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Benzocyclobutene and Benzo[1,2:4,5]dicyclobutene: The Possibility of Valence Isomerism

Jerome M. Schulman* and Raymond L. Disch

Contribution from the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367

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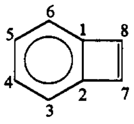
Abstract: Ab initio calculations are reported on Kekulé forms of the title compounds. For benzocyclobutene, the HF and RMP2 quinoid structure **1b** is much higher in energy than the expected benzenoid isomer **1a**. CASSCF π calculations, however, do not support the quinoid structure as a local minimum. In the case of benzodicyclobutene, a C_{2v} form, **3b**, is ca. 10 kcal/mol higher in energy than the D_{2h} form, **3a**. Both structures are obtained at the GVB level in a small basis set. While isomerism between Kekulé forms of **3** may exist, the phenomenon will be difficult to demonstrate experimentally. Heats of formation are computed for all species, including pentalene. The heat of hydrogenation of benzocyclobutene **1a** to dihydrobenzocyclobutene **2** is calculated to be 52.6 kcal/mol.

Benzocyclobutene (**1**) opposes the antiaromatic cyclobutadiene to the classic aromatic benzene in an overall 8-π-electron system. The fusion of these antithetical π systems, together with severe angle strain, leads to a highly reactive molecule[1] that has been isolated only in an argon matrix at low temperature, wherein it dimerizes above 75 K.[1a] An X-ray structure of a derivative of **1** having methyls on the benzene ring and *tert*-butyls on the cyclobutadiene shows short (essentially double) bonds between C_7 and C_8 in addition to a shortening of C_1C_6 relative to C_1C_2,[2] the so-called Mills–Nixon effect.[3] Recent HF/3-21G calculations have produced a geometry for **1** consistent with the experimental geometry.[4,5] Thus, both X-ray and theoretical results imply structure **1a** for benzocyclobutene.



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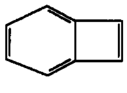
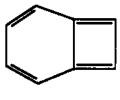


1a

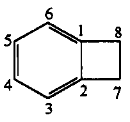


1b

We were therefore intrigued by a recent flow-NMR study which found the chemical shifts of **1** to be similar to those of *o*-xylylene, suggesting that the geometry of benzocyclobutene is of the quinoid form **1b**.[6] While substituted benzenes do not form two 6-π-electron Kekulé isomers,[7] benzocyclobutene structures **1a** and **1b** have HOMO–LUMO π–π^* configurations $1b_1^2 2b_1^2 1a_2^2 3b_1^2 2a_2^0$ and $1b_1^2 2b_1^2 1a_2^2 2a_2^2 3b_1^0$, respectively, in C_{2v} symmetry, and this orbital crossing implies the possibility of a barrier making possible the existence of both forms.

These considerations led us to undertake an ab initio study of valence isomerization in **1**, for even if **1b** is not the lower-energy isomer, its existence would be of interest. A prior study of the two isomers at the MNDO level by Dewar and Merz[8] found **1a** to be more stable than **1b** by 26 and 24 kcal/mol at the RHF and HE/CI levels, respectively. UMNDO calculations showed that **1b** is not a minimum on the C_8H_6 potential surface.

In addition to **1a** and **1b**, we have included the lowest triplet state of benzocyclobutene, **1t**, as well as dihydrobenzocyclobutene **2**. The calculated heat of hydrogenation of the lowest-energy form of **1** should be consistent with values expected for a strained olefin. Finally, in an effort to locate other possible Kekulé isomerizations involving benzene, we also studied benzo[1,2:4,5]-dicyclobutene (**3**).



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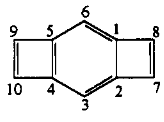

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Computational Methods

This work was carried out using programs developed by us and the GAUSSIAN90 (IBM) and GAUSSIAN92 (SGI) program packages.[9] Results are reported here using the notations of Pople: // means at the geometry of and / means in the basis. Calculations of electron-correlation energy at the second-order Møller–Plesset (MP2) level using the frozen-core approximation are identified by FC; those which use all the molecular orbitals (full calculations) are identified by FU. Vibrational frequency calculations were carried out with numerical finite differencing in GAUSSIAN90 and checked with GAUSSIAN92, which uses analytic second derivatives. CASSCF calculations were performed with both GAUSSIAN programs. AM1 calculations were also performed on all the molecules reported here.[10] We have not included differential zero-point and thermal effects in the calculated energies, as they are expected to be very small. Planar carbon frameworks are assumed throughout.

