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Puckered Structures of 1,3-Dihydro-1,3-diboretes and Bicyclobutane-2,4-dione: Nonplanar Hückel 2π-Electron Aromatic Molecules**

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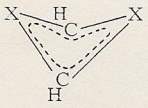
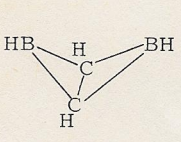
Krogh-Jespersen's[1a] calculational discovery that the cyclobutadiene dication prefers a puckered **1** rather than a planar structure initiated interest in the isoelectronic 1,3-dihydro-1,3-diborete **2**. Ab initio molecular orbital theory predicted a nonclassical folded geometry for this molecule as well[1b].



1, X = $CH^{\oplus}$
2, X = BH

Structure **2**, calculated (4-31G basis set) to have an unusual C–C distance of 1.86 Å, was favored over classical **3** and planar Hückel 2π aromatic **4** alternatives. The repulsive 1,3-interactions in **4** are reduced or eliminated in **2**. Due to orbital mixing, other electronic features of **2** are also more favorable than those in **4**[1b].



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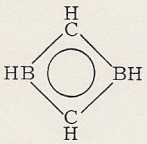

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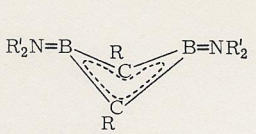
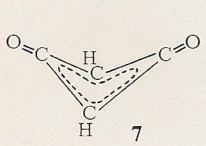


5, R = $C(CH_3)_3$, R' = CH_3
6, R = R' = H

Quite recently the first syntheses of 1,3-dihydro-1,3-diborete derivatives were achieved in three different laboratories[2–4], and the first X-ray determination carried out. *Siebert*'s puckered structure of **5**[4] is in remarkably close agreement with our 1981 predictions of **2** (Table 1). Thus the experimental distance, 1.81 Å, is much longer than the normal C–C bond length found in bicyclobutane (1.50 Å)[5]. The short exocyclic BN bonds in **5** (1.41 Å) indicate considerable B=N double bond character. Nevertheless, the very good π-donor $N(CH_3)_2$ substituents in **5** evidently alter the geometry of **2** only to a small extent. To examine this matter further, we have now calculated the structure of **6**, a simple analog of **5**, with the 3-21G basis set[6]. The geometry of **2** was redetermined at that level. The work has been further extended to the isoelectronic "organic" counterpart of **6**, bicyclobutane-2,4-dione **7**.



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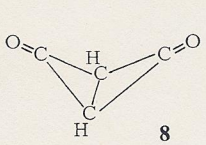

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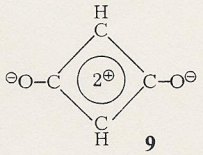

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As can be seen from the data collected in Table 1, the calculated structure of **6** agrees even more closely than that of **2** with the experimental structure of **5**[4]. The long C···C and the B=N distances are essentially identical, and the calculated puckering angle, α, is only 4° smaller than the experimental value. In view of the bulky substituents in **5**, better agreement could hardly be expected.

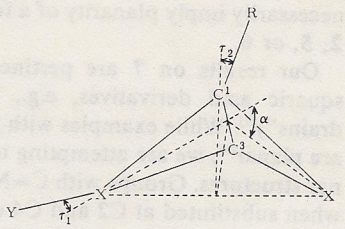

Table 1. Comparison of calculated and experimentally determined structures.

Compound	Data source [a]	Distances [Å] $C^1\cdots C^3$	C^1–X	Angles [°] HCC	α	τ_1	τ_2
1 (D_{2d})	4-31G opt. [1a]	1.973	1.431	160.6	35.8		1.5
	6-31G* opt. [1a]	1.928	1.414	157.1	42.6		1.6
2 (C_{2v})	STO-3G opt. [1b]	1.754	1.477	140.6	54.9	6.2	7.4
	4-31G part. opt. [1b]	1.858	1.510	141.0	48.2	5.2	11.4
	3-21G opt. [b]	1.883	1.521	141.4	47.6	5.1	11.5
5	exp. [4]	1.814	1.504 [c]		52	2–3	12
6 (C_{2v})	3-21G opt.	1.794	1.528 [d]	133.9	48.4	6.4	16.7
7 (C_{2v})	3-21G opt.	1.762	1.464 [e]	139.4	45.8	6.9	13.3
Bicyclo-butane	exp. [5]	1.497	1.498	128.3	58.3	−0.7	11.5
	3-21G opt.	1.484	1.513	134.7	61.8	1.4	3.0
	6-31G* opt. [f]	1.466	1.489	132.5	59.9	1.4	6.0

[a] The basis sets used for geometry optimizations are indicated. STO-3G is a minimal basis, 3-21G and 4-31G split valence bases, and 6-31G* a polarization basis. The accuracy of the results obtained at these levels are generally expected to increase in the order given. [b] T. Clark, unpublished. [c] BN distance 1.410 Å av. [d] BN distance 1.403 Å, CH 1.075, NH 1.000 Å; angles, BNH 122.6°; CBNH 171.8°. [e] CO distance 1.196 Å (in **9** 1.208 Å), CH 1.066 Å. [f] For 4-31G and 6-31G* geometries see K. B. Wiberg, *J. Am. Chem. Soc. 105* (1983) 1227.

The donation of ca. 0.2π electron from nitrogen to boron in **6** only results in a decrease of ca. 0.04e in the C→B donation. The inversion barrier though the planar structure increases by 4 kcal/mol (**2** vs **6**) as a consequence, but the other effects are small. Because of the electropositive character of boron, other electronegative substituents (like OR or F) also are not expected to alter the geometry appreciably.

We now predict that bicyclobutane-2,4-dione **7**[7], like **1**, **2**, **5**, and **6**, will also prefer a nonclassical folded structure (Table 1). The 3-21G optimized central C1···C3 distance in **7** (1.76 Å) excludes the classical formulation **8**. This distance is halfway between that in bicyclobutane (1.50 Å)[5] and that calculated for planar **9** (2.01 Å). Analysis of the electron distribution $\rho(r)$ reveals a considerable build-up of negative charge between C1 and C3 in going from **9** to **7**. The properties of $\rho(r)$ in **7** are typical for a situation preceding the formation of a C–C bond[8]. The C–O electronegativity difference is nearly the same as that between B

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and N; the bonding situations in **6** and **7** are rather similar.

As suggested by the formal structure **9**, a planar form would be expected to benefit from the Hückel 2π character of the four-membered ring. Nevertheless, **9** is 14.6 kcal/mol less stable than **7** with the larger 6-31G* basis set (13.2 kcal/mol; 3-21G). The inversion barrer for **6** is indicated to be even larger, 20.6 kcal/mol (6-31G*//3-21G; 18.4 kcal/mol, 3-21G). According to the properties of $\rho(r)$, electron delocalization in puckered **6** and **7** is still large and is supported by the now favorable 1,3-interaction. Both π and σ effects contribute to the stability of the puckered forms[1]. Once again, our calculational observations emphasize that an aromatic 2π electron ensemble does not necessarily imply planarity of a four-membered ring like **1**, **2**, **5**, or **6**.

Our results on **7** are pertinent to a large number of squaric acid derivatives, e.g., the "squaraines" ("quadrains")[7]. While examples with good π donor substituents are planar[9], we are attempting to find cases with non-planar structures. Groups with C=N or C=C double bonds[10] when substituted at C2 and C4 of bicyclobutane may also lead to partially opened structures like **7** with elongated C1–C3 bonds[11].

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