fused to two cyclobutadiene rings; its properties are the sum of aromatic and antiaromatic components, like benzocyclobutadiene. Ring-opening transition states for both **3** and **12** have been located, and these are conrotatorily twisted. The ring-opening barrier for **12** is more than twice that for **3**. Ring-opening of **20** involves ring inversion as the only barrier.

Introduction

The Bergman rearrangement of enediynes to *p*-benzynes (e.g., **1** to **2**) continues to receive experimental and theoretical attention.[1] The possibility that butalene (**3**), a “valence isomer” of **2**, could have an independent existence was recognized over 25 years ago, when it was introduced as a theoretical species less stable than **2** and insulated from conversion to **2** by a 4.6 kcal/mol barrier (MINDO 3).[2,3] The Breslow lab has reported experimental results implicating **3** as an intermediate.[4,5] Briefly summarized, chloro-Dewar benzene **4** was treated with strong base to afford, in the presence of diphenylisobenzofuran, 10−15% of amino-Dewar benzene adduct **6**. The remainder of the product mixture was variously deuterated dimethylanilines. A second paper dealt with the formation of both *meta* (**9**) and *ortho* (**10**) aniline derivatives starting from **7**; the intermediacy of methylbutalene (**8**) was suggested, although other pathways could not be ruled out.

On the theoretical side, Dewar revised the ring-opening barrier for **3** to only 3 kcal/mol using MNDO.[6] The first ab initio calculations involving **3** appeared in 1979.[7] These authors were primarily focused on the relative stability of **2** and **3**. Although they found the former to be more stable (as have all credible calculations), their use of unpolarized basis sets and geometry optimizations without electron correlation make their results outdated by current standards. Later, Nicolaides and Borden revisited the earlier work using the 6-31G* basis set, with similar results; they optimized **3** at only the RHF/6-31G* level, but, using QCISD(T)/6-31G*, found it to lie 37.0 kcal/mol above **2**, a value that is similar to that reported here (vide infra).[8] Most recently, Ohta and Shima used a GVB wave function with the 4-31G basis set to study **3** and its ring-opening transition state to **2**.[9] These results are considered in more detail later.



Theoretical consideration of the aromaticity or antiaromaticity of **3**, particularly within the context of comparisons with cyclobutadiene (**11**) and bicyclobutadienylene[10] (**12**), were made as early as 1971.[11] These semiempirical PMO[12] and modified PMO methods[13] all agreed that **3** was more aromatic (less antiaromatic) than either **11** or **12**. Although semiempirical consideration of condensed cyclobutadienes have continued to appear relatively recently,[14] and **11** has received considerable attention at the ab initio level,[15] the only attempt at an ab initio treatment of **12** appears to be as a footnote in Vollhardt’s 1982 paper, where minimal basis set HF results of partial optimizations were reported.[16] The issue of aromaticity could not be

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(2) Dewar, M. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974**, *96*, 5569.

(3) Mention of **3** goes back to at least 1968, when it was called butylene: Wilcox, C. F., Jr. *Tetrahedron Lett.* **1968**, 795.

(4) (a) Breslow, R.; Napierski, J.; Clarke, T. C. *J. Am. Chem. Soc.* **1975**, *97*, 6275. (b) Breslow, R.; Khanna, P. L. *Tetrahedron Lett.* **1977**, 3429.

(5) Attempts to observe **3** under matrix isolation conditions were apparently unsuccessful: Bergman, R. Personal communication, 1980. See, also: Jones, R. R. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1976.

(6) Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 3162.

(7) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

(8) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 11951.

(9) Ohta, K.; Shima, T. *Chem. Phys. Lett.* **1994**, *217*, 7.

(10) Fritch, J. R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3643.

(11) Dewar, M. J. S.; Kohn, M. C.; Trinajstic, N. *J. Am. Chem. Soc.* **1971**, *93*, 3437.

(12) Herndon, W. C.; Ellzey, L. M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.

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10.1021/ja011134v CCC: $20.00

addressed. We are unaware of any high-level theoretical appraisals of the next homologue, **20**, which may be called “butalobutalene” (in analogy to “benzo” nomenclature); however, in light of its calculated properties, we prefer “dicyclobutenobutalene”.


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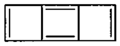
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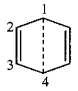

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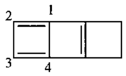

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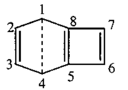

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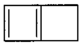
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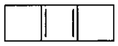
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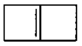
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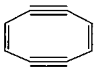
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20

In this paper we use density functional theory (DFT) to address questions regarding **3**, **12**, and **20**, including their geometries, energies, aromaticity, and stability.