Benzocyclobutene

Structures **1a** and **1b** were optimized at the STO-3G, 3-21G, MP2(FU)/3-21G, 6-31G, MP2(FU)/6-31G, and 6-31G* levels

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Table I. 6-31G* and MP2(FU)/6-31G Geometric Parameters[a] of Benzocyclobutene and Dihydrobenzocyclobutene

parameter	**1a**[b,c]	**1b**[b]	**1t**	**2**[b,d]
C_1C_2	1.422 [1.445] (1.401)	1.526 [1.558]	1.413 [1.485]	1.380 [1.415] (1.391)
C_1C_6	1.342 [1.379] (1.367)	1.455 [1.458]	1.390 [1.418]	1.378 [1.401] (1.385)
C_3C_4	1.440 [1.449] (1.445)	1.333 [1.375]	1.382 [1.404]	1.393 [1.421] (1.400)
C_4C_5	1.358 [1.400] (1.370)	1.497 [1.503]	1.408 [1.451]	1.392 [1.420] (1.399)
C_7C_8	1.333 [1.379] (1.357)	1.596 [1.657]	1.516 [1.507]	1.573 [1.609] (1.576)
C_1C_8	1.518 [1.553] (1.529)	1.323 [1.373]	1.441 [1.445]	1.519 [1.544] (1.518)
C_6H_6	1.075 [1.091]	1.075 [1.092]	1.075 [1.091]	1.076 [1.092]
C_4H_4	1.076 [1.091]	1.076 [1.092]	1.076 [1.091]	1.076 [1.092]
C_8H_8	1.072 [1.087]	1.072 [1.088]	1.070 [1.085]	1.085 [1.098]
$C_1C_6C_5$	115.5 [115.7] (115.1)	115.7 [115.8]	115.9 [115.8]	116.0 [115.9] (116.0)
$C_3C_4C_5$	121.8 [121.8] (121.2)	124.1 [123.8]	122.2 [122.7]	121.7 [121.7] (121.7)
$C_2C_1C_6$	122.8 [122.5] (123.8)	120.2 [120.4]	121.9 [121.5]	122.3 [122.4] (122.3)
$C_2C_1C_8$	88.3 [88.8] (89.1)	91.5 [92.1]	92.0 [90.4]	93.6 [93.6] (93.5)
$C_1C_8C_7$	91.7 [91.2] (91.1)	88.5 [87.9]	88.0 [89.6]	86.4 [86.4] (86.5)
$H_6C_6C_1$	124.0 [123.8]	122.4 [122.7]	122.8 [123.0]	123.1 [123.3]
$H_5C_5C_6$	118.7 [118.9]	119.8 [119.6]	119.4 [119.4]	119.5 [119.4]
$H_8C_8C_1$	134.3 [134.8]	136.6 [137.0]	136.4 [135.8]	115.6 [115.9]
$H_8C_8C_7$				114.6 [114.3]

[a] Bond lengths are in Å, and angles are in degrees. C_{2v} geometries were assumed for all molecules. [b] MP2(FU)/6-31G values are given in square brackets. [c] X-ray values of di-*tert*-butyltetramethylbicyclobutene, ref 2, are in parentheses. [d] X-ray values of ref 12 are in parentheses.

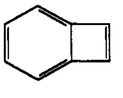
Table II. Total Energies of Benzocyclobutene and Dihydrobenzocyclobutene (–au)

level	**1a**	**1b**	**1t**	**2**
HF/STO-3G	302.59007	302.50166 (55.5)[a]	302.56564 (15.7)	303.85332
HF/3-21G	304.61153	304.52914 (51.7)	304.58141 (18.9)	305.84646
MP2(FU)/3-21G	305.31854	305.24409 (46.7)	305.25524 (39.7)	306.55897
HF/6-31G	306.21785	306.13514 (51.9)	306.19113 (16.8)	307.44953
MP2(FU)/6-31G	306.92076	306.84613 (46.8)	306.86013 (38.0)	308.15777
HF/6-31G*	306.33569	306.25707 (49.3)	306.30630 (18.4)	307.56542
MP2(FC)/6-31G*//HF/6-31G*	307.33806	307.25905 (49.6)	307.27900 (37.1)	308.57922

