Long Interbridgehead Bonds in Acceptor-Substituted Bicyclobutanes

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Abstract: The structures of bicyclobutane **4** and its dimethylene, diimino, and dioxo derivatives **5–7** as well as those of diboretene **8** and diaminodiboretene **9** were determined by ab initio MO theory at the RHF and GVB levels with use of the split-valence 3-21G basis set. The substituted cyclopropanes and cyclopropenes **10–21** were studied for comparison. Bicyclobutane itself has a short C(1)–C(3) bond between the bridgeheads; the introduction of doubly bound =CH$_2$, =NH, or =O groups at C(2) and C(4) results in a progressive opening of the C(1)–C(3) bond which acquires more π character. In bicyclobutane, planarization to the D_{2h} structure **4b** produces a biradicaloid species. The planar molecules **5b–9b** have much less biradical character, and **7b–9b** are aromatic species rather than biradicals. All molecules prefer nonplanar structures, but the planarization energies for **5–9** are very small at the GVB level, indicating easy inversion. Bicyclobutanedione **7**, cyclopropenone **13**, the diboretenes **8** and **9**, and borirenes **14** and **15** exhibit the large stabilization associated with aromatic molecules; dimethylenebicyclobutane **5** and methylenecyclopropene **11** are not aromatic. Facile ring-opening of bicyclobutanedione is expected on the basis of MNDO results.

Despite the high strain energy of 66.6 kcal/mol,[2] both types of C–C bonds in bicyclobutane (**4**) have nearly the same length (1.50 Å)[3]: the molecule is best represented by structure **1**.[4] However, the central bond between the C(1) and C(3) bridgeheads is broken relatively easily, and the resulting planar species (**4b**) is a biradicaloid (structure **2**).[5] Substitution of the methylene bridges by the strong acceptors BH or CH⁺ results in only partial opening of the molecule toward the planar structure **3**.[6,7] These acceptor-substituted bicyclobutanes are formally Hückel 2π-aromatic molecules; nevertheless, they prefer puckered rather than planar structures. This nonplanarity is favored by a partial 1,3-σ-bonding in the puckered structures and by the relief of the strong nonbonded 1,3-repulsions which are present in the planar structures.[6,7]

In this paper, we examine the structures of some bicyclobutane derivatives (**5–9**) bearing weaker acceptor groups in the bridge positions. These acceptor groups (X=Y = C=CH$_2$, C=NH, C=O, B=NH$_2$) are 2π-fragments, so that the planar geometries of these species have 6 π-electrons. However, the aromatic delocalization would be opposed by the resulting separation of charge in the open structure **3**: puckered structures may be more stable. On the other hand, the increase in ring strain caused by the sp²-hybridized X=Y groups favors opening toward **2**. The objective of this paper is to analyze how the different forces (ring strain, π-delocalization, nonbonded repulsions) find a balance. For comparison, we have also examined the substituted cyclopropenes **11–15**. Like the bicyclobutane derivatives, these are potentially aromatic molecules, but they lack the complications

of nonplanarity and biradical contributions.

Several theoretical studies on bicyclobutane (**4**),[2,4,5,8] diboretene (**8**),[6,9,10] and borirene (**14**)[6,11] have appeared, and the (potential) aromaticity of bicyclobutanedione (**7**),[10] methylenecyclopropene **11**,[8,12] and cyclopropenone (**13**)[13,14] also has been considered. Gassman et al. have studied the inversion of bicyclobutane[5] and Borden and Davidson have examined planar and nonplanar

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Table I. Geometrical Data for 4–27

	RHF/3-21G						GVB/3-21G					
	C(1)C(3)	CX	XY	α^f	τ_1	τ_2	C(1)C(3)	CX	XY	α	τ_1	τ_2
4a	1.484	1.513	1.075	61.8	5.0	3.0	1.529	1.514	1.075	60.0	1.1	6.0
5a	1.593	1.470	1.305	55.6	7.1	9.6	1.775	1.480	1.306	44.7	3.4	29.6
6a	1.667	1.466^b	1.240	52.2	6.4	12.2	1.813	1.478^b	1.241	42.4	4.1	24.3
7a	1.762	1.464	1.195	45.9	6.9	13.3	1.888	1.477	1.196	36.1	4.8	17.9
8a^c	1.883	1.521	1.174	47.6	5.1	11.5	1.967	1.530	1.176	43.2	2.6	12.0
9a^c	1.794	1.528	1.403	48.4	6.4	16.7	1.912	1.539	1.405	43.5	4.0	19.2
4b	1.927	1.520	1.093				2.103	1.541	1.084			
5b	1.971	1.468	1.328				2.068	1.499	1.314			
6b	1.988	1.471^b	1.257				2.057	1.496^b	1.248			
7b	2.010	1.472	1.208				2.058	1.492	1.201			
8b^c	2.183	1.543	1.184				2.197	1.552	1.184			
9b^c	2.174	1.546	1.421				2.213	1.562	1.414			

	RHF/3-21G										
	CC	CX	XY		CC	CX	XY			CX	XY
10^e	1.282	1.523	1.075	16^e	1.513	1.513	1.072	22^e		1.541	1.085
11^e	1.308	1.448	1.311	17	1.545	1.472	1.301	23^e		1.515	1.318
12	1.320	1.440^b	1.248	18	1.559	1.470^b	1.241	24		1.515^b	1.258
13	1.333	1.428	1.203	19	1.572	1.469	1.195	25^e		1.515	1.211
14^d	1.348	1.485	1.171	20^d	1.559	1.545	1.175	26^d		1.586	1.196
15^d	1.343	1.496	1.400	21^d	1.580	1.542	1.387	27		1.595	1.411

