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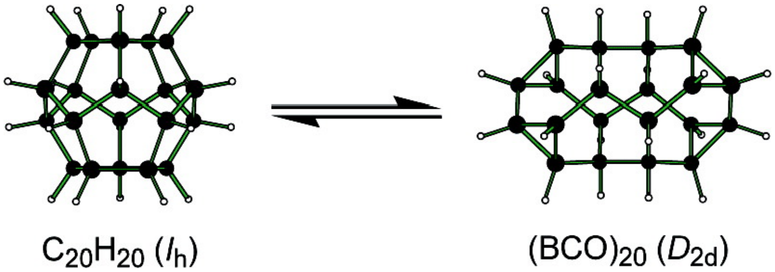

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Structures and Energies of Isolobal $(BCO)_n$ and $(CH)_n$ Cages

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Abstract: The structures and energies of isolobal $(CH)_n$ and $(BCO)_n$ polyhedral species, computed at the B3LYP density functional theory level, reveal contrasts in behavior. The strain energies of the $(BCO)_n$ cages are much smaller. Also unlike the $(CH)_n$ cages, the most stable $(BCO)_n$ polyhedra ($n \geq 10$) prefer structures with the largest number of three-membered rings. The planar (or nearly planar) faces of the cage systems were modeled by computations on planar, isoelectronic $(CH_2)_n$ (D_{nh}) and $(HBCO)_n$ (C_{nv}) rings. While the strain energies of all the planar carbon rings, relative to the most stable D_{5h} $(CH_2)_5$, were large, the strain energies of all the planar $(HBCO)_n$ (C_{nv}) rings were small. Remarkably, the three-membered $(HBCO)_3$ (C_{3v}) ring was the most stable. Finally, large $(BCO)_n$ systems prefer tubelike rather than cage structures.

Introduction

Polyhedral hydrocarbons, $(CH)_n$, comprised only of CH groups, stimulate aesthetic pleasure due to their high symmetries, challenge synthetic chemist's ingenuity, and test physical organic chemists' understanding of the relationship between structure and energy. Exciting examples of polyhedral hydrocarbons $(CH)_n$ include tetrahedrane (**1**, C_4H_4, T_d), [3]prismane (**2**, C_6H_6, D_{3h}), cubane (**3**, C_8H_8, O_h), cuanane (**4**, C_8H_8, C_{2v}), [5]prismane (**5**, $C_{10}H_{10}$, D_{5h}), diademane (**6**, $C_{10}H_{10}$, C_{3v}), and dodecahedrane (**13**, $C_{20}H_{20}$, I_h).[1] While their strain energies per CH group generally decrease with increasing cage size,[2] e.g., from tetrahedrane[3] to dodecahedrane (Table 1),[4] remarkable magnetic anomalies were recently revealed by their nucleus-independent chemical shifts (NICS):[5] tetrahedrane is indicated to be highly aromatic, whereas cubane is strongly antiaromatic.[6]

The remarkable isolobal[7] relationship between the $^4\Sigma^-$ CH excited state and the $^4\Sigma^-$ BCO ground state[8] in the same symmetry has wide applicability.[9,10] Thus, H_3BCO, the first-prepared (1937)[11] of the many boron carbonyls known today,[12] is isolobal with CH_4, $(CO)BH_2{-}BH_2(CO)$ is the counterpart of C_2H_6, OCBBCO[13] is the acetylene equivalent, and $(CH)_5BCO$[14] mimics benzene. Further examples are the monocyclic boron carbonyls,[15] $(BCO)_3{}^+$, $(BCO)_4{}^{2+}$, $(BCO)_5{}^-$, $(BCO)_6$, and $(BCO)_7{}^+$, which are isolobal with the Hückel aromatic series, $C_3H_3{}^+$, $C_4H_4{}^{2+}$, $C_5H_5{}^-$, C_6H_6, and $C_7H_7{}^+$.

Extending isolobal analogies between organometallic compounds and polyhedranes,[7] we explore similar relationships involving structures, energies, and magnetic properties between polyhedral $(BCO)_n$ boron carbonyls and their $(CH)_n$ hydrocarbon relatives. As we find important differences in the strain energies of these two sets of cage molecules, the isolobal monocyclic $(CH_2)_n$ and $(HBCO)_n$ rings also were studied in order to facilitate analysis.