[a] Values in parentheses are energies relative to that of **1a**, in kcal/mol.

in C_{2v} symmetry. At all levels of calculation, the energy of **1a** is considerably lower than that of **1b**. SCF energy differences in the larger basis sets range from 49.3 to 51.9 kcal/mol. The MP2(FU)/3-21G and MP2(FU)/6-31G energy differences are 46.7 and 46.8 kcal/mol, respectively, smaller than their SCF counterparts but still quite large. These values are larger than that calculated with AM1, 31.5 kcal/mol, and larger still than the reported MNDO value, 26.3 kcal/mol.[8] As noted previously, **1a** and **1b** differ in the occupancies of their π orbitals, as shown in Figure 1.

The geometric parameters of benzocyclobutene are given in Table I and the total energies in Table II. The 6-31G* CC bond lengths (in Å) for **1a** are C_1C_2, 1.422; C_1C_6, 1.342; C_3C_4, 1.440; C_4C_5, 1.358; C_1C_8, 1.518; and C_7C_8, 1.333. The 6-31G* geometry is in good agreement with the previously reported 3-21G values[4,5] as well as with the X-ray structure of di-*tert*-butyltetramethylbenzocyclobutene.[2] The calculated length of C_7C_8 confirms a double bond, while the large single-bond length C_1C_8 is consistent with the avoidance of cyclobutadiene character in **1a**. The CC bond lengths within the benzene ring of **1a** alternate in length in a manner consistent with the Mills–Nixon effect (e.g., C_1C_2, C_3C_4 > C_1C_6, C_4C_5),[3] implying a greater contribution from resonance form **4** than from **5**. From their natural resonance theory analysis[11] at the 3-21G level, Faust et al.[5] found the ratio of these two Kekulé forms to be 2.7:1.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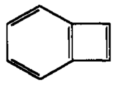
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The MP2(FU)/3-21G frequencies of **1a** are all real, the lowest being 149 (b_1) and 198 (a_2) cm^{-1}. The b_1 vibration is transformed like an out-of-plane coordinate, while the a_2 vibration involves torsional motion about the C_2 axis. Strong b_1 CH bending modes are calculated to occur at 739 and 651 cm^{-1} for the benzenoid and cyclobutadiene hydrogens, respectively. These are in reasonable agreement with the experimental values,[1a] 737 and 700 cm^{-1}, although scaling by a factor of ca. 0.91 would reduce the agreement somewhat.

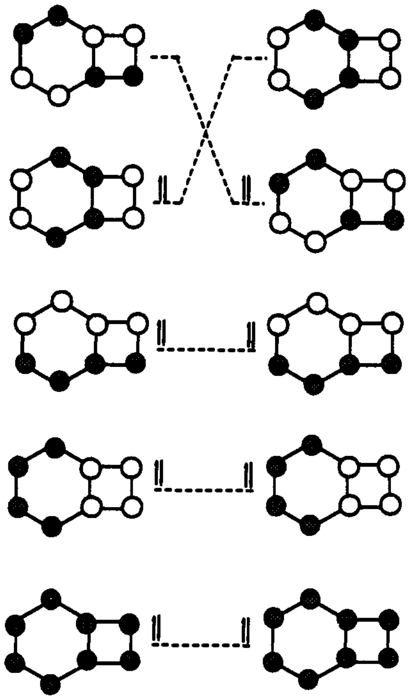

Figure 1. Top view of the four doubly occupied π orbitals and the lowest unoccupied (π*) orbitals of benzocyclobutene **1a** (left) and **1b** (right). The isomerization, symmetry forbidden at the orbital level, is indicated by the crossed dotted lines.

When the geometry of **1b** was optimized within C_{2v} symmetry, energy minima were found at all levels of HF and RMP2

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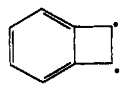
calculations. The geometric parameters (Table I) are entirely consistent with this structure, especially the short C_1C_8 bonds, 1.323 and 1.373 Å, and the very long C_7C_8 bonds, 1.596 and 1.657 Å. It is interesting that the bond angles of **1a** and **1b** are quite similar despite their different bond lengths, particularly in the four-membered ring.