Computational Methods

Molecular geometries for all species were initially optimized using the BLYP functional,[17,18] as implemented in the Gaussian 98 program package;[19] all optimizations employed the 6-31G* basis set. The BLYP functional was used so comparisons to previous work on **2**[1] could be made. However, optimizations of **2**, **3**, and their connecting transition state were also carried out with the B3LYP hybrid functional.[20] All stationary points were characterized by frequency analysis; minima have no imaginary frequencies (NIMAG = 0), while transition states have 1 (NIMAG = 1). The calculated zero point energies (ZPE) are reported without correction. As part of the frequency analysis, Gaussian 98 also generates enthalpies and free energies via standard statistical mechanical methods. Electronic energies of optimized structures were also obtained using the extended 6-311+G** basis set. Enthalpies at the 6-311+G** level are based on electronic energies at that level and rovibrational corrections at the 6-31G* optimization level. The barrier height between **2** and **3** was also evaluated using the CCSD(T) approach.[21] All new singlet minima reported herein have stable restricted DFT wave functions, a fact ascertained by wave function stability calculations.[22] Such is not true, however, for their HF wave functions, and we use $\langle S^2\rangle_{\mathrm{UHF/6-31G*}}$ values as a measure of diradical character.[23]

The transition state between **2** and **3** could not be easily located using the usual synchronous transit-guided quasi-Newton methods (QST2 or QST3),[24] possibly because the nature of the transition region changes from restricted to unrestricted as the ring opens. We had to locate a structure very close to the actual transition state using optimizations with frozen 1,4 bond distances, which were subsequently optimized using QST3.

Diamagnetic susceptibilities were calculated using the continuous set of gauge transformations method at the B3LYP/6-311+G** level for all cases.[25]

Results and Discussion

Geometries. The geometries of key structures are shown as ball-and-stick drawings in Figure 1 (Cartesian coordinates (CC) of all geometries are available as Supporting Information). While **11** equilibrates between two identical rectangular structures [BLYP/6-31G* (B3LYP/6-31G*) CC distances of 1.345 Å (1.335 Å) and 1.592 Å (1.578 Å)], **3** is calculated to have only one planar structure with a long central bond somewhere between 1.592 Å (BLYP) and 1.571 Å (B3LYP);[26] the previous RHF/6-31G* value of 1.536 Å was somewhat short,[8] whereas the GVB value of 1.58 Å was essentially correct.[9] The fusion of a cyclobutane ring around **3**, to give **14**, results in a butalene derivative which is nonplanar at all three double bonds, although the pyramidalization is not so extreme as recently reported for some fused cyclopropenes.[27] The structure of **12** is also singular and cis-puckered, although it lies only 0.9 kcal/mol (0.8 kcal/mol with ZPE) below the planar transition state for its inversion (**12p**). The longest bond in **12** is the central (1,4) bond at 1.513 Å. The geometries (and properties, vide infra) of the triplet states of **3** and **12** contrast sharply with the singlet ground states (much as the square planar triplet state of **11** [BLYP/6-31G* (B3LYP/6-31G*) CC distance of 1.452 Å (1.441 Å)] contrasts with the rectangular ground state). The triplet state of butalene (**3t**) is nonplanar with more bond alternation than for **3**, while the triplet state of **12** (**12t**) is planar with almost no bond alteration. Thus, the idea that **11** and **12** resemble each other, whereas **3** is different, is supported by the geometries.

Next higher homologue **20** can potentially exist as a planar or bent structure; the latter may be cis-bent or trans-bent. The calculations find the cis-bent structure to be a minimum, while the trans-bent is a nonstationary point along the optimization pathway that ultimately leads to the dicyclobuteno-*p*-benzyne (**30**) minimum (which lies some 73 kcal/mol lower in energy). The planar version of **20** (**20p**) is a second-order saddle point which lies some 10 kcal/mol above the **20** minimum; its imaginary modes are for symmetrical (56*i*) and antisymmetrical (201*i*) bending of the outer rings. The corresponding triplet (**20pt**) is a similar second-order saddle point. Both planar structures have a “butalobutalene” structure, with short central bonds and long adjacent cross-ring distances. Comparison of the singlet and triplet structures, **20** and **20t**, is instructive. It is seen that the end rings of **20** are quite rectangular, like cyclobutadiene, whereas the central two rings resemble butalene with the long central bond. Although we could find only a single geometry for the **20** minimum, like benzene, it clearly cannot be represented adequately by a single resonance structure. Thus, the geometry of **20** indicates it is a butalene fused to two cyclobutadiene rings (which is also supported by its other

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(26) These two methods appear to bracket bond distances given by the most accurate methods; for example, the B3LYP distances reported by Jiao et al. (Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921) are mostly shorter than their best CASPT2N values, while our BLYP values for the same compounds (unpublished) are almost uniformly longer.