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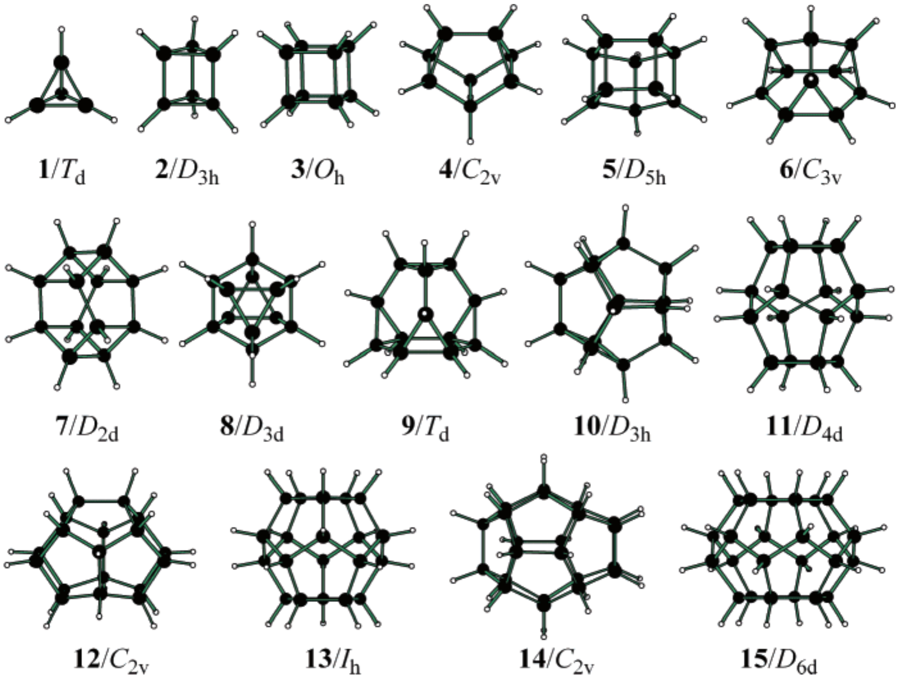
Table 1. Number of Different Rings (F_3, F_4, F_5, and F_6), NICS Values at the Cage Centers at GIAO-B3LYP/6-31G* (ppm), and Analysis of B3LYP/6-311+G*//B3LYP/6-31G* Data (in kJ/mol) for the Corresponding $(CH)_n$ and $(BCO)_n$ Cages[a]

isomer	n	symm	ΔE/CH[b]	ΔE/BCO[b]	$F_3 + F_4 + F_5 + F_6$	NICS (CH)	NICS (BCO)	ΔE_{dis}/CH[c]	ΔE_{dis}/BCO[c]
1	4	T_d	128.6	44.2	4 + 0 + 0 + 0	−46.1	−46.2	437.2	379.5
2	6	D_{3h}	87.1	25.6	2 + 3 + 0 + 0	2.2	−10.9	475.3	397.9
3	8	O_h	70.3	28.3	0 + 6 + 0 + 0	23.9	−6.6	490.7	395.8
4	8	C_{2v}	50.8	10.2	2 + 2 + 2 + 0	−8.0	−6.5	510.4	413.0
5	10	D_{5h}	45.2	15.1	0 + 5 + 2 + 0	7.3	2.1	515.0	408.4
6	10	C_{3v}	32.9	−1.0	3 + 0 + 3 + 1	−10.5	−4.2	527.9	423.9
7	12	D_{2d}	27.5	8.6	0 + 4 + 4 + 0	2.1	1.3	532.1	414.7
8	12	D_{3d}	18.4	−1.0	2 + 0 + 6 + 0	−6.0	−2.6	540.9	423.9
9	12	T_d	27.6	−8.5	4 + 0 + 0 + 4	−14.7	−11.5	531.7	431.4
10	14	D_{3h}	16.3	4.4	0 + 3 + 6 + 0	0.1	−8.1	543.0	418.8
11	16	D_{4d}	9.0	2.0	0 + 2 + 8 + 0	−0.1	4.1	549.7	421.3
12	18	C_{2v}	8.5	2.2	0 + 2 + 8 + 1	0.1	3.4	550.1	421.3
13	20	I_h	0.0	0.0	0 + 0 + 12 + 0	1.7	7.9	558.0	423.4
14	22	C_{2v}	5.6	2.5	0 + 1 + 10 + 2	−0.7	2.9	552.6	417.2
15	24	D_{6d}	3.4	2.8	0 + 0 + 12 + 2	−0.1	3.0	554.3	421.0

[a] The most stable $(CH)_n$ isomers have been chosen for each value of n; the $(BCO)_n$ entries correspond to these species. Relative energies (in kJ/mol) per CH or BCO (ΔE/CH and ΔE/BCO) are based on $n = 20$ (dodecahedrane and its $(BCO)_{20}$ analogue). The dissociation energies (see text), ΔE_{dis}/CH and ΔE_{dis}/BCO, also are given per CH or BCO. [b] Based on I_h $(CH)_{20}$ and $(BCO)_{20}$ (**13**) as references. Dissociation into the CH doublet ground state ($^2\Pi$) or the BCO quartet ground state ($^4\Sigma^-$).