The very high energy of **1b** raises the question of whether the minima obtained are artifacts, although the HOMO–LUMO gap in **1b**, 0.286 au, is not small. The frequencies of **1b** at the MP2 and HF/3-21G levels are all real. The lowest MP2 frequencies are 149 (HF, 205) and 198 (HF, 255) cm^{-1} for b_1 and a_2 modes, respectively. The lowest totally symmetric frequency is 537 (HF, 599) cm^{-1}. In order to study further the a_1 motions, which link **1a** to **1b**, we performed a synchronous transit based upon geometries that were linearly interpolated between the MP2/3-21G structures of the two isomers. The energy along this pathway (Figure 2) shows a maximum at ca. 80% of the transit to **1b**, with only a ca. 3 kcal/mol barrier for passage back from **1b** to **1a**. In order to assess whether the barrier is dependent upon the use of a single root configuration, CASSCF geometry optimizations of **1b** were attempted using an active space of eight π and π^* orbitals. All the optimizations led to structure **1a**. Moreover, calculations of CASSCF frequencies at the STO-3G HF geometry of **1b** produced a single imaginary frequency. These results strongly imply that the quinoid structure of benzocyclobutene is not a local minimum.

In view of the tendency of $4n$-π-electron systems to have low-energy triplet states (e.g., cyclobutadiene itself), the $^3B_2$ triplet level of configuration $3b_12a_2$ was considered. Geometry optimization of this triplet, **1t**, starting from either **1a** or **1b** led to the same structure, which, at the HF/6-31G* and MP2(FU)/6-31G* levels, is respectively 18.4 and 37.1 kcal/mol higher than **1a**. The reported MNDO value is 21.6 kcal/mol,[8] and our AM1 value is 24.8 kcal/mol. At all levels of calculation, the triplet state has a lower energy than **1b**. This is consistent with its instability in unrestricted HF calculations such as UMNDO.[8]

The geometry of **1t** shows little bond alternation within the six-membered ring at the HF/6-31G* level, but a pronounced bond alternation is found at the MP2(FU)/6-31G level. However, both calculations find values of the C_7C_8 bond length (1.516 and 1.507 Å) to be midway between those of **1a** and **1b**. Since the π bond between C_7 and C_8 is broken in **1t** and since there are large spin densities on these carbons (0.95, HF/6-31G*; 1.19, MP2(FU)/6-31G*) and much smaller spin densities on the other carbons, it is reasonable to conclude that **1t** is represented by structure **6**.



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Heats of Formation and Heats of Hydrogenation

As part of our study of **1**, the geometry and energy of its dihydrogenated counterpart, dihydrobenzocyclobutene **2**, was determined; the results are given in Tables I and II. Geometries calculated at the various levels are in good agreement with those of previous ab initio studies[3c,5] and with the experimental X-ray structure.[12] There is little CC bond alternation around the benzene ring. Bonds C_1C_2 and C_1C_6 are of almost equal lengths, their difference being 0.006 (expt) and 0.002 (6-31G*) Å. Faust et al.[5] in their interesting study of the Mills–Nixon effect found that the extent of bond alternation in **2** is less than that in **1a** due to the shorter C_7C_8 distance in **1a** and to the conjugation of the antiaromatic π system to the benzene ring. Thus, in contrast to **1a**, there is little difference in the contribution of the two Kekulé structures in the case of **2**. This interpretation of the lack of significant bond alternation in **2** differs from that of Stanger,[3f] who has ascribed it to outwardly bent bonds C_1C_8 and C_2C_7, which allow the nominally stringent rehybridization demands at C_1 and C_2 to be met.

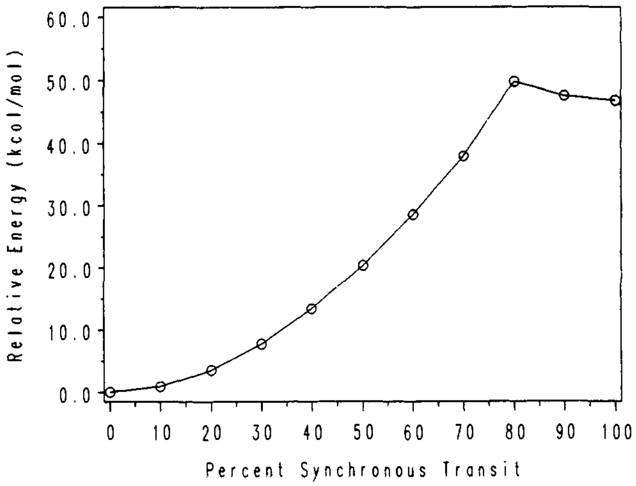

Figure 2. MP2/3-21G energies for a linear synchronous transit between **1a** and **1b**. Energies are relative to that of **1a**.