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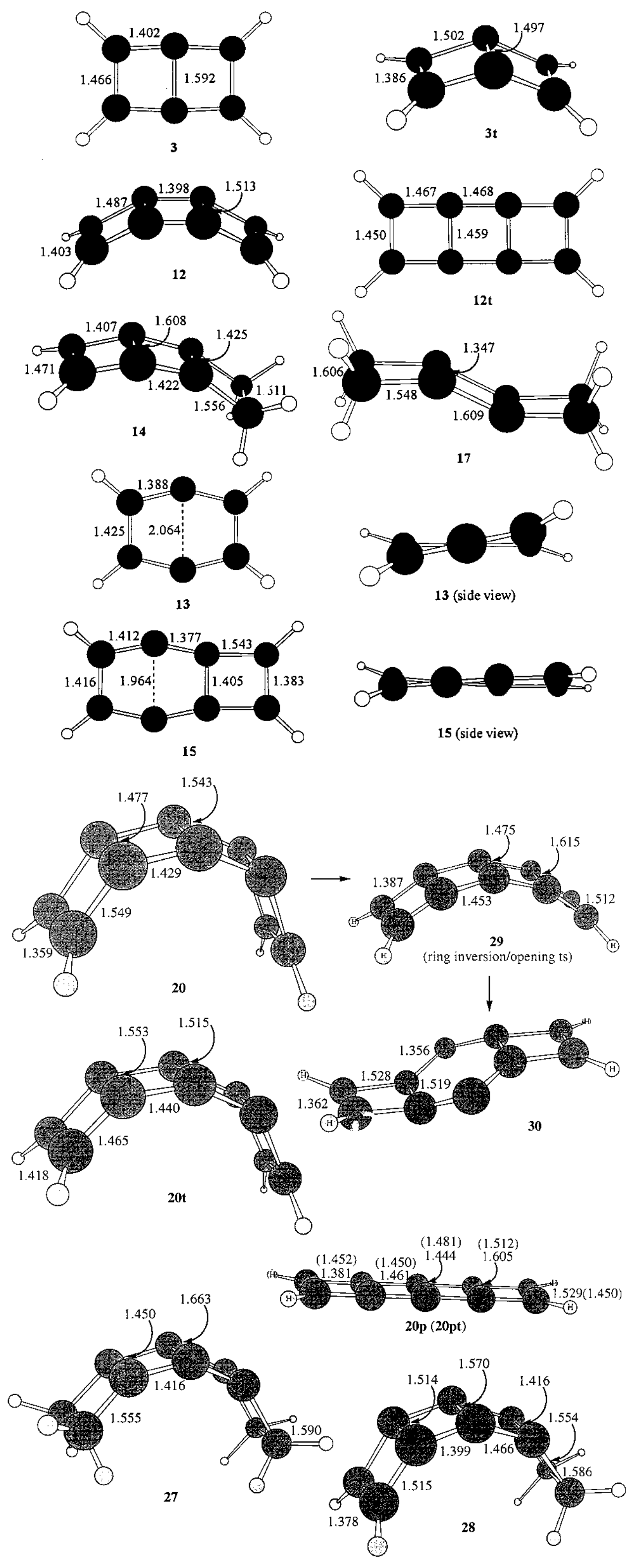

Figure 1. Ball and stick drawings of key compounds−BLYP/6-31G* optimizations.

properties, vide infra). The triplet, **20t**, has end rings that are much closer to square planar, again like cyclobutadiene, although the relatively short central bond (1.515 Å) gives it a butalobutalene flavor.

The 1,4 distance ($r_{1,4}$) in transition-state **13** was previously estimated at 1.85 Å (MINDO 3)[2] and 1.76 Å (GVB).[9] Our results bracket this distance between 2.064 Å (BLYP, $n_i = -912.8$ cm^{-1}) and 2.001 Å (B3LYP, $n_i = -1073.4$ cm^{-1}). More interestingly, both DFT methods show **13** to be twisted out of planarity in the sense required for a conrotatory ring-opening [i.e., **13** has C_2 symmetry with dihedral angle $HC_2C_3H = 31.0°$ (33.0°, B3LYP)]. A study of the transition region over the range from $r_{1,4} = 1.99-2.08$ Å revealed that $r_{1,2}$ remained constant at 1.387 Å (1.374 Å, B3LYP), while $r_{2,3}$ decreased as $r_{1,4}$ increased, and the aforementioned dihedral angle peaked at the transition state. Also, on the "**2** side" of the transition state it was easy to find a higher electronic state that became more and more twisted, and stayed electronically restricted, whereas the lower reaction pathway returned toward planarity and became electronically unrestricted (see discussion of energies). Borden previously discussed the orbital changes that occur near the transition state,[8] and the upper pathway may lead to the spurious nonplanar, electronically restricted *p*-benzyne structure we previously discussed.[1]