Scheme 1. Most Stable $(CH)_n$ Structures (the $(BCO)_n$ Topologies in the Same Symmetries)



Computational Methods

All structures were optimized at the B3LYP/6-31G* level of density functional theory with the Gaussian 98 program.[16] Vibrational frequency computations characterized all structures to be minima, at B3LYP/6-31G* for the $(CH)_n$ set, but at various levels of theory for the related $(BCO)_n$ set due to their large sizes (at B3LYP/6-31G* for $n \leq 20$, at B3LYP/3-21G for $n = 22$, and at HF/STO-3G for $n = 24$). The basis set and method dependencies were probed by single-point energies computed at B3LYP/6-311G*, B3LYP/6-311+G*, and MP2/6-31G* (the last only for $(BCO)_n$ up to $n = 18$) using the B3LYP/6-31G* optimized geometries. These dependencies of $(CH)_n$ on the theoretical level are known.[2] As given in the Supporting Information, the relative energies for $(BCO)_n$ with $n = 4-18$ at B3LYP differ from those at MP2/6-31G* (especially for small cages), but they show the same order and trend in a qualitative way. Thus, only the relative energies at B3LYP/6-311+G*//B3LYP/6-31G* for $(CH)_n$ and $(BCO)_n$ are discussed and compared for consistency. The monocyclic planar $(CH_2)_n$ and $(HBCO)_n$ ($n = 2-6$) reference systems have been computed at B3LYP/6-311+G**, respectively.

In addition to the structure and energy, nucleus-independent chemical shifts (NICS)[5] at the cage and at the ring centers have been computed at B3LYP/6-31G*//B3LYP/6-31G* with the gauge-including atomic orbital (GIAO) method. The Supporting Information summarizes the computed total electronic and relative energies at various levels of theory and NICS values for $(CH)_n$ and $(BCO)_n$ species, as well as data on the structural isomers of $(BCO)_n$ ($n = 10$, 12, 14) and on the monocyclic planar $(CH_2)_n$ (D_{nh}) and $(HBCO)_n$ (C_{nv}) ring systems. The B3LYP/6-31G* Cartesian coordinates for the $(CH)_n$ and $(BCO)_n$ cages are included.

Results and Discussion

Cage Structures and Stabilities. Scheme 1 shows the most stable $(CH)_n$ structures; these also represent the best $(BCO)_n$ topologies. The relative strain energies of $(CH)_n$ or of $(BCO)_n$ species, defined as the energy per unit, ΔE/CH or ΔE/BCO

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(16) Frisch, M. J. et al. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

relative to the values for $C_{20}H_{20}$ and $(BCO)_{20}$, respectively, are given in Table 1. The relative strain of the $(CH)_n$ species agrees well with previous results[2] and decreases gradually with the increasing cage size. The least strained system in this set is dodecahedrane (**13**), and the most strained system is tetrahedrane (**1**).

In anticipation of the full discussion in a later section below, we stress here that all the rings comprising the faces of the cage polyhedra in Scheme 1 are planar or nearly so. Consequently, the energies of these cages reflect the 1885 strain energy concept of Baeyer, which was based on the deviations of *planar* ring bond angles from the tetrahedral value.[17] Baeyer predicted that planar cyclopentane would be the most stable planar ring. This is exactly what we find here for the $(CH)_n$ cages, e.g., for dodecahedrane (**13**).

The BCO systems are much less strained than their $(CH)_n$ counterparts. Note the much smaller ΔE/BCO than the corresponding ΔE/CH data in Table 1. For $(CH)_4$ and $(BCO)_4$ (**1**), for example, the corresponding ΔE/CH and ΔE/BCO are 128.6 and 44.2 kJ/mol, respectively, and those of $(CH)_6$ and $(BCO)_6$ (**2**) are 87.1 and 25.6 kJ/mol.