The use of group equivalents with the ab initio energies of **1** and **2** enables computation of their heats of formation. The 6-31G* CH_2 and =C— group equivalents of Schulman et al.,[13] −39.02681 and −38.45385 au, and the aromatic group equivalents of Disch et al.,[14] $=C_bH— = -38.45576$ au and $=C_b< = -37.88263$ au, give $\Delta H_f°$ values of 48.6 and 100.6 kcal/mol for **2** and **1a**. These values lead to a ΔH_h for **1a** → **2** of −52.0 kcal/mol, a large but reasonable value considering the strain energy and the antiaromatic character removed in the process.

The energy difference between **1** and **2** can be compared with that calculated for the conversion of cyclobutadiene to cyclobutene. At the MP2(FC)/6-31G*//HF/6-31G* level, this energy difference is 1.2653 au;[15] the energy difference between **1a** and **2** at this same level is 1.2412 au. Since ΔH_h of cyclobutadiene → cyclobutene is calculated to be −65.2 kcal/mol,[15] that of benzocyclobutene to dihydrobenzocyclobutene is −50.1 kcal/mol, only slightly different from the value obtained by the group-equivalent method.

It is interesting to note that the hypothetical isomerization

biphenylene + cyclobutadiene → 2(benzocyclobutene **1a**)

is only slightly exothermic, −5.5 kcal/mol, at the MP2(FC)/6-31G*//6-31G* level. The heats of formation of cyclobutadiene and biphenylene have been calculated to be 103.7[15] and 99.9[16] kcal/mol, respectively. These values are quite similar to the value of 100.6 kcal/mol found for **1a**.

The $\Delta H_f°$ of dihydrobenzocyclobutene is significantly lower than that of its nonaromatic isomer, bicyclo[4.2.0]octa-2,4,7-triene (**7**), which can be estimated to be 76.6 kcal/mol from the $\Delta H_f°$ of cyclooctatetraene (COT)[17] and the heat of isomerization of **7** to COT, 5.5 kcal/mol.[18]

The heat of formation of **1a** is slightly higher than that of (C_{2h}) pentalene (**8**). Use of the 6-31G* and MP2(FC)/6-31G*//HF/6-31G* energies of C_{2h} pentalene, respectively −306.34598 and −307.34891 au, with the corresponding values of **1a** gives an energy difference of 6.5 and 6.8 kcal/mol, respectively. The heat of

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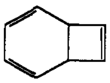
Table III. 6-31G* and 3-21G Geometric Parameters[a] of Benzodicyclobutene

parameter	**3a**[b]	**3b**[c]	**3t**[b]
C_1C_6	1.380 [1.384]	1.327 [1.331]	1.389 [1.391]
C_1C_2	1.393 [1.386]	1.540 [1.518]	1.513 [1.489]
C_5C_6	1.380 [1.384]	1.447 [1.448]	1.389 [1.391]
C_4C_5	1.393 [1.386]	1.568 [1.552]	1.513 [1.489]
C_5C_9	1.568 [1.539]	1.334 [1.329]	1.478 [1.460]
C_1C_8	1.568 [1.539]	1.477 [1.460]	1.478 [1.460]
C_7C_8	1.331 [1.327]	1.359 [1.356]	1.366 [1.362]
C_9C_{10}	1.331 [1.327]	1.595 [1.556]	1.366 [1.362]
C_8H_8	1.065 [1.072]	1.066 [1.073]	1.066 [1.073]
C_9H_9	1.065 [1.072]	1.066 [1.073]	1.066 [1.073]
C_6H_6	1.070 [1.075]	1.071 [1.075]	1.071 [1.075]
$C_6C_1C_2$	123.9 [124.1]	126.3 [126.5]	124.1 [124.3]
$C_5C_6C_1$	112.1 [111.8]	111.7 [111.3]	111.8 [111.4]
$C_4C_5C_6$	123.9 [124.1]	121.8 [122.3]	124.1 [124.3]
$C_2C_1C_8$	88.9 [88.9]	86.5 [86.8]	87.2 [87.5]
$C_4C_5C_9$	88.9 [88.9]	90.3 [90.1]	87.2 [87.5]
$H_8C_8C_1$	134.1 [134.5]	133.1 [133.5]	133.6 [134.0]
$H_9C_9C_5$	134.1 [134.5]	135.7 [135.7]	133.6 [134.0]
$H_6C_6C_1$	123.9 [124.1]	125.0 [125.0]	124.1 [124.3]
HF/3-21G	379.79155	379.77226	379.80483
MP2(FU)/ 3-21G// HF/3-21G	380.67520	380.65762	380.62629
HF/6-31G*	381.95389	381.94061	381.97370
MP2(FC)/ 6-31G*// HF/6-31G*	383.21549	383.20019	383.17179