The ring-opening transition state for **12** (**15**) is notable in two respects: (a) there is one breaking bond (1,4), and its distance (1.964 Å, BLYP, $n_i = -408.3$ cm^{-1}) is about the same as in transition state **13**, and (b) it is conrotatorily twisted to about the same degree as **13** on the disubstituted double bond side ($HC_2C_3H = 28.9°$), but, due to the additional ring, virtually not at all on the other side ($C_6C_5C_8C_7 = 1.9°$). The energetic result of this geometric restriction is discussed later. A brief study of the transition region revealed that the wave function became unrestricted at $r_{1,4} > 2.1$ Å. This is interesting because the structure appears to be evolving into cyclobuteno-*p*-benzyne. However, in a separate study,[28] this benzyne was not a stationary point on either the restricted or unrestricted surfaces. However, it seems likely that the pathway from **12** joins the Bergman cyclization pathway that ultimately leads to **19**, a species previously considered by Vollhardt.[16]

The ring-opening of **20** is significantly different from its lower homologues. Structures with artificially stretched central CC distances (1.9−1.95 Å) (partially) optimized to **20**-like *cisoid* geometries with energies above **20p**; full optimization of these led back to **20**. Stretching of the noncentral cross-ring bond (potentially toward a butalo-*p*-benzyne) led to inversion of the partially opened ring at the end, but full optimization of this structure led to re-closing of the terminal rings and opening of the central bond to afford dicyclobuteno-*p*-benzyne (**30**). Thus, there appears to be no ring-opening pathway that is analogous to what was found for **3** and **12**. Ultimately we located the ring-inversion transition state, **29**, which lies 7.6 kcal/mol (BLYP/6-311+G** + ZPE) above **20**. Optimization of **29** to a minimum leads directly to **30**.

Ancillary cyclobutadienes **16** and **17**, necessary for energetic comparisons, are geometrically interesting in that they are both nonplanar. For **16**, this contrasts with **18**, which is planar.[29] This geometric diversity is due to the relatively greater strain energy in **16**. Cyclobutadiene **17** has both cis-puckered and trans-puckered forms; the degree of puckering is about the same in both, with the former about 1.0 kcal/mol less stable than the latter. Another contrast with the condensed cyclobutadiene structures is that **17** has short cross-ring bonds and very long side bonds (like known cyclobutadienes with similarly fused, but larger, rings).[15b] Compounds **14** and **27** are cyclobutano-fused butalenes, which fusion induces *cisoid* puckering. Last, the long (1.570 Å) central bond of **28** suggests that it and **12** should also be viewed as butalenes with an additional fused

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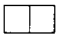
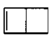
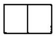
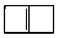
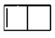
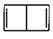
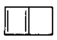
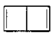
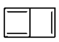
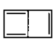
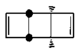
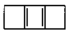
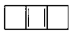
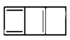
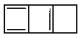
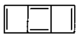
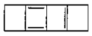
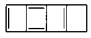
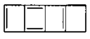
Table 1. Isodesmotic Stabilization Energies

Compound				Stabilization Energies (incl. ZPE)[a]
X		X-H$_2$		
21		**22**		-1.1 (-1.3)
22		**11**		33.1 (32.1)
23		**24**		-1.6 (-1.5)
23		**18**		24.4 (24.0)
24		**25**		1.8 (1.7)
18		**16**		27.7 (27.1)
25		**3**		32.5 (32.2)
16		**3**		-19.5 (-18.6)
26a		**17**		81.5 (80.2)
17		**14**		-16.3 (-15.9)
14		**12**		8.6 (8.5)
27		**28**		9.5 (9.4)
28		**20**		16.3 (15.8)

[a] "Stabilization energies" are from isodesmic eq 1, where the value in parentheses includes the ZPE correction; electronic energies are from BLYP/6-311+G**//BLYP/6-31G* calculations, while zero point energies (ZPE) are from frequency calculations at the BLYP/6-31G* level; −78.567 83 au (31.2 kcal/mol) and −79.792 38 au (46.0 kcal/mol) are the relevant values for ethylene and ethane, respectively; all other absolute energies and ZPE's are contained in the Supporting Information.

cyclobutadiene ring; the energies are also in accord with this idea (vide infra).