^{a} Distances in Å, angles in deg. ^{b} Average of the two nonequivalent C–N bonds. ^{c} RHF data from ref 10. ^{d} From ref 11. ^{e} From ref 21. ^{f} For the meaning of α, τ_1, and τ_2, see Figure 1.

structures of dimethylenebicyclobutane 5.[13] Gleiter and Hoffmann considered classical nonplanar (1) and planar (2, 3) structures for bicyclobutanedione but did not discuss the possibility of intermediate situations.[15]

Systems for which biradical contributions are important cannot be treated adequately at the closed-shell restricted Hartree–Fock (RHF)[16] level but require a multi-configuration-SCF (MCSCF) or an equivalent generalized valence-bond (GVB) treatment.[17] Therefore, we have optimized the geometries of 4–9 at the RHF/3-21G and GVB/3-21G levels. This allows the importance of biradical contributions to both energies and geometries to be evaluated.

1   **2**   **3**

nonplanar   planar

XY =	4a (C_{2v})	4b (D_{2h})
CH₂		
C=CH₂	5a (C_{2v})	5b (D_{2h})
C=NH	6a (C_2)	6b (C_{2h})
C=O	7a (C_{2v})	7b (D_{2h})
B—H	8a (C_{2v})	8b (D_{2h})
B=NH₂	9a (C_{2v})	9b (D_{2h})

XY = CH₂	10	16	22	C_{2v}
C=CH₂	11	17	23	C_{2v}
C=NH	12	18	24	C_s
C=O	13	19	25	C_{2v}
B—H	14	20	26	C_{2v}
B=NH₂	15	21	27	C_{2v}

Methods

The geometries of 4–9 were optimized completely, subject only to overall molecular symmetry constraints, using the restricted Hartree–

Table II. Total Energies (au) for 4–27^a

	RHF		GVB/3-21G
	3-21G	6-31G*	
4a	−153.98664	−154.86957	−154.00505
5a	−229.23183	−230.54097	−229.25433
6a	−261.04456	−262.55082	−261.06912
7a	−300.52519	−302.24931	−300.55137
8a	−126.64963	−127.36623	−126.66968
9a	−236.22714	−237.52427	−236.24937
4b	−153.84197	−154.72028	−153.95862
5b	−229.17831	−230.48493	−229.23966
6b	−261.00694	−262.51340	−261.05982
7b	−300.50436	−302.22599	−300.54759
8b	−126.62994	−126.34138	−126.65844
9b	−236.19783	−237.49141	−236.23874

		RHF/3-21G			
10	−115.16201	16	−116.40121	22	−117.61330
11	−152.79232	17	−154.01872	23	−155.24714
12	−168.70316	18	−169.92037	24	−171.15031
13	−188.44973	19	−189.65330	25	−190.88722
14	−101.52267	20	−102.68696	26	−103.91768
15	−156.30779	21	−157.49096	27	−158.72142

^{a} Data for 8 and 9 (RHF) were taken from ref 10, for 14, 15, 20, 21, 26 from ref 11 and for 10, 11, 16, 22, 23, 25 from ref 21.

Table III. Occupation Numbers of the C(1)–C(3) π^* Natural Orbital in GVB Calculations

	structures	
compd	a	b
4	0.04	0.94
5	0.11	0.59
6	0.11	0.40
7	0.12	0.27
8	0.07	0.15
9	0.08	0.24

Fock (RHF)[16] and generalized valence-bond (GVB)[17] methods with the small split-valence 3-21G basis set.[18a] The GAUSSIAN-80 program[19] was employed for the RHF calculations, while the GVB calculations, using one pair function for the bridgehead C–C bond, were carried out with

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the GAMESS program package.[20] The influence of polarization functions was checked at the RHF level by single-point calculations at the RHF/3-21G optimized geometries with the 6-31G* basis set.[18b] Since the effects of polarization functions were found to be minor and GVB calculations in such a large basis would be very time-consuming, we did not carry out single-point GVB/6-31G* calculations. The RHF/3-21G geometries and energies of the compounds **10–27** were obtained for comparison purposes; data on some of these were already available[11,21] (see the footnotes to Tables I and II).

The most important geometrical details are summarized in Table I: complete specifications of all geometries (Z-matrices and coordinates) are available as supplementary material. Total energies are collected in Table II; the occupation numbers for the C(1)C(3)-antibonding π^* natural orbitals in **4–9**, which reflect the amount of biradical character, are given in Table III.

Comparisons of bond lengths are frequently made in the discussion. Unless otherwise noted, these data refer to 3-21G optimized geometries (GVB for **4–9**, RHF for **10–27**) and not to experimental bond lengths, which are in most cases unavailable.