Note that the *negative* ΔE/BCO values of **6** ($(BCO)_{10}$, C_{3v}), **8** ($(BCO)_{12}$, D_{3d}), and **9** ($(BCO)_{12}$, T_d), indicate that these cages are *less strained* than I_h $(BCO)_{20}$ in contrast to the behavior of the corresponding hydrocarbon systems. With $\Delta E/\mathrm{BCO} = -8.5$ kJ/mol, **9** is the most stable $(BCO)_n$ species showing that its three membered rings actually are favorable. Likewise, the NICS value of **9** also is the most negative of the entire BCO set, except for tetrahedral $(BCO)_4$, which has only three-membered rings. Clearly, the most stable $(BCO)_n$ species do not mimic the $(CH)_n$ hydrocarbons.

To understand this behavior, the number of constituent three-(F_3), four-(F_4), five-(F_5), and six (F_6)-membered rings are given in Table 1. This method has been used to identify the most stable fullerene cages.[18] As expected, the $(CH)_n$ structures with F_3's and/or F_4's are strained more highly that those with fewer or without any F_3's and/or F_4's, while isomers with F_5's and F_6's are more stable than other alternatives.

For $(BCO)_n$, however, structures with F_3's are more stable than those with F_4's; both planar and cage boron compounds prefer deltahedral bonding in general.[19] To confirm this relationship between structure and energy, we have computed complete sets of structural alternatives with only F_3's, F_4's, F_5's, and F_6's for $(BCO)_{10}$ (five isomers), for $(BCO)_{12}$ (10 isomers), and for $(BCO)_{14}$ (fifteen isomers). The energies and structures are summarized in Table 2 and in the Supporting Information.

The stability of the five $(BCO)_{10}$ isomers decreases with the smaller number of F_3's and the larger number of F_4's. The most stable $(BCO)_{10}$ isomer, structure **6** (C_{3v}), has three F_3's and no F_4; the least stable isomer **5** (D_{5h}), with five F_4's and no F_3, is 160.8 kJ/mol higher in energy. The stability of the other three isomers is between **6** and **5**, as expected.

The most stable $(BCO)_{12}$ isomer (of the 10 in Table 2) is **9** with four F_3's and four F_6's, while the least stable isomer is [6]prismane (D_{6h}) with six F_4 and two F_6's; the energy difference is 255.8 kJ/mol. The regular structure with two F_4 and two F_5 in D_{2d} symmetry (**7**) is higher in energy than **9** by 205.6 kJ/mol. Other isomers become less stable with the decreased number of F_3's and increased number of F_4's, respectively. However, note that the corresponding **7** and **9** $(CH)_{12}$ isomers are within 0.6 kJ/mol in energy.

Table 2. Relative Energies (ΔE, kJ/mol) of $(BCO)_n$ ($n = 10, 12, 14$, m = the Order Number of Isomers) and the Number of Different Rings (F_3, F_4, F_5, and F_6)

n–m	symm	$F_3 + F_4 + F_5 + F_6$	E_{rel}[b]
		$(BCO)_{10}$	
10−1 (**6**)[a]	C_{3v}	3 + 0 + 3 + 1	0.0
10−2	C_2	2 + 2 + 2 + 1	64.7
10−3	C_{2v}	2 + 3 + 0 + 2	83.6
10−4	C_{3v}	1 + 3 + 3 + 0	102.3
10−5 (**5**)[a]	D_{5h}	0 + 5 + 2 + 0	160.8
		$(BCO)_{12}$	
12−1 (**9**)[a]	T_d	4 + 0 + 0 + 4	0.0
12−2 (**8**)[a]	D_{3d}	2 + 0 + 6 + 0	90.6
12−3	C_s	3 + 1 + 1 + 3	92.2
12−4	C_{2v}	2 + 1 + 4 + 1	103.5
12−5	C_{2v}	2 + 2 + 2 + 2	129.2
12−6	C_2	2 + 2 + 2 + 2	143.9
12−7	C_s	1 + 3 + 3 + 1	165.8
12−8	C_s	1 + 4 + 1 + 2	195.0
12−9 (**7**)[a]	D_{2d}	0 + 4 + 4 + 0	205.6
12−10	D_{6h}	0 + 6 + 0 + 2	255.8
		$(BCO)_{14}$	
14−1 (**16**)[a]	C_{3v}	3 + 0 + 3 + 3	0.0
14−2	C_s	3 + 0 + 3 + 3	9.6
14−3	C_s	2 + 1 + 4 + 2	50.1
14−4	C_2	2 + 1 + 4 +2	50.8
14−5	C_2	2 + 2 + 2 + 3	66.7
14−6	C_{2v}	2 + 3 + 0 + 4	68.6
14−7	C_s	2 + 2 + 2 + 3	72.2
14−8	C_s	1 + 2 + 5 + 1	81.2
14−9	C_2	2 + 2 + 2 + 3	82.8
14−10	C_1	1 + 3 + 3 + 2	101.0
14−11 (**10**)[a]	D_{3h}	0 + 3 + 6 + 0	113.7
14−12	C_s	1 + 4 + 1 + 3	126.8
14−13	C_{2v}	0 + 4 + 4 + 1	138.6
14−14	C_{2v}	0 + 5 + 2 + 2	170.3
14−15	D_{3h}	0 + 6 + 0 + 3	189.5
[7]prismane	D_{7h}	2 F_7 + 7 F_4	313.1