Energies and Magnetic Properties of Ground States. Evidence Regarding Aromaticity. (1) Energies.

$$X + H_2C{=}CH_2 \rightarrow X{-}H_2 + H_3C{-}CH_3 \qquad (1)$$

The best way to study the energies of the various structures is to compare the energetic cost (benefit) of introducing a double bond at a previously saturated position. This can be accomplished by the double bond "stabilization" energies of isodesmic eq 1. A negative energy for this equation means the double bond is more stable in the molecule under consideration relative to ethylene. The data are collected in Table 1. For the simplest case of cyclobutane, the conversion to cyclobutene produces a stabilization of 1.3 kcal/mol (including ZPE). This is not to be confused with the fact that cyclobutene is 2−4 kcal/mol more strained than cyclobutane.[30] It is seen that **11** is destabilized severely: it costs 32.1 kcal/mol to introduce the second double bond. Apparently even worse is bent cyclobutadiene derivative **16**, which suffers a 52.7 kcal/mol double bond introduction penalty relative to **24**. However, much of that is due to strain; the cost of converting **18** to **16** is only 27.1 kcal/mol, somewhat less than for the parent system. From the 24.0 kcal/mol double bond introduction cost of going from **23** to **18**, it is seen that the high energy of **16** is about half due to the strain of the central double bond and half due to "normal" cyclobutadiene destabilization (antiaromaticity). Some of the extra energy of **16** must be due to "strain", since **16** is puckered, whereas **18** is planar. It is also very costly to generate cyclobutadiene **17**. Based on anti-cyclobutadiene dimer **26a**,[15c] **17** is 80.2 kcal/mol less stable (the value calculated from the data on the bicyclo[2.2.0] series is 78.2 kcal/mol, where syn or anti stereochemistry cannot be taken into account).

The comparisons for the condensed cyclobutadienes are most interesting. It is seen that adding a double bond to **16** to make **3** is *beneficial* by 18.6 kcal/mol. Another way of looking at it is that it takes only 8.3 kcal/mol to add the two double bonds to go from **18** to **3**. Obviously **3** is more stable than can be expected on the basis of viewing it as a cyclobutadiene. This gives credence to the "two wrongs make a right" idea that **3** might be aromatic (or at least not antiaromatic). A similar energetic story is evident for fused butalene **14**, whose formation from **17** is energetically beneficial by 15.9 kcal/mol (appropriately slightly less than for the parent system, since **14** is strained to the point of being puckered). Quite the opposite picture emerges for **12**, whose formation from **14** costs an additional 8.5 kcal/mol. It is clear that the electronic destabilization endured by **12** is less than for the cyclobutadiene system. For example, the conversion of **17** to **12** would be *beneficial* by 7.4 kcal/mol. Appropriately, conversion of double-fused butalene **27** to fused bicyclobutadienylene **28** is associated with an energetic cost, 9.4 kcal/mol, similar to that of **14** to **12**. Perhaps most interesting is that formation of **20** from **28** is associated with a destabilization of 15.8 kcal/mol, consistent with the formulation of **20** as a dicyclobutenobutalene rather than an aromatic system implicit in merely counting its 10 π electrons.

(2) Magnetic Properties. Schleyer has vigorously recommended the use of magnetic susceptibility exaltations as a unique criterion for aromaticity (negative exaltations relative to simple model compounds, from which "susceptibility group increments" are derived)[31] and antiaromaticity (positive exaltations).[32] The CSGT method employed here (and elsewhere)[33] gives magnetic susceptibilities that are closer to experimental values than does the IGLO[34] method which has been more commonly used. The disadvantage of the CSGT method is that a fairly large basis set must be used; we use the standard 6-311+G** basis. Schleyer has reported positive exaltations for a few antiaromatic systems, including a value of 18.0 for cyclobutadiene.[35] He has also pointed out that the triplet state will show magnetic behavior in the opposite direction from the corresponding singlet state of an aromatic or antiaromatic compound.[36]

Our results, gathered in Table 2, are consistent with expectations for the simple compounds. It is seen that cyclobutanes, in general, have somewhat positive exaltations of about the same magnitude as the negative exaltations seen for cyclopropanes. Cyclobutadiene (**11**, +15.9), cyclobutadiene **16** (+18.1; planar form, +25.6), and cyclobutadiene **17** (trans-bent, + 23.2; cis-bent, +17.2) all have the large positive exaltations expected of

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[30] (a) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395. (b) Schleyer, P. v. R.; Williams, J. E., Jr.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

[31] For a particularly clear explanation of this approach, see the paper given in ref 26.

[32] Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

[33] Manoharan, M.; De Proft, F.; Geerlings, P. *J. Org. Chem.* **2000**, *65*, 7971.

[34] Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.

[35] (a) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A. Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[36] See also ref 14b.