The Bonding in Bicyclobutane

Bicyclobutane (**4**) is a highly strained molecule. Because of the unusual bond angles, the paths of maximum electron density do not follow the bond vectors, i.e., the C–C bonds are "bent bonds"[4] like those in cyclopropane.[22] As a consequence, the C–C distances are smaller than those in unstrained analogues. The peripheral bonds in **4** are virtually identical with those in cyclopropane calculated at the same level of theory (1.513 Å at RHF/3-21G): the contraction with respect to ethane is 0.030 Å. The bridgehead bond is part of two cyclopropane rings, and the calculated bond length of 1.484 Å is very close to that of ethane minus twice this contraction. The difference between peripheral and bridgehead bond lengths persists even at the RHF/6-31G* level (calcd.: 1.489, 1.466 Å[2]), which usually produces C–C bond lengths accurate to ca. 0.02 Å. Experimentally, however, the two bond types have the same lengths (1.498, 1.497 Å[3]).

The C(1)C(3) bridgehead bond in **4** is the most highly strained part of the molecule. According to Newton and Schulman,[4] it is formed from hybrid orbitals of nearly pure p character inclined at an angle of ca. 30° with respect to the bond vector; in other words, it is a single bond with ca. 25% π-character. Because of the high strain in the bond, the molecule cannot be adequately described by a single-determinant wave function.[5] A proper description requires a two-configuration wave function composed of the ground state plus the HOMO → LUMO double excitation;[13] equivalently, one can use a GVB pair function to represent the C(1)C(3) bond.[5] At the GVB/3-21G optimized geometry, **4** is calculated to have ca. 4% biradical character (Table III). The bridgehead bond has been lengthened by 0.045 Å with respect to RHF/3-21G and is now slightly longer than the peripheral C(1)C(2) bonds; the other geometrical changes are minor (Table I). Because of computation-time limitations, we have not been able to carry out a GVB/6-31G* optimization for **4**, which should give a more accurate geometry. Estimated GVB/6-31G* values can be obtained by assuming additivity of the RHF → GVB and 3-21G → 6-31G* corrections: the comparison with the experimental data for bicyclobutane (Table V) is seen to be satisfactory.

Substituted Bicyclobutanes 5–7

The bridgehead bond in **4** has ca. 25% π-character, hence the C(1)–C(3) bonding orbital will be stabilized and its π-character increased by π-acceptor orbitals in the 2- and 4-positions. We have studied dimethylene-, diimino- and dioxobicyclobutane (**5–7**), where the π-acceptor orbitals are the X–Y π^*-antibonding orbitals. In the extreme, π-donation from the C(1)C(3)-bond to these π^* orbitals would produce the zwitterionic structure **2**, expected to have some degree of aromatic stabilization. For comparison, we have also examined derivatives of cyclopropane (**16–21**) which

Table IV. Partitioning (in Å) of the Increase in the Bridgehead Bond Length in **5–9** from That in **4**[a]

molecule	Δ_{tot}	Δ_{birad}	Δ_{strain}	Δ_π
5a	0.246	0.182	0.064	0.000
6a	0.284	0.146	0.092	0.046
7a	0.359	0.126	0.118	0.115
8a	0.438	0.084	0.092	0.262
9a	0.383	0.118	0.134	0.131

[a] Definition of terms (see text): Δ_{tot} = increase in C(1)C(3) bond length with respect to **4**; Δ_{birad} = difference in bond length between GVB and RHF structures; Δ_{strain} = twice the increase in distal bond length in the corresponding cyclopropanes **17–21** with respect to **16**; Δ_π = $\Delta_{tot} - \Delta_{birad} - \Delta_{strain}$.

should provide a reasonable reference point for the strain effects in the bicyclobutanes.

The three molecules **5–7** show a gradual opening of the bridgehead bond with increasing electronegativity of the atoms Y. These bonds are 0.25–0.35 Å longer than the value in **4**, taken to be "normal". The large elongations can be attributed to biradical, strain, and π-delocalization effects (see Table IV). Easiest to evaluate is the biradical contribution, i.e., the difference between the GVB/3-21G and RHF/3-21G bond lengths; this amounts to 0.18–0.12 Å. The X═Y substituents increase strain at the bridgehead bond. As the same effect is present in the corresponding substituted cyclopropanes, the strain contribution can be estimated as twice the elongation (0.03–0.06 Å) of the distal bond in **17–19** with respect to **16**. What remains can be interpreted as the π-delocalization contribution: this amounts to 0.00–0.12 Å. Biradical contributions, ring strain, and π-effects cooperate to produce extremely long bridgehead bonds but are not strong enough in these systems to result in planar structures. An extremely long bridgehead bond (1.78 Å), comparable to those calculated for **5–7**, is found in 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethyl-2,4-disilabicyclobutane.[23] The elongation of the C(1)C(3) bond has been attributed to the π-acceptor-character of the bridges, in this case the dimethylsilyl groups.[24]

Diboretenes 8 and 9

The π-acceptor orbitals in **5–7** are X–Y antibonding orbitals. Such X═Y groups are poor acceptors compared to BH, which has a vacant π-orbital. Accordingly, the bridgehead "bond" in **8** (XY = BH) is calculated to be nearly 0.45 Å longer than that in **4**, and this elongation is largely (0.26 Å, 58%) due to the π-effect. The C–C distance of 1.967 Å can hardly be called a bonding distance any more.[25]

The structure of 1,3-bis(dimethylamino)-2,4-di-*tert*-butyl-1,3-diboretene (**28**) has been determined by Siebert et al.[26] The diboretene skeleton is puckered, as predicted earlier for the parent **8**.[6] The geometrical parameters from the X-ray determination agree reasonably well with the calculated values for **8**. In order to assess the effects of the amino substituents, we have also optimized diaminodiboretene **9** at the RHF/3-21G and GVB/3-21G level. Compared with **8**, the bridgehead bond is shorter and the peripheral bonds are slightly longer in **9**, as expected because of the poorer acceptor character of the BNH$_2$ groups.