[a] Numbers in bold correspond to numbers in Schemes 1 and 2. [b] At B3LYP/6-311+G*//B3LYP/6-31G*.

The same trends are found for the fifteen $(BCO)_{14}$ isomers in Table 2. For example, **16** is the most stable isomer and has three F_3's, three F_5's, and three F_6's; the regular structure (**10**, D_{3h}), with three F_4's and six F_5's, is 113.7 kJ/mol higher in energy. The analogous $C_{14}H_{14}$ isomers behave differently; **16-CH** is 39.5 kJ/mol higher in energy than **10-CH**. The least stable $(BCO)_{14}$ structure with six F_4's and three F_6's in D_{3h} symmetry is 189.5 kJ/mol higher in energy, respectively. In addition, the [7]prismane $(BCO)_{14}$ structure with seven F_4's and two F_7's is computed to be higher in energy than **16** by 313.1 kJ/mol, respectively.

Intrigued by this interesting finding, we have computed a series of $(BCO)_n$ structures with as many F_3's as possible and compared them with their "regular" isomers in Scheme 1. The results are given in Table 3, and the topologies of the most stable $(BCO)_n$ structures are shown in Scheme 2.

Since the number of possible isomers increases rapidly with the larger number of BCO or CH units, the computations focused on cage structures with the maximum number of F_3's. For $(BCO)_{16}$, **17** (T_d) with four F_3's and six F_6's was 83.6 kJ/mol more stable than **11** (D_{4d}) with two F_4's and eight F_5's;

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(17) *Lehrbuch der Organischen Chemie*; Beyer and Walter, S. Hirzel; Verlag Stuttgart: 1991; pp 387−388.

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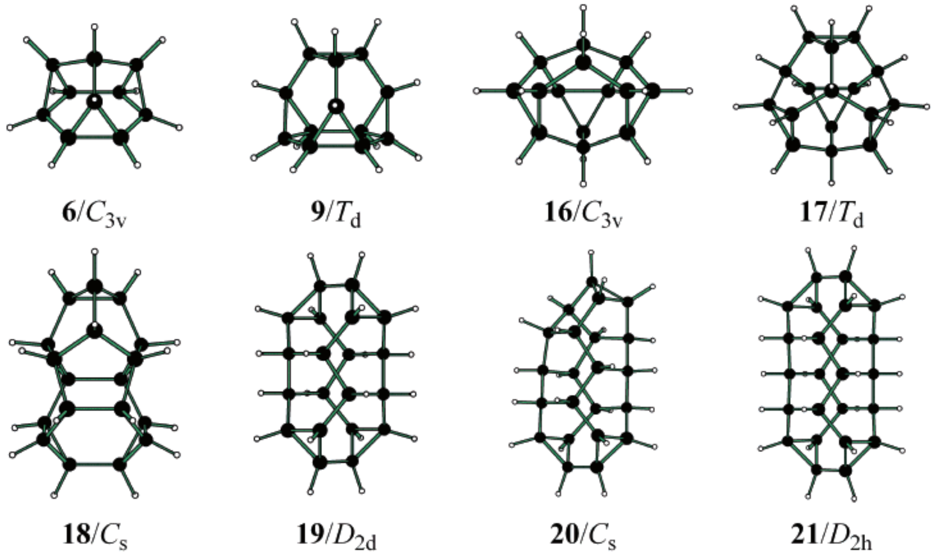
Table 3. B3LYP/6-311+G*//B3LYP/6-31G* Relative Energies (ΔE, kJ/mol) and Dissociation Energies (ΔE_{dis}, kJ/mol) per BCO (or CH) of the Most Stable $(BCO)_n$ Cages (for $(CH)_n$ with the Same Symmetry as $(BCO)_n$) and the Number of Different Rings (F_3, F_4, F_5, and F_6) and NICS Values at the Cage Center at GIAO-B3LYP/6-31G* (ppm)

