

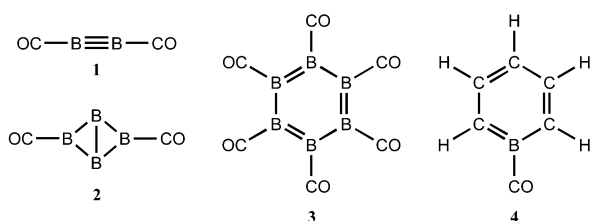
Monocyclic Boron Carbonyls: Novel Aromatic Compounds

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Akin to carbonyl transition metal complexes,¹ borane carbonyl compounds offer intriguing structural possibilities.² The H₃B–CO adduct was discovered in 1937; some two dozen BCO complexes have been described subsequently. Recent highlights are tris(trifluoromethyl)borane carbonyl, (CF₃)₃BCO³ and the two new borane carbonyls, B₂(CO)₂ (**1**) and B₄(CO)₂ (**2**) of Zhou et al.^{4,5} Combined matrix isolation infrared spectroscopy and quantum chemical computations established **1** to have a linear singlet ground state with some boron–boron triple bond character. The related triplet state was very high in energy.⁴ In contrast, **2** is a new aromatic σ – π diradical which favors an open-shell singlet over a triplet state, but only slightly. Zhou et al also investigated the triplet boron carbonyl (BBCO).⁶



Interestingly, **1** is formed from the dimerization of BCO, rather than from reaction of B₂ with CO.⁴ This suggests that higher BCO oligomers also might be viable. The six-membered, fully CO coordinated B₆ ring, (BCO)₆ (**3**), is especially intriguing as a benzene analogue. Its relationship to the borabenzene–CO complex **4** (see below) is obvious. We⁶ have called attention to the isolobal relationship⁷ of a BCO fragment to a CH group. Thus, **1** and acetylene are isolobal as are **3**, **4**, and benzene. Each boron atom in **3** has formal sp² hybridization involving a CB and two in-plane BB bonds, as well as one out-of-plane electron participating in the six-electron π delocalization.

In contrast, (BH)₆²⁻ is well-known to favor an *O_h* *closo* rather than a planar *D_{6h}* structure. Planar (BH)₆²⁻ (also (BF)₆²⁻) has only two π electrons; computationally, it is a higher-order saddle point with three imaginary frequencies (NImag = 3). The planar neutral form, (BH)₆, has NImag = 5, and (BF)₆ has NImag = 3. Unlike **3**, these species have too few valence electrons to serve as benzene surrogates. While the parent borabenzene (C₅H₅B) is still elusive, neutral Lewis base adducts (C₅H₅B–L) are well-known experimentally,⁸ but the best information on L = CO (**4**) is computational.⁹ Our calculations on **4** confirm a large (38.7 kcal/mol) CO binding energy to C₅H₅B and a CO stretching frequency of 2080 cm⁻¹.

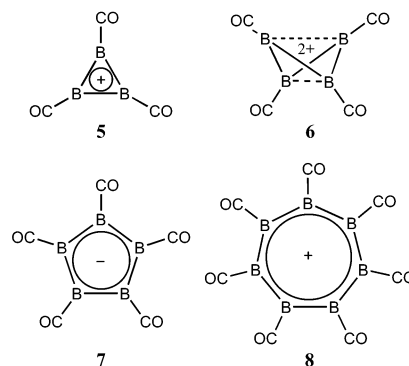
In addition to **3**, we now describe a homologous set of new aromatic monocyclic boron compounds where all the borons are

Table 1. Computed Natural Boron Charges (*q*) Scaled Vibrational Frequencies (ν , cm⁻¹), and Bond Lengths (*r*, Å)

	<i>q</i> _B ^a	ν_{CO} ^{a,b}	$\nu_{\text{B-B}}$ ^b	<i>r</i> _{B-B} ^c	<i>r</i> _{B-C} ^c	<i>r</i> _{CO} ^c
(BCO) ₃ ⁺ (5 , <i>D</i> _{3h})	−0.133	2176	1117	1.560	1.480	1.126
(BCO) ₄ ²⁺ (6 , <i>D</i> _{2d})	−0.090	2240	1170	1.597 ^d	1.527	1.117
(BCO) ₅ [−] (7 , <i>D</i> _{5h})	−0.294	1941	1135	1.659	1.455	1.163
(BCO) ₆ (3 , <i>D</i> _{6h})	−0.250	2039	1089	1.642	1.478	1.146
(BCO) ₇ ⁺ (8 , <i>D</i> _{7h})	−0.200	2098	1002	1.644	1.508	1.136