It is not useful to compare the GVB/3-21G structure for **9** directly with the experimental structure for its substituted derivative. Polarization functions are required to calculate accurate bond lengths and angles, but a GVB/6-31G* optimization would be excessively time-consuming. We can, however, use the available RHF/3-21G and GVB/3-21G structures for **8** and **9** and the RHF/6-31G* structure fo **8**[9] to obtain an extrapolated GVB/6-31G* structure for **9**. The results are compared with the ex-

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Table V. Extrapolated GVB/6-31G* Geometries for 4, 8, and 9[a]

	CC	CX	XY	α	τ_1	τ_2
4, RHF/3-21G	1.484	1.513		61.8		
4, corr RHF → GVB	0.045	0.001		-1.8		
4, corr 3-21G → 6-31G*[b]	-0.018	-0.024		-1.9		
4, GVB/6-31G* est	1.511	1.490		58.1		
4, exptl[c]	1.497	1.498		58.3		
8, RHF/3-21G	1.883	1.521		47.6	5.1	11.5
8, corr RHF → GVB	0.084	0.009		-4.4	-2.5	0.5
8, corr 3-21G → 6-31G*[d]	-0.096	-0.021		3.2	0.7	0.4
8, GVB/6-31G* est	1.871	1.509		46.2	3.3	12.4
9, RHF/3-21G	1.794	1.528	1.403	48.4	6.4	16.7
9, corr RHF → GVB	0.118	0.011	0.002	-4.9	-2.4	2.5
8, corr 3-21G → 6-31G*[d]	-0.096	-0.021	-0.011[e]	3.2	0.7	0.4
9, GVB/6-31G* est	1.816	1.518	1.394	46.7	4.7	19.6
28, exptl[f]	1.814	1.504	1.410	52	2-3	12

[a]Distances in Å, angles in deg. [b]From ref 3. [c]6-31G* geometry for 4 from ref 2. [d]6-31G* geometry for 8 from ref 10. [e]3-21G → 6-31G* correction for H₂BNH₂, taken from ref 21. [f]From ref 26.

perimental data in Table V, and the agreement suggests that the extrapolation procedure is reasonable.

t-Bu
t-Bu
Me₂N≔B⟨⟩B≕NMe₂

28
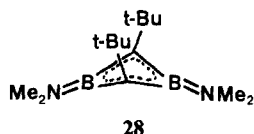
Singlet–Triplet Separations

Earlier theoretical work by Dougherty[27] indicates that opened bicyclobutanes (e.g., **4b**) might have triplet ground states, and the triplet 1,3-dimethyl-1,3-cyclobutadiyl biradical has recently been detected by ESR spectroscopy.[28] There is little doubt that the corresponding singlet would rapidly decay to a closed bicyclobutane (**4a**) derivative much lower in energy than the triplet.[27] For the more highly strained dimethylenebicyclobutane **5**, however, Borden and Davidson calculated the singlet *at its equilibrium geometry* to be close in energy to the triplet[13] (triplet **5** has also been detected recently[29]).

In the present work, we have not investigated the triplet states of **4–9**. The HOMO–LUMO separation will increase with increasing acceptor strength of the X=Y groups: the C(1)C-(3)-bonding π-HOMO delocalizes to the X=Y groups, whereas the C(1)C(3)-antibonding π*-LUMO has a node through these groups. Thus, the HOMO–LUMO separation will increase in the order **5b** < **6b** < **7b** < **9b** < **8b**. This is reflected by the decreasing amount of biradical character of the singlet states (Table III); the stability of the singlet relative to the triplet will increase in the same order. Since singlet and triplet **5** are close in energy,[13] **6–9** would be expected to have singlet ground states; this has been confirmed experimentally for the diboretene derivatives.[26,30,31]

Planarization Energies

The bicyclobutane skeleton is rather flexible, and a derivative (1,3-diphenyl-2,4-bis(methoxycarbonyl)bicyclobutane) has been reported to undergo thermal inversion at 120° (ΔH* = 26 ± 2 kcal/mol).[32] During the inversion process, the bridgehead bond must open. Gassman and co-workers studied the inversion process

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(28) Jain, R.; Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7294.
(29) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774.
(30) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-Van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem.* **1983**, *95*, 61.
(31) Wehrmann, R.; Pues, C.; Klusik, H.; Berndt, A. *Angew. Chem.* **1984**, *96*, 372.
(32) D'Yakanov, I. A.; Razen, V. V.; Komendantov, M. I. *Tetrahedron Lett.* **1966**, 1127, 1135.

Figure 1. Definition of geometrical parameters for structures **4a–9a**.