isomer	n	symm	ΔE/BCO	ΔE/CH[a]	$F_3 + F_4 + F_5 + F_6$	NICS (CH)	NICS (BCO)	ΔE_{dis}/CH[b]	ΔE_{dis}/BCO[b]
9	12	T_d	0.0	27.6	4 + 0 + 0 + 4	−14.7	−11.5	531.7	431.4
16	14	C_{3v}	4.8	18.9	3 + 0 + 3 + 3	−8.3	−5.9	540.1	426.4
17	16	T_d	4.7	23.3	4 + 0 + 0 + 6	−10.0	−8.5	535.5	426.8
18	18	C_s	5.8	15.4	3 + 0 + 3 + 6	−6.1	−4.9	543.4	425.9
19	20	D_{2d}	6.4	19.8	4 + 0 + 0 + 6	−5.6	−7.3	538.8	425.1
20	22	C_s	7.6	13.2	3 + 0 + 3 + 7	−4.2	−5.1	545.1	419.3
21	24	D_{2h}	8.3	16.9	4 + 0 + 0 + 10	−3.6	−6.0	541.3	423.4

[a] Relative to dodecahedrane (**13**, Table 1). [b] Dissociation into the CH doublet ground state ($^2\Pi$) or the BCO quartet ground state ($^4\Sigma^-$).

Scheme 2. Most Stable $(BCO)_n$ Structures (the $(CH)_n$ Topologies in the Same Symmetries)



this order is reversed for $C_{16}H_{16}$, where **11-CH** is 227.0 kJ/mol lower in energy than **17-CH**.

The larger $(BCO)_n$ structures in Scheme 2 (**18**, **19**, **20**, and **21**) prefer tubelike forms over their alternative cage isomers (Scheme 1), **12**, **13**, **14**, and **15**, by 83.3, 35.7, 10.7, and 60.0 kJ/mol, respectively. In contrast, the $(CH)_n$ cage structures **12**−**15** are more stable than the tubelike **18**−**24** forms by 120.1, 386.8, 159.8, and 310.0 kJ/mol, respectively. Note that both $(CH)_n$ and $(BCO)_n$ isomers in Scheme 2 have negative NICS values (Table 2).

Based on the dissociation energies (ΔE_{dis}) into the respective ground state ($^2\Pi$) CH and ($^4\Sigma^-$) BCO fragments (Tables 1 and 3), the $(CH)_n$ systems are much more stable thermodynamically (Tables 1 and 3). For example, the ΔE_{dis} per CH or BCO unit for the most stable $(CH)_{20}$ (**13**) and $(BCO)_{12}$ (**9**) are 558.0 and 431.4 kJ/mol, respectively. The ΔE_{dis} of $(CH)_4$ is 231.6 kJ/mol larger than $(BCO)_4$. This difference is due to a combination of two effects: the greater thermodynamic stability of $(CH)_n$ over $(BCO)_n$ cage bonding and the instability of CH relative to BCO fragments. Since the cage CC bonds are inherently stronger and "stiffer," deformations into strained geometries are resisted more strongly. This also is demonstrated by the results on monocyclic planar $(CH_2)_n$ and $(HBCO)_n$ rings, presented in the forthcoming sections.

Relative to their $(CH)_n$ counterparts, the lower strain of $(BCO)_n$ structures (compare columns 4 and 5 of Table 1) can be attributed to the greater radial extension of the orbitals of the more electropositive boron. This favors deltahedral and delocalized bonding in general and stabilizes structures with three-membered rings. Furthermore, the electrons donated from CO to the boron cage are compensated by the corresponding back-donation into the CO LUMO,[9c] and this synergetic interaction results in further stabilization of the boron cages.