Table 2. Magnetic Susceptibilities ($\chi_{\text{tot.}}$) and Magnetic Susceptibility Exaltations ($\Lambda_{\text{tot.}}$, ppm Cgs) Calculated at CSGT-B3LYP/6-311+G**//BLYP/6-31G*, Including Reference Molecules Used To Generate Group Increments[a]

molecules and group increments	$\chi_{\text{tot.}}$	$\Lambda_{\text{tot.}}$
$-CH_3$	−12.2[b]	
$-CH_2$-	−10.4[c]	
$-CH<$	−10.1[d]	
$>C<$	−9.7[e]	
	−4.3[f]	
$-CH{=}CH-$ (cis)	−13.5[g]	
$>C{=}C<$	−11.3[h]	
ethane	−24.4 (−26.8)	
propane	−34.8 (−38.6)	
isobutane	−46.7 (−50.5)	
neopentane	−58.5 (−63.1)	
ethylene	−17.1 (−18.8)	
tetramethylethylene	−60.1 (−65.9)	
cis−2-butene	−37.9	
cyclopropane	−37.2 (−39.9)	−6.0 (−4.5)
tert-butyl radical	−40.9	
benzene	−52.9 (−54.7)	−12.4 (−13.7)
byclobutane (**21**)	−39.2	2.4
cis−1,2-dimethylcyclobutane	−60.4	5.0
cis−1,3-dimethylcyclobutane	−61.4	4.0
cyclobutene (**22**)	−30.0	4.3
cyclobutadiene (**11**)	−11.1	15.9
cyclobutadiene, square singlet	−10.7	16.3
cyclobutadiene, square triplet	−24.8	2.2
bicyclo[2.2.0]hexane (**23**)	−51.5	10.3
1,4-dimethylbicyclo[2.2.0]hexane	−77.0	8.2
bicyclo[2.2.0]hex-2-ene (**24**)	−46.2	8.3
bicyclo[2.2.0]hex-1(4)-ene (**18**)	−40.7	12.2
bicyclo[2.2.0]hex-1,3-diene (**16**)	−31.1	18.1
planar form of **16** (NIMAG = 1)	−23.6	25.6
Dewar benzene (**25**)	−39.0	8.2
butalene (**3**)[i]	−37.0	1.3
triplet butalene (**3t**)	−28.3	10.0
p-benzyne (**2**)	−48.5	−12.9
3 to **2** transition state (**13**)	−34.9	3.4
anti-cyclobutadiene dimer (**26a**)	−55.5	11.9
syn-cyclobutadiene dimer (**26s**)	−57.9	9.5
cyclobutadiene **17** trans-bent	−41.0	23.2
cyclobutadiene **17** cis-bent	−47.0	17.2
butalene **14**	**−51.7**	5.2
bicyclobutadienylene (**12**)	−38.5	11.1
triplet bicyclobutadienylene (**12t**)	−44.5	5.1
ring-opening transition state **15**	**−28.9**	20.7
dicyclobutanobutalene (**27**)	−69.8	5.7
cyclobutanobicyclobutadienylene (**28**)	−59.1	9.1
dicyclobutenobutalene (**20**)	−46.2	14.7
triplet dicyclobutenobutalene (**20t**)	−52.9	8.0
planar dicyclobutenobutalene (**20p**)	−54.2	6.7
planar triplet dicyclobutenobutalene (**20pt**)	−38.8	22.1
dicyclobuteno-*p*-benzyne (**30**)	−39.1	19.1

[a] Parenthetical experimental values for $P_{\text{tot.}}$ and $\Lambda_{\text{tot.}}$ were taken from ref 29. [b] From ethane. [c] From propane−ethane. [d] From isobutane−3CH$_3$. [e] From neopentane−4CH$_3$. [f] From *tert*-butyl radical−3CH$_3$-used for the *p*-benzyne calculation. [g] From *cis*-2-butene−2CH$_3$. [h] From tetramethylethylene−4CH$_3$. [i] Group increment *P* from 2(−CH=CH-cis, entry 6) + >C=C<, entry 7.

Table 3. Singlet−Triplet Energy Gaps and $\langle S^2\rangle_{\text{UHF/6−31G*}}$ Values

compound	$\langle S^2\rangle_{\text{UHF/6−31G*}}$	ΔE(T−S)[a]	compound	$\langle S^2\rangle_{\text{UHF/6−31G*}}$	ΔE(T−S)[a]
21	0.00		**3**	0.00	33.5
22	0.07		**14**	0.00	
25	0.15		**27**	0.00	
18	0.00		**12**	0.05	42.9
11	0.98	6.7	**28**	2.04	29.1
16	1.07		**20**	2.54	8.2
17	1.05				

[a] Positive values, in kilocalories per mole, indicate the singlet state lies below the triplet; all values are for energies at the BLYP/6-311+G**//BLYP/6-31G* level and include ZPE corrections at the geometry optimization level.

antiaromatic compounds. The ring-opening transition state from **12** (**15**, +20.7) has the positive exaltation consistent with the cyclobutadiene portion of the molecule that is being generated (which also accounts for the higher barrier for ring-opening of **12**; see below). *p*-Benzyne (**2**), on the other hand, has a negative exaltation (−12.9) consistent with its aromatic structure. It is known that benzene diatropicity is relatively insensitive to geometry.[35b,37] The data for square planar (+16.3) and rectangular (+15.9) cyclobutadiene show that the antiaromaticity of this molecule is also fairly insensitive to geometry. The triplet state of **11** (+2.2), however, is not antiaromatic.