Table VI. Planarization Energies for **4–9** (kcal/mol)

molecule	$E_{\text{planarization}}$		
	RHF/3-21G	RHF/6-31G*	GVB/3-21G
4	90.8	93.7	29.1
5	33.6	35.2	9.2
6	23.6	23.5	5.8
7	13.1	14.6	2.4
8	12.4	15.6	7.1
9	18.4	20.6	6.7

of bicyclobutane at the RHF/PRDDO and GVB/PRDDO levels.[5] The RHF and GVB methods were found to give similar changes in energy and geometry near the equilibrium geometry of **4**. However, for smaller values of the folding angle α (see Figure 1) the RHF energy increases much too steeply and this leads to an unrealistically high barrier of over 50 kcal/mol. The calculated potential energy curve indicates the existence of a second, very shallow C_{2v} local minimum with pyramidalized carbon atoms in the vicinity of the planar D_{2h} structure, similar to the near-planar local minimum found by Borden and Davidson for **5**.[13] Gassman et al. did not optimize the structure of this second minimum. For inversion, the molecule probably still has to pass through the planar structure. The precise shape of this region of the potential energy surface is bound to be very sensitive to the basis sets and computational methods employed, so that an extensive study of the surface would not be very useful. Therefore, we have refrained from exploring the inversion paths of **4–9** in detail. Instead, we have calculated the puckered equilibrium structures **4a–9a** and the planar structures **4b–9b**: the energy differences between the puckered and planar structures are given in Table VI. Our ab initio results on **4** agree with the PRDDO results of Gassman: in particular, the unrealistically high barrier of ca. 90 kcal/mol at RHF is reduced to ca. 30 kcal/mol at the GVB level. Clearly, RHF is inadequate here! Qualitatively, the same trends are observed for **5–9**: planarization energies are reduced by a factor of 3–5 at the GVB level. The calculated barriers are all rather low (2–9 kcal/mol, see Table VI) and are not expected to become much higher at higher levels of theory.

Planar singlet bicyclobutane is a biradical (see Table III). The planar species **5b–9b** are not pure biradicals, but the population of the π* orbital is in all cases much higher in the planar species than in the puckered ones, although the energy differences between the planar and puckered structures are rather small. Thus, it seems likely that singlet **5** and **6** can behave as biradicals even though the equilibrium structures have only ca. 11% biradical character. The remaining molecules **7–9** are more nearly closed-shell species even in the planar geometries (Table III).

Bicyclobutanedione **7** has the smallest inversion barrier of the molecules studied here. Even so, it definitely prefers a nonplanar structure, and this preference is expected to become somewhat greater at higher levels of theory. The closest relatives to **7** are the squaraines,[33] which carry π-donor substituents in the 1- and 3-positions. Squaraines prefer planar structures, which we have attributed to strong π-bonding with the substituents.[34] Such

(33) For a recent review, see, e.g.: Schmidt, A. H. In "Oxocarbons"; West, R., Ed.; Academic Press: New York, 1981; Chapter 10. Schmidt, A. H. *Synthesis* **1980**, 961.
(34) Budzelaar, P. H. M.; Dietrich, H.; Macheleid, J.; Weiss, R.; Schleyer, P. v. R. *Chem. Ber.* **1985**, *118*, 2118.

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π-bonding makes the "bridgehead" carbon atoms unavailable for 1,3 σ-bond formation, and the extended conjugation also opposes ring puckering.

The Aromaticity of Bicyclobutane and Cyclopropene Derivatives

No simple, unequivocal definition of aromaticity, or of the degree of aromaticity, has met general acceptance.[35] The assignment of "aromatic", "nonaromatic", or "antiaromatic" character can be based on energy relationships and bond length changes with respect to certain reference compounds; the difficulty lies, of course, in the selection of the proper reference compounds.[36]

We will take borirene (14) and 1,3-diboretene (8) as examples. The resonance energy of borirene has been estimated to be 47 kcal/mol[6,11] from reaction 1. This large resonance energy cer-

(1)
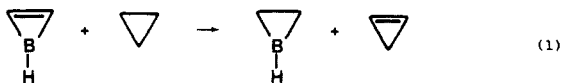
tainly justifies classifying it as an "aromatic" molecule. The resonance energy of 1,3-diboretene was calculated from eq 2 as

(2)
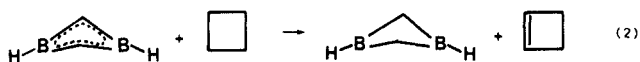
14 kcal/mol,[6] which would imply a much smaller degree of aromaticity for 8. However, if one considers 8 to be a bicyclobutane derivative there are more appropriate choices for reference compounds, as in eq 3 or 4. Evaluation of these equations gives

(3)

(4)
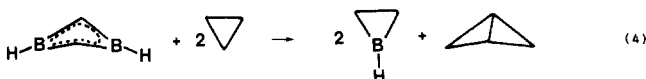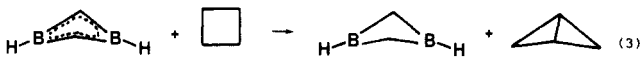
much higher resonance energies, viz., 32 and 58 kcal/mol. While recognizing that there are good arguments in favor of each of these three choices, we prefer the last one in the present context. We are examining the effect of acceptor substituents on the bridgehead-bonding orbital of bicyclobutane, so comparisons between substituted and unsubstituted bicyclobutanes are needed. This excludes reaction 2. In addition, ring strain in bicyclobutanes is one of the factors which promote ring opening. A classical diborabicyclobutane would have somewhat more than twice the ring strain of borirane, just as bicyclobutane has somewhat more than twice the ring strain of cyclopropane.[2,37] However, borirane is more strained than cyclopropane,[10] so that the ring strain relief accompanying ring-opening is represented better by eq 4 than by eq 3. Thus, we conclude that 1,3-diboretene has a very large resonance energy of ca. 58 kcal/mol.