^a At B3LYP/6-31G*. ^b The scaled computed frequency of CO is 2138 cm⁻¹. ^c At B3LYP/6-311+G*. ^d The 1,3-B–B distance is 2.079 Å

coordinated to CO's. These systems, (BCO)₃⁺ (**5**), (BCO)₄²⁺ (**6**), (BCO)₅[−] (**7**), and (BCO)₇⁺ (**8**), mimic the monocyclic aromatic



hydrocarbons. While **5**, **7**, and **8** have planar minima and the *D*_{3h}, *D*_{5h}, and *D*_{7h} symmetries of the isolobal cyclopropenyl cation (C₃H₃⁺), the cyclopentadienyl anion (C₅H₅[−]), and the tropylium ion (C₇H₇⁺), **6** favors the same puckered *D*_{2d} structure as that of the cyclobutadienyl dication (C₄H₄²⁺).¹⁰ The computed natural boron charges and bond lengths are summarized in Table 1.

At B3LYP/6-311+G*,¹¹ (BCO)₆ (**3**) is an energy minimum in *D*_{6h} symmetry. The computed B–B bond length, 1.642 Å, is longer than the formal BB triple bond of **1** (1.444 Å) and the formal BB double bond (1.590 Å) in *trans*-OCBH=BHCO (isolobal with ethene), but is shorter than the BB length of 1.790 Å (1.78 Å experimental¹²) in *C*_{2h} OCBH₂–BH₂CO (isolobal with ethane). The HOMO–LUMO gap of **3**, 2.55 eV and its stable wave function indicate a closed shell singlet ground state. The two intense infrared active vibrational frequencies in the 1000–2200 cm⁻¹ range (Table 1)¹³ are 2039 cm⁻¹ for CO stretching and 1089 cm⁻¹ for in-plane BB stretching. The CO vibrational frequency of **1** (2046 cm⁻¹) is nearly the same as **3**, but its infrared active BB mode (1050 cm⁻¹) is 39 cm⁻¹ smaller than **3**. Note that the computed CO frequency of 2039 cm⁻¹ resembles those of neutral transition metal complexes, e.g., cobalt tetracarbonyl (Co(CO)₄; 2015, 2027, 2095 cm⁻¹).¹³

In addition to the equal B–B distance, the aromaticity of **3** is verified by its energy and magnetic properties. The trimerization

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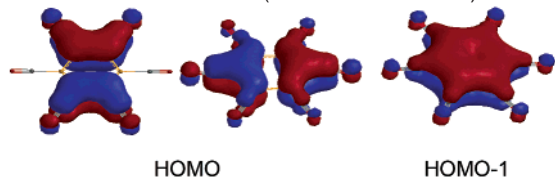
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Table 2. GIAO-HF/6-31+G* and PW91/IGLOIII Total NICS(1) and Dissected Values (ppm) of **3–8** (Related Aromatic Hydrocarbon Data Are in Parentheses)

	NICS(0, π) ^a	NICS(1) ^a	NICS(1) ^b
C ₅ H ₅ BCO (4 , C _{2v})	-18.3 (-20.7)	-9.1 (-10.6)	-10.2 (-10.7)
(BCO) ₃ ⁺ (5 , D _{3h})	-18.1 (-26.0)	-14.1 (-15.0)	-16.6 (-16.0)
(BCO) ₄ ²⁺ (6 , D _{2d})	-14.0 (-17.4)	-17.1 (-15.5)	-19.0 (-16.5)
(BCO) ₅ ⁻ (7 , D _{5h})	-15.9 (-22.7)	-5.2 (-11.5)	-6.6 (-10.6)
(BCO) ₆ (3 , D _{6h})	-14.4 (-20.7)	-6.8 (-10.6)	-8.2 (-11.5)
((BCO) ₇) ⁺ (8 , D _{7h})	-12.6 (-13.2)	-4.1 (-8.8)	-6.5 (-10.7)

^a IGLO data. ^b GIAO data.