The butalenes (**3**, +1.3; **14**, +5.2; **27**, +5.7) are revealed as not antiaromatic, in accord with the energetic results discussed above. If one uses alkene **18** as a reasonable model for **3**, one would conclude that the magnetic results classify butalene as aromatic. Consistently, the parent butalene triplet state, **3t** (+10.0), has a more positive exaltation. Bicyclobutadienylene (**12**, +11.1) falls between **3** and **11**, just as it did energetically. Its triplet state, **12t** (+5.1), has a lower exaltation, which is consistent with **12** being more antiaromatic than aromatic. Finally, dicyclobutenobutalene (**20**, +14.7) is more antiaromatic than **12**, while the triplet (**20t**, +8.0) is less antiaromatic than the singlet. This again reinforces the geometric and energetic results discussed above. The effects of the cyclobutadiene and butalene rings oppose each other, much as in benzocyclobutadiene.[35a,38] However, the expectation that **20** might be just like butalene (**3**) is not met, perhaps due to the nonplanarity induced by other than "aromaticity" factors. This idea is supported by the exaltations of the planar stereoisomers of **20**: **20p** (+6.7) is considerably less antiaromatic than **20pt** (+22.1). Thus, the geometric characterization of these structures as butalobutalenes is reinforced by the electronic structure as revealed by the magnetic property calculations.

Singlet−Triplet Gaps and Diradical Character. Another measure of aromatic character involves examination of the singlet−triplet gaps and the diradical character of the singlet state. The expectations are for large singlet−triplet gaps and virtually zero diradical character for aromatics, with the contrary for antiaromatics. Table 3 summarizes the relevant data for the cases studied herein. The singlet−triplet gap for butalene is quite large, as expected for an aromatic compound. Consistent with this is the zero diradical character seen for the butalenes (the effective number of unpaired electrons is $2\langle S^2\rangle^{23}$). The simple cyclobutadienes all have essentially two unpaired electrons, which is in accord with viewing them as diradicals.[15c] Dicyclobutenobutalene has a singlet−triplet gap appropriate for a cyclobutadiene (compounds with two separated cyclobutadiene rings have a singlet−triplet gap like cyclobutadiene because the excitation involves only 1 ring) and the diradical character of approximately two cyclobutadienes. Bicyclobutadienylene has a surprisingly large singlet−triplet gap with a consistently zero diradical character. The effect on apparent diradical character on going from **12** to **28** is not readily explicable, and may represent a failure of this approach. On the other hand, the singlet−triplet gap remains quite large.

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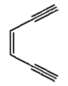
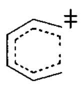
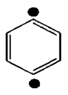
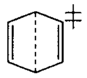
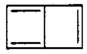
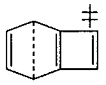
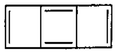
(37) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Muhlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(38) Dicyclobuteno-*p*-benzyne is another case of aromatic/antiaromatic ring interactions. The diamagnetic exaltation of +19.1 (see Table 2) indicates that it is net antiaromatic.

Table 4. Comparison of Transition State Enthalpies (Free Energies) with Relevant Ground States[a]

Theoretical Method	Relative Enthalpy, H_{rel} (Relative Free Energy, G_{rel}), kcal/mol				
	 1	 1ts	 2	 13	 3
BLYP/6-31G*//BLYP/6-31G*	0.0 (0.0)	24.3 (26.3)	7.3 (10.0)	43.1 (45.6) [4.5 (4.7)]	38.6 (40.9) [0.0 (0.0)]
BLYP/6-311+G**//BLYP/6-31G*	0.0 (0.0)	27.4 (29.4)	14.3 (17.0)	51.0 (53.5) [3.4 (3.6)]	47.6 (49.9) [0.0 (0.0)]
B3LYP/6-31G*//B3LYP/6-31G*	0.0 (0.0)	29.9 (31.8)	3.9 (7.3)	45.5 (47.8) [6.4 (6.5)]	39.1 (41.3) [0.0 (0.0)]
B3LYP/6-311+G**//B3LYP/6-31G*	0.0 (0.0)	32.9 (34.8)	11.0 (14.4)	52.8 (55.1) [5.5 (5.7)]	47.3 (49.4) [0.0 (0.0)]
CCSD(T)/6-31G*//BLYP/6-31G*	-	-	-	[3.0 (3.2)]	[0.0 (0.0)]
CCSD(T)/6-31G*//B3LYP/6-31G*	-	-	-	[4.0 (4.1)]	[0.0 (0.0)]
Experiment	0.0	28.7	8.5	-	-
				 15	 12
BLYP/6-31G*//BLYP/6-31G*				[10.7 (9.7)]	[0.0 (0.0)]
BLYP/6-311+G**//BLYP/6-31G*				[10.6 (9.6)]	[0.0 (0.0)]
B3LYP/6-311+G**//BLYP/6-31G*				[12.5 (11.5)]	[0.0 (0.0)]

[a] Electronic energies calculated at the level indicated; rovibrational and entropic corrections at the optimization level.