A similar conclusion can be drawn from analysis of the bond lengths in borirene and diboretene. The C=C bond in 14 is 0.07 Å longer than that in cyclopropene (10). A small part of this is caused by the increased ring strain in the boron compound, but most of it is due to the 2π-delocalization. In general, the change in hybridization from sp³ to sp² results in a decrease of the covalent radius of carbon, presumably because of the increased amount of s-character in the bonds. Because three-membered ring framework bonds are largely formed from p-orbitals,[4,22] this effect would not be expected in cyclopropane derivatives: indeed the C(sp³)–C(sp²) bond in cyclopropene is calculated to be ca. 0.01 Å longer than the C(sp³)–C(sp³) bond in cyclopropane (both at 4-31G² or 3-21G, Table I). Applying the same argument to borirene, we conclude that the shortening of the B–C bonds by 0.06 Å with respect to borirane 20 is not caused by hybridization

Table VII. Resonance and Strain Energies (kcal/mol)[a]

XY	reaction				
	5	6	7	8	9
C=CH₂	8.9	8.0	−10.2	−11.5	−2.2
C=NH	16.1	13.8	−11.2	−6.2	+2.6
C=O	26.4	22.3	−13.7	−1.0	+8.7
BH	58.4	47.0	−11.7	+35.1	+35.3
B=NH₂	40.6	35.1	−11.5	+17.6	+23.6

[a] Using GVB/3-21G data for 4–9 and RHF/3-21G data for 10–27.

effects but rather by the aromatic delocalization in 14.

In diboretene, the effects of delocalization will be spread over four single bonds and will therefore be more attenuated. Also, it is not easy to select the right reference bond lengths. In the absence of delocalization effects, three-membered rings have shorter bonds than open-chain compounds, whereas four-membered rings tend to have slightly longer bonds.[37] For a classical diboretene (type 1 structure), one would therefore expect B–C single bonds close to those in borirane (1.545 Å). For the opened, delocalized form, the expected single bond length would be ca. 1.59 Å, the B–C single bond calculated for 1,3-diboretane at 4-31G.[6] In four-membered rings, however, changes in hybridization cause significant changes in bond lengths, cf. the C-(sp³)–C(sp²) bonds in cyclobutene with the C(sp³)–C(sp³) bonds in cyclobutane (1.526 and 1.554 Å, both at 4-31G²). Assuming the same contraction on going from C(sp³)–B(sp²) to C(sp²)–B-(sp²), one obtains a reference bond length of 1.56 Å, still 0.03 Å longer than that calculated for 8. That all four bonds contract by 0.03 Å certainly indicates a significant delocalization!

We will now consider the aromaticity of substituted bicyclobutanes and cyclopropenes. Table VII lists the resonance energies, estimated by means of eq 5 and 6. Also given are the strain

(5)

(6)
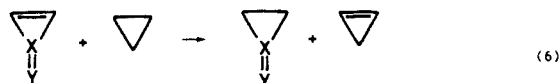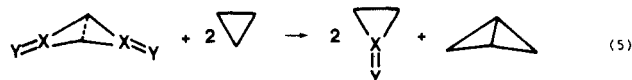
energies relative to the parent compounds of each series. While basis sets without polarization functions are not suitable for calculating absolute strain energies, comparisons at lower levels involving isodesmic reactions usually provide consistent results.[38a] Accordingly, the 3-21G energies for reactions 7–9 should be reasonably accurate. Clearly, all X=Y substituents increase the
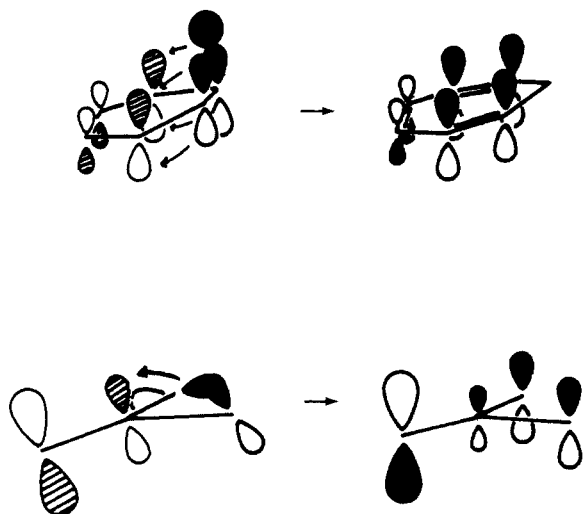
(7)

(8)

(9)
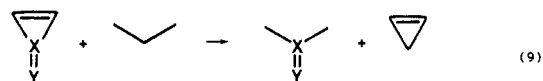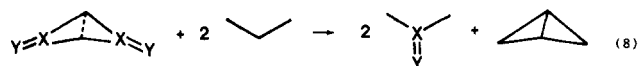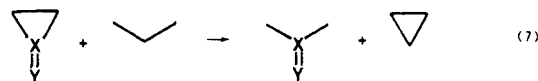
strain energy of cyclopropane. For the cyclopropenes and bicyclobutanes, however, the increased ring strain is partly compensated for by "aromatic" delocalization. The methylene com-

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(35) Garratt, P. J. "Aromaticity"; McGraw-Hill: London, 1971.
(36) Binsch, G. *Naturwissenschaften* **1973**, *60*, 369.
(37) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

(38) (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. Actually, reactions 7–9 do not represent pure changes in strain energies as defined by George et al.,[38b] since changes in the bond separation energies of the alicyclic reference compounds also contribute. However, these contributions should be small for the species considered here. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. George, P.; Trachtman, M.; Brett, A. M.; Bock, W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.