Scheme 1 π Molecular Orbitals (HOMO and HOMO-1) of **3**



energy of three molecules of **1** to give **3**, -155.5 kcal/mol, is even more exothermic than the -139.5 (expt -143.6) kcal/mol acetylene trimerization energy to give benzene!¹⁴ The dissociation of a single CO from **3** (to give C_{2v} B(BCO)₅, the isolobal counterpart of borabenzene) is endothermic by 31.9 kcal/mol. For comparison, our computed dissociation energies (in kcal/mol) of experimentally known² boron carbonyls are: 24.9 for H₃BCO, 22.7 and 21.7 (first and second CO) for OCBHBHCO, 41.4 for B₃H₇CO, and 43.6 for B₄H₈CO. Clearly, **3** is stable thermodynamically.

The widely employed nucleus-independent chemical shift (NICS) method was applied at two levels: GIAO-HF/6-31+G* (which gives nearly the same results as those at B3LYP) and the standard IGLO-PW91/III.¹⁵ The latter dissects the total NICS values into localized π , σ , and lone pair orbital contributions. The best aromaticity indexes are NICS(0, π) (in the ring center) and total NICS(1) (1 Å above the ring), since the influence of the σ contributions is eliminated or reduced.^{15b,c} (This also is shown by the behavior of the in-plane and out-of-plane contributions to the GIAO anisotropies. See Supporting Information.) Accordingly, **3** is only somewhat less aromatic than benzene. The same is true of **4–8**, which mimic their aromatic hydrocarbon counterparts (Table 2).

The aromatic character of **3** also is shown by the three benzene-like π frontier orbitals in Scheme 1. The degenerate HOMO and HOMO-1 reveal binding between the ring borons and carbons and the antibonding carbon–oxygen interactions, due to the back-donation from boron to carbon.⁹ These reduce the 2138 cm⁻¹ vibrational frequency computed for CO itself to 2039 cm⁻¹ for **3**.

Interestingly, the boron natural charges are negative (Table 1) and correlate (Figure 1) with the CO vibrational frequencies (and with the CO separations): the less negative the boron center the higher the CO frequency. For example, (BCO)₄²⁺ (**6**) has the least negative charge on boron (-0.090), but the highest CO frequency (2232 cm⁻¹); in contrast, (BCO)₅⁻ (**7**) has the largest negative charge on boron (-0.294), but the lowest CO frequency (1962 cm⁻¹).

In conclusion, (BCO)₆ (**3**) and other monocyclic boron carbonyl compounds (**5–8**) with $4n + 2$ delocalized π electrons are aromatic and should be viable species. The isolobal equivalence of a BCO with a CH group appears to be capable of considerable extension and predicts a new family of molecules, akin to the metal carbonyls. In the conceptual design of possibilities, BCOs simply replace one or more CH groups. “Boron carbonyl chemistry” also offers variations, since the CO groups can be substituted by other ligands

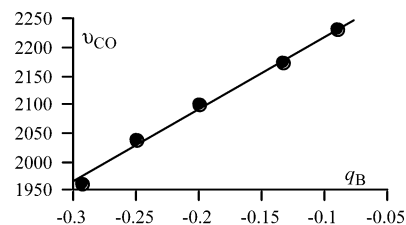


Figure 1. Correlation between $q(\text{B})$ and $\nu(\text{CO})$.

(as in **4**). Experimentalists should take into consideration that CBO isomers can be more stable than the BCO species, for example, (CBO)₆ is 213.6 kcal/mol more stable than (BCO)₆.

Acknowledgment. This paper is dedicated to G. Maier. We thank M. Zhou for stimulating our interest in BCO chemistry. This work was supported by the special funds of the Shanxi Normal University, by the Leibnizgesellschaft, and by National Science Foundation Grant CHE-0209857.

Supporting Information Available: Cartesian coordinates, total electronic energies, and complete NICS analysis of **3–8** (in-plane and out-of-plane contributions to the anisotropies) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA034605H