Transition-State Energies. The only previous ab initio estimation of the butalene ring-opening barrier found it to lie as little as 1.6 kcal/mol above **3**; this did not include any ZPE correction.[9] The level of that calculation (incomplete correlation correction, unpolarized basis sets) is now seen to be inadequate for this problem. Nicolaides and Borden[8] detected the presence of a ring-opening barrier for **3**, but did not locate it. Our results for the ring-openings of **3** and **12** are given in Table 4. Transition-state **13** is essentially a closed-shell structure (S^2 = 0.03, BLYP; 0.075, B3LYP), whereas **2** is open-shell (S^2 = 0.80, BLYP; 0.95, B3LYP); **15** is completely closed-shell. Since the DFT methods under consideration do not adequately treat structures such as **2** (the BLYP/6-31G* enthalpy is only fortuitously close to experiment), the focus should be on comparisons with enediyne **1** and its cyclization transition state (**1ts**), both of which are closed-shell structures. As can be seen from the data in Table 4, B3LYP enthalpies are a bit high and tend to get more so with the better basis set, while BLYP enthalpies are somewhat low, but get closer to experiment with the larger basis set. Thus, as with geometries, these DFT methods appear to bracket experimental reality. Thus, the barrier to ring-opening of **3** can confidently be placed between 3.5 and 5.5 kcal/mol. The values obtained from the coupled clusters approach [CCSD(T)] are near the low end of the DFT range. Interestingly, contrary to perhaps naive expectations, the inclusion of entropy actually increases the barrier slightly. We surmise this reflects a loss of aromaticity at the transition state; this effect is not seen for the ring-opening of **12**, but **12** is not aromatic. The overall larger barrier for ring-opening of **12** can be attributed to the difficulty in generating a pure cyclobutadiene ring and is also reflected in the magnetic exaltation data for **15**. Although comparison of these barriers with the ring-inversion initiated opening of **20** does not seem very useful, it appears that the cis-bent structure of **20** inhibits the style of ring-opening apparent for **3** and **12**.

It is seen that **3** lies about 39 kcal/mol above **2** (BLYP/6-311+G** enthalpy for **3** minus experimental[39] enthalpy for **2**), in good agreement with Nicolaides and Borden's QCISD(T) result mentioned earlier.[8] What is not clear is the product to be expected from **13**, since we did not perform a full intrinsic reaction coordinate analysis. The imaginary vibration of **13** certainly involves separation of the "*para*" carbons. However, the energy of **13** is at least 20 kcal/mol above **1ts**, which could be easily reached, geometrically, by stretching of the 2,3-bond. Thus **1** would be a reasonable product, although one cannot be certain without knowledge of the dynamics of the system.

Last, two pathways were considered for the formation of **6**. The first involved trapping of **3** by Me_2ND, followed by Diels–Alder reaction with DPIBF, while the second reversed the order of Diels–Alder and solvent addition. Our results appear to be not in accord with Diels–Alder trapping of **3** at the disubstituted double bond, since that would generate a derivative of **16**, which is much less stable than **3**.

Conclusion

We have carried out DFT calculations on butalene (**3**), bicyclobutadienylene (**12**), their respective ring-opening transition states (**13** and **15**), dicyclobutenobutalene (**20**), and related compounds for comparison. Both **3** and **12** are minima; the ring-opening barrier from **3** is only 3.5–5.5 kcal/mol, while that from **12** is at least twice as high. *Cisoid* puckered **20** is a minimum, the ring-opening of which involves an initial ring inversion process via **29**; the *transoid* puckered isomer of **20** is a nonstationary point along the path to ring-opened dicyclobuteno-*p*-benzyne (**30**). The structures of the ring-opening

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(39) (a) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401. (b) Roth, W. R.; Hopf, H.; Wasser, T.; Zimmermann, H.; Werner, C. *Liebigs Ann.* **1996**, 1691.

transition states are twisted in a conrotatory fashion. On the basis of energetic comparisons, magnetic criteria, and singlet–triplet gaps, **3** has to be classified as aromatic, whereas **12** is nonaromatic to slightly antiaromatic and **20** is somewhat more so. The ordering for the first two is consistent with resonance energies previously gleaned from semiempirical PMO treatments.

Acknowledgment. This paper is dedicated to Professor Ronald Breslow on the occasion of his 70th birthday. Dr. Breslow's mentoring of the senior author when he was a Columbia freshman in 1964 was inspirational.

Supporting Information Available: Cartesian coordinates of optimized geometries, absolute energies, enthalpies, and free energies for all compounds studied (17 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA011134V