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Figure 2. Schematic representations of the orbital interactions accompanying the ring-opening of norcaradiene and acceptor-substituted bicyclobutane.

pounds **5** and **11** have only small delocalization energies and are conjugated, nonaromatic molecules. In contrast, the resonance energies of **7** and **13** are sizable, and one can certainly assign these molecules some aromatic character.[10,12,39,40] The BH compounds **8** and **14** are the most aromatic ones of the series. Introduction of amino groups at boron decreases delocalization because of the competing N→B π-donation, but the effect is not large and both **9** and **15** are still aromatic.[10,11]

A Comparison with Norcaradienes and Methano[10]annulenes

The partial opening of bicyclobutanedione **7** and of the diboretenes **8** and **9** can be compared to the Woodward-Hoffmann-allowed ring-opening reactions of norcaradiene **29** and of methano[10]annulene **30**.[41-47] In all these reactions, the presence of a π-acceptor orbital adjacent to a bridgehead C–C bond assists the ring-opening: the C–C σ-bonding orbital mixes with the π-acceptor orbital, and in the final situation only a weak π-interaction between the bridgehead carbon atoms remains (Figure 2). Bürgi was able to trace a path for these reactions by examining a number of crystal structures of derivatives of **29** and **30**,[41] and the more recent series of X-ray studies of derivatives of **30** by Simonetta[42] shows a nearly continuous transition from the

(39) Fitzpatrick and Fanning (Fitzpatrick, N. J.; Fanning, M. O. *J. Mol. Struct.* **1975**, *25*, 197) found a total C≡C → C—C π-donation of 0.22 e and C—C π-overlap populations of 0.338 (C≡C) and 0.064 (C—C) for **13** and concluded from these data that cyclopropenone is not aromatic. However, even in borirene, which certainly has a large resonance energy, the π-electron distribution is rather uneven, with a C≡C → B—H π-donation of 0.33 e and π-overlap populations of 0.37 (C≡C) and 0.18 (C—B). Thus, the calculated resonance energy of 22 kcal/mol for **13** seems reasonable, being slightly less than half of that of **14**, and we conclude that even relatively small amounts of π-electron delocalization may lead to sizable resonance energies.

(40) In this extensive discussion of cyclopropene derivatives,[14] F. H. Allen argues that the bond lengths in cyclopropenone do not indicate a significant degree of delocalization. Although we agree with his argument that the C≡C single bond lengths in **10** are not very suitable references, we feel that the geometrical changes with respect to **11** are more significant here and do indicate some effects of delocalization on bond lengths. In any case, even a relatively small amount of π-electron delocalization, with correspondingly small geometric effects, may result in a considerable resonance stabilization,[39] so geometric arguments alone are not enough to exclude aromatic character.

(41) Bürgi, H. B.; Shefter, E.; Dunitz, J. D. *Tetrahedron* **1975**, *31*, 3089.

(42) Bianchi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr.* **1973**, *B29*, 1196. Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr.* **1978**, *B34*, 2157. Bianchi, R.; Pilati, T.; Simonetta, M. *J. Am. Chem. Soc.* **1981**, *103*, 6426. Vogel, E.; Scholl, T.; Lex, J.; Hohlneicher, G. *Angew. Chem.* **1982**, *94*, 878; *Suppl.* **1982**, 1882.
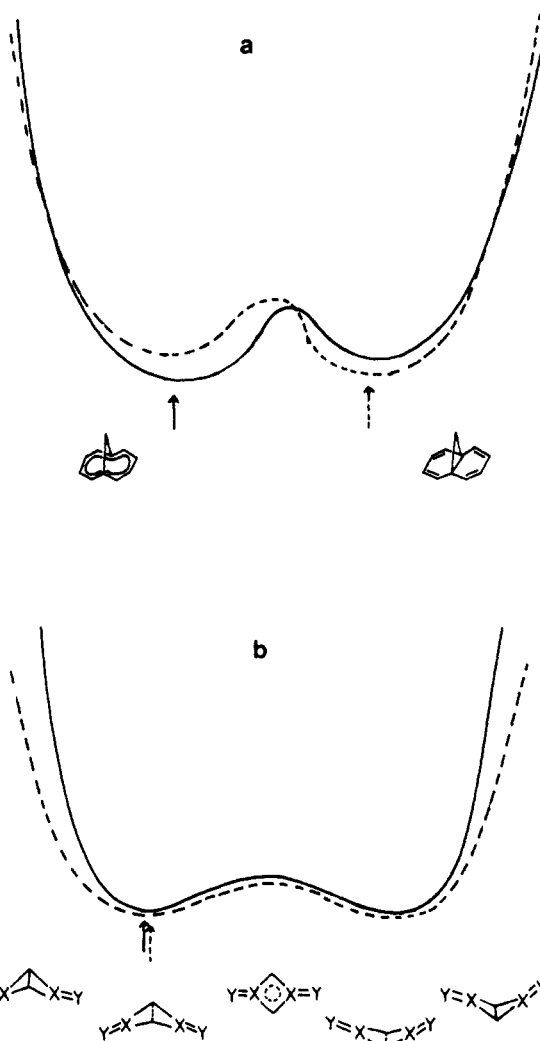
(43) Gatti, C.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1985**, *107*, 878.