[a] Bond lengths are in Å, angles are in degrees, and energies are in –au. 6-31G* values are in square brackets. [b] D_{2h} symmetry. The HF/3-21G bond lengths are in good agreement with those reported by Faust et al., ref 5. [c] C_{2v} symmetry.

formation of pentalene should be ca. 93.8 kcal/mol. The AM1 method gives slightly larger $\Delta H_f°$ values for **1a** and pentalene, 114 and 106 kcal/mol, respectively, while the MNDO values of Dewar and Merz are 91 and 87 kcal/mol.[8]



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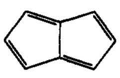
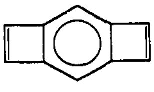


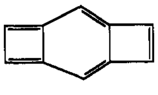
8

Benzo[1,2:4,5]dicyclobutene

In order to find a system exhibiting valence isomerization, we studied benzodicyclobutene, which could have both a D_{2h} isomer, **3a**, and a pair of C_{2v} isomers, **3b**. Isomer **3a**, with equal C_1C_6 and C_5C_6 bond lengths, cannot exhibit bond alternation in its aromatic ring. Furthermore, since each of the principal resonance structures of **3a** contains a cyclobutadiene ring (as do those of **3b**), avoidance of antiaromatic character in the manner of **1a**, namely by having larger contributions from resonance form **4** than from **5**, would not be possible. Both these factors could reduce the energy difference between **3a** and **3b**.



3a



3b

Optimizations of benzodicyclobutene led to minimum-energy structures in both symmetries at the HF/3-21G and 6-31G* levels. The total energies of the D_{2h} and C_{2v} forms predict energy differences of 12.1 (HF/3-21G), 8.3 (HF/6-31G*), 11.0 (MP2/3-21G), and 9.6 (MP2/6-31G*) kcal/mol in favor of the higher-symmetry form **3a**. Geometric parameters and energies of both forms are summarized in Table III. Isomer **3a** shows very little bond alternation in its benzene ring and typical double-bond lengths for C_7C_8. In contrast, **3b** exhibits pronounced bond alternation around its periphery.

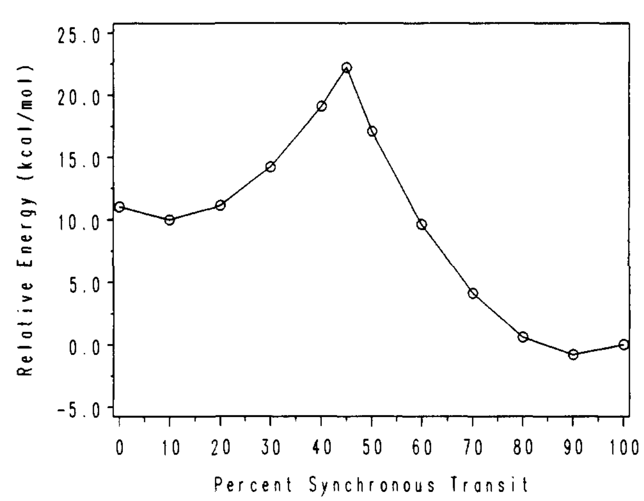


Figure 3. MP2/3-21G energies for a linear synchronous transit between **3a** and **3b**. Energies are relative to that of **3a**.