Table 4. Relative (ΔE) and Dissociation (ΔE_{dis}) Energies (kJ/mol) and Energies Per CH_2 or HBCO Unit for Planar Cycloalkanes $(CH_2)_n$ and $(HBCO)_n$ Rings (B3LYP/6-311+G**)

$(CH_2)_n$	ΔE/ CH_2[a]	ΔE_{dis}/ CH_2[b]	$(HBCO)_n$	ΔE/ HBCO[c]	ΔE_{dis}/ HBCO[d]
$(CH_2)_2/D_{2h}$	34.6	372.0	$(HBCO)_2/C_{2v}$	33.6	178.2
$(CH_2)_3/D_{3h}$	27.9	378.7	$(HBCO)_3/C_{3v}$	−4.6	214.5
$(CH_2)_4/D_{4h}$	18.3	388.3	$(HBCO)_4/C_{4v}$	5.1	205.3
$(CH_2)_5/D_{5h}$	0.0	406.6	$(HBCO)_5/C_{5v}$	0.0	209.9
$(CH_2)_6/D_{6h}$	9.3	397.3	$(HBCO)_6/C_{6v}$	4.4	205.3
$CH_2\,^3B_1/C_{2v}$	415.0		HBCO $^3\Sigma/C_{\infty v}$	200.1	

[a] Relative to D_{5h} $(CH_2)_5$. [b] $\Delta E_{dis} = [E(CH_2)_n - nE(CH_2)]/n$. [c] Relative to C_{5v} $(HBCO)_5$. [d] $\Delta E_{dis} = [E(HBCO)_n - nE(HBCO)]/n$.

Strain Energies of Planar D_{nh} $(CH_2)_n$ Rings ($n = 2, 3, 4, 5, 6$). As stressed above, planar (or nearly planar) rings comprise the faces of the cage polyhedra in Schemes 1 and 2. Consequently, the usual ring strain analysis based on the fully relaxed ring geometries is not appropriate here. For example, note the *exactly planar cyclohexane rings* in **6**, **9**, and **15**. Following von Baeyer's original concept, cyclopentane is the least strained planar ring, since its CCC bond angles (108°) deviate least from 109.5°.[17] This concept agrees very well with the relative energies per CH_2 group ($\Delta E/CH_2$) computed for the planar cycloalkanes in Table 4 (ethylene is included for comparison). As planar cyclopentane had the lowest $\Delta E/CH_2$, its strain energy was taken as the reference zero. Planar cyclohexane is more strained than

Table 5. NICS for Planar $(HBCO)_n$ C_{nv} Rings; Values for Points Away from the Center on the H Side Are Followed by Those on the CO Side (in Parentheses)

NICS(x Å)	$(HBCO)_3/C_{3v}$	$(HBCO)_4/C_{4v}$	$(HBCO)_5/C_{5v}$	$(HBCO)_6/C_{6v}$
NICS(0)	−38.9	−5.3	+0.7	−4.9
NICS(0.5)	−26.7 (−27.2)	−3.7 (−4.2)	−1.1 (+1.0)	−5.0 (−4.3)
NICS(1)	−11.1 (−13.5)	−2.2 (−1.7)	−1.7 (−0.2)	−4.2 (−3.8)
NICS(1.5)	−4.8 (−6.2)	−1.3 (−1.0)	−1.2 (−0.5)	−3.0 (−3.0)
NICS(2)	−2.4 (−3.0)	−0.7 (−0.4)	−0.7 (−0.5)	−2.0 (−2.0)

planar cyclopentane, while cyclobutane and cyclopropane are most strained. Note also that all the planar rings have only eclipsed conformations, which increases their energies. This energetic analysis explains perfectly the stability of dodecahedrane (**13**) with its twelve planar cyclopentane rings.

Strain Energies of Planar C_{nv} $(HBCO)_n$ Rings ($n = 2, 3, 4, 5, 6$). The HBCO group is isolobal with CH_2; both have triplet ground states. $(HBCO)_n$ rings are isolobal with cycloalkanes but have lower symmetries and many more conformational and configurational alternatives (see the Supporting Information). On the basis of the structures in Schemes 1 and 2, the present objective of modeling the faces of the $(BCO)_n$ cages is best achieved by imposing C_{nv} symmetry, with all CO's on one side of a planar B_n ring and the H's on the other. Although these C_{nv} arrangements are not the most stable (see the Supporting Information), they mimic those found on the cage ring faces quite well and serve as the basis for our energy analysis (Table 4). The ethene analogue C_{2v}, $(HBCO)_2$, has been included in this set. For comparison with $(CH_2)_n$, the C_{5v} five-membered ring, $(HBCO)_5$, was chosen as the reference zero for the strain energy evaluations in Table 4. Surprisingly, *the three-membered C_{3v} ring, $(HBCO)_3$, was less strained.* On the basis of this energetic analysis, it is easy to understand the stability of $(BCO)_{12}$ (**9**) containing four three-membered rings and four planar six-membered rings.