(44) Cremer, D.; Dick, B. *Angew. Chem.* **1982**, *94*, 877.

(45) Farnell, L.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 7650.

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

(47) An extensive list of references is given in the following: Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.
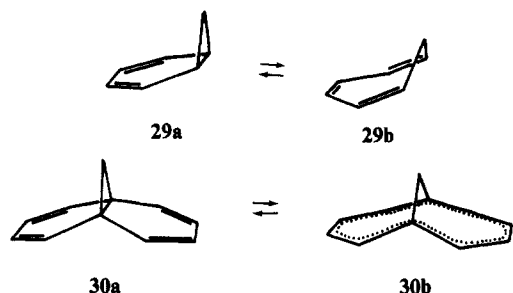

Figure 3. Schematic representations of substituent effects on the potential-energy curves for ring-opening of 1,6-methano[10]annulene (a) and acceptor-substituted bicyclobutane (b).

dinorcaradienic to the annulenic structure.[43] Theoretical studies by Cremer and Dick[44] and Farnell and Radom[45] indicated a double-minimum potential-energy curve for this valence tautomerization, with a very low activation energy for interconversion. In view of the large influence of both basis set size and electron correlation effects on the relative energies of the isomers,[46] the barrier might disappear at higher levels of theory. Most consistent with the experimental data is a broad potential energy well, for which small substituent effects might cause large structural changes (Figure 3a).[45]

In the bicyclobutane systems **5–9**, the destabilization of the closed type **1** structure appears to be so large that any acceptor substituent causes a sizable ring-opening. On the other hand, the destabilization of the planar structure with respect to the puckered one seems to be little affected by the specific nature of the acceptor group, so that a planar structure will not be obtained by minor substituent variations (see Figure 3b). Thus, whereas substituent effects in methano[10]annulenes tend to produce either dinorcaradienic or annulenic structures,[45] with intermediate situations only found for special choices of substituents,[42,43] the acceptor-substituted bicyclobutanes will nearly invariably show partially opened structures.

Decomposition Routes

The bicyclobutanes **5–9** studied in this work are all strained molecules. The 1,3-diboretenes **8** and **9** are aromatic, and some stable derivatives have now been reported.[26,30,31] This leads one to wonder whether derivatives of **5–7** might not also be stable enough to allow isolation. As we have noted above, **5** and **6** require

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29a   29b

30a   30b

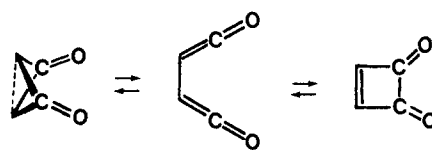|	7	32	33
RHF/3-21G:	42.0	0	4.1
E_{rel} (kcal/mol)		(T.S.)	(T.S.)
MNDO:	40.3	63.2	0	40.5	0

very little energy to convert to a structure with a large amount of biradical character. Hence, derivatives will probably be extremely reactive, and the best one can hope for may well be generation and detection in an inert matrix.

Bicyclobutanedione (7) is more nearly a closed-shell molecule and moreover possesses appreciable aromatic stabilization, so here the prospects appear more favorable. Apart from biradicaloid behavior, two decomposition routes should be considered. The first is loss of carbon monoxide, leading to cyclopropenone derivatives. A second route is suggested by the analogy between BH and CO compounds. The isomerization of 1,2-diboretene (31) to 1,3-diboretene (8) has been calculated to proceed with a very low activation energy, passing through a diborabutadiene-like transition state.[9] The CO group is a weaker acceptor than a BH

31   8
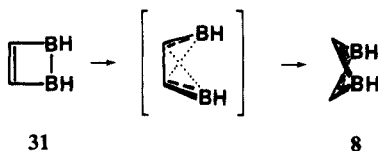
group. Therefore, the equilibrium for 7 lies on the other side; also, the diketene 32 is a stable intermediate instead of a transition state. We have optimized the diketene and cyclobutenedione 33 at the RHF/3-21G level, and all three minima plus the two transition states at the MNDO[48] level. The MNDO barrier of 23 kcal/mol indicates that the ring-opening of 7 to reactive open-chain products should be facile. Hence, preparation of bicyclobutanediones will certainly not be an easy task. The low barriers for ring-opening of acceptor-substituted bicyclobutanes should be contrasted with

the much higher values for the parent 4. The ring-opening of bicyclobutane to butadiene has an activation energy of ca. 41 kcal/mol[49] and has been calculated to proceed via a biradical intermediate.[50]

Conclusions

The bicyclobutane derivatives 5–7 and diboretenes 8 and 9 are all rather flexible molecules preferring nonplanar structures with very long bridgehead C–C bonds. The barriers for inversion are small. The planar singlet structures have a considerable amount of biradical character and cannot be adequately described by a closed-shell restricted Hartree–Fock method.

(48) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

(49) Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* 1969, *61*, 90. Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* 1965, *69*, 1775.

(50) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* 1975, *97*, 2931. Dewar, M. J. S. *J. Am. Chem. Soc.* 1984, *106*, 209.