The HF/3-21G vibrational frequencies of **3b** are real, the lowest being 157 cm^{-1} for a b_1 (in-plane) mode. An energy barrier separates the two singlet isomers of **3a** and **3b** due to a change in orbital configuration at the RHF level. Taking the molecular plane as *xz*, where the *x* axis passes through C_3 and C_6, the configuration of the occupied π orbitals of the D_{2h} structure is $1b_{3u}^2 1b_{1g}^2 1b_{2g}^2 2b_{3u}^2 2b_{1g}^2$, with the π^* LUMO being $1a_u$. (In the representations of C_{2v}: $1b_1^2 2b_1^2 1a_2^2 2a_2^2 3b_1^2$ for the occupied orbitals and $3a_2$ for the LUMO). The orbital ordering in the C_{2v} isomer **3b** is $1b_1^2 2b_1^2 1a_2^2 3a_2^2 4a_2^2$, the LUMO being a π^* $3b_1$ orbital. The HOMO–LUMO gaps are respectably large for the optimized structures, being 0.31 au in both cases. There is a barrier of ca. 10 kcal/mol (in the single-configuration approximation) in passing from **3b** to **3a**, as seen from the linear synchronous transit shown in Figure 3. CASSCF geometry optimizations of **3a** and **3b** in the STO-3G basis, correlating two electrons in two π orbitals (GVB level), produced structures of each symmetry. The GVB energy difference, 20 kcal/mol, in favor of **3a** is similar to the HF value in the same basis, 17.9 kcal/mol. Benzodicyclobutene appears to exhibit Kekulé isomerism. However, this problem will have to be investigated with larger basis sets and a larger CASSCF active space as well as with the calculation of vibrational frequencies.

It was also possible to locate a low-energy triplet state, **3t**, starting from a geometry approximately midway between those of **3a** and **3b** (i.e., near the orbital crossing point). The symmetry of the triplet is D_{2h}, and its HF/3-21G and 6-31G* energies are 8.3 and 12.4 kcal/mol lower than those of the singlet **3a**. However, at the MP2/3-21G and MP2/6-31G* levels, the triplet is higher than **3a** by 30.7 and 27.4 kcal/mol. (The AM1 $\Delta H_f°$ values for **3a**, **3b**, and **3t** are 211, 219, and 224 kcal/mol.) Despite the highly strained structure of **3**, Toda et al.[19] have succeeded in preparing a derivative having *tert*-butyls on C_3 and C_6 and phenyls on C_7, C_8, C_9, and C_{10}. Their NMR and EPR investigations show that this air-sensitive compound is a singlet.

The spin density of the triplet resides mainly on the carbon atoms of the six-membered ring. A curiosity of the triplet calculation is the unusually high value of S^2, 2.4, in contrast to 2.04 found for **6**. This implies that the triplet has significant contamination from a state of higher multiplicity, possibly a quintet. All calculations on the quintet state led to structures of significantly higher energy.

Conclusion

From the viewpoints of energy, geometry, and infrared spectra, the benzenoid isomer **1a** is clearly the isolated form of benzo-

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[19] (a) Toda, F.; Ohi, M. *J. Chem. Soc., Chem. Commun.* **1975**, 506. (b) Toda, F.; Takahara, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2515. (c) Toda, F.; Mukai, K. *Chem. Lett.* **1975**, *7*, 778.

Table IV. Heats of Formation (kcal/mol)

molecule	$\Delta H_f°$	molecule	$\Delta H_f°$
1a	100.6	**8**, C_{2h}	93.8
1b	150.6[a]	**3a**	199.8
2	48.6	**3b**	209.4[a]

[a] Based upon MP2(FC)/6-31G* energies.

cyclobutene. Unlike cyclobutadiene, which exists in two distinct rectangular forms having a small barrier between them, the fusion of a benzene ring onto cyclobutadiene leads to benzocyclobutene with only one stable form.

A more promising case of valence isomerism is benzodicyclobutene **3**, for which the energies of the two singlets do not differ greatly. This problem should ultimately be studied at higher levels of calculation, as noted above. In general, Kekulé isomerization involving benzene rings appears to require, at the least, involvement in an extended π-electron system where forbidden orbital crossings lead to a barrier that "protects" the less stable form.

In this work, various heats of formation have been computed. They are summarized in Table IV.

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