Note also that the strain energies of the other rings as well as all the $(HBCO)_n$ dissociation energies are much smaller than those of the $(CH_2)_n$ systems. Unlike the cycloalkanes, both the four- and six-membered C_{nv} $(HBCO)_n$ rings are strained modestly, to a similar extent (Table 4).

NICS Analysis. The extent of electron delocalization is revealed by NICS computed at the centers of the $(CH)_n$ and $(BCO)_n$ cages (as well as in their their ring faces, see the Supporting Information). The NICS values of the $(CH)_n$ cages (Tables 1 and 3) agree with the available data.[6] Compounds with three-membered rings (σ aromatic) have large negative NICS, whereas positive NICS values characterize compounds with four-membered rings (σ anti-aromatic).[6,20] The same is true for the monocyclic, planar $(CH_2)_n$ (D_{nh}) rings. In contrast, both three- and four-membered rings of the $(BCO)_n$ systems have negative NICS values due to their σ-aromaticity (see the NICS values at the individual ring centers in the Supporting Information). Note that structures **2**, **3**, and **10** for $(CH)_n$ have positive NICS, while those of $(BCO)_n$ systems have negative NICS values (Table 1). Along with the difference in strain, this reveals the similarities and differences of $(CH)_n$ and $(BCO)_n$.

NICS data on the planar $(HBCO)_n$ (C_{nv}) rings in Table 5 corroborate these differences. The NICS values computed along the normal fall off away from the ring center but are nearly the same on the H− as on the CO sides. NICS in the centers are representative: like cyclopropane a very large negative value characterizes the three-membered $(HBCO)_3$ ring indicating significant aromatic stabilization. This helps explain the remarkably small strain and low energy associated with the three-membered rings in the cage compounds as well as the monocycles. However, in contrast to cyclobutane, the four-membered $(HBCO)_4$ also has a negative NICS, albeit modest in magnitude. Dissected localized MO NICS analysis[21] shows that the BB bond contributions are nearly zero, so that the diatropic NICS arises from other contributions. In contrast, more than half the diatropic −38.9 NICS value at the ring center is due to the three BB bonds. Like $(HBCO)_4$, the five- and six-membered $(HBCO)_n$ rings also can be considered to be nonaromatic.

Conclusions

Polyhedral $(BCO)_n$ cages are considerably less strained than their $(CH)_n$ analogues. For $n = 4$, 6, 8, and 10, $(CH)_n$ and $(BCO)_n$ have the same structural patterns and the same order of strain. However, the ($n = 12$, 14, 16) sets are different; the $(CH)_n$ set prefers cage structures with five- and six-membered rings, while the $(BCO)_n$ analogues favor cages combining three- and six-membered rings. For $n = 18$, 20, 22, and 24, the most stable $(BCO)_n$ structures are tubelike.

The rings comprising the faces of all these cage compounds are planar, or nearly so. Consequently, planar isolobal $(CH_2)_n$ and $(HBCO)_n$ rings provide the best models. As Baeyer predicted 120 years ago, D_{5h} cyclopentane is the least strained planar cycloalkane ring. Similarly, dodecahedrane (**13**) is the most stable $(CH)_n$ cage. The $(HBCO)_n$ rings in C_{nv} symmetry are much less strained than their carbon counterparts, and remarkably, the three-membered $(HBCO)_3$ ring is the least strained and the most stable. Therefore, the stability of $(BCO)_{12}$ (**9**) can be understood easily.

NICS shows that this can be attributed to its σ aromaticity, at least in part, and it extends to the stabilizing effect of the three-membered ring faces in the $(BCO)_n$ cages. The four-, five-, and six-membered rings in the $(HBCO)_n$ set are nonaromatic. In the carbon cages, three-membered ring faces are also strongly diatropic, but four-membered ring faces are paratropic.

Besides the cage boron carbonyl compounds, new $(CH)_n$ structures (Scheme 2), especially **16** and **17** with low strain energies, are reported here for the first time. All of these provide synthetic challenges.

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Supporting Information Available: Total electronic energies, relative energies at various levels of theory and NICS values for $(CH)_n$ and $(BCO)_n$ species, and the energies of the structural isomers of $(BCO)_n$ ($n = 10$, 12, 14) as well as the monocyclic $(CH_2)_n$ and $(HBCO)_n$ ring systems. The B3LYP/6-31G* Cartesian coordinates for the $(CH)_n$ and $(BCO)_n$ cages are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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