

Density functional studies of the stepwise substitution of pyrrole, furan, and thiophene with BCO

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Abstract The structures, stabilities, and aromaticities of a series of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$), $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$), and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=0-4$) clusters were investigated at the B3LYP density functional level of theory. The most stable positional isomers of the individual clusters were obtained. All of the calculated CO binding energies were exothermic, suggesting that these BCO-substituted species are stable. Calculated differences in strain energy between the BCO-substituted structures and their corresponding hydrocarbon clusters were all exothermic, indicating that the BCO-substituted structures are less strained. The negative nucleus-independent chemical shift (NICS) values obtained show that these BCO-substituted clusters are aromatic compounds, in good agreement with the aromaticities of the corresponding hydrocarbon species. To aid further experimental investigations, CO-stretching frequencies were also computed.

Keywords Borane carbonyl compounds · Stability · DFT · Aromaticity

Introduction

Borane carbonyl compounds offer intriguing structural possibilities [1], akin to carbonyl transition metal complexes [2]. The $\text{H}_3\text{B}-\text{CO}$ adduct was discovered in 1937 [3]; some two dozen BCO complexes have since been described. Tris

(trifluoromethyl)borane carbonyl, $(\text{CF}_3)_3\text{BCO}$ [4], $\text{B}_2(\text{CO})_2$ [5], $\text{B}_4(\text{CO})_2$ [6], and triplet boron carbonyl (BBCO) [7] have also been investigated. Interestingly, $\text{B}_2(\text{CO})_2$ is formed upon the dimerization of BCO, rather than the reaction of B_2 with CO. This suggests that higher BCO oligomers might also be viable.

The remarkable isolobal relationship [8] of the $^4\Sigma^- \text{CH}$ excited state with the $^4\Sigma^- \text{BCO}$ ground state [9] of the same symmetry has wide applicability. Following this analogy, H_3BCO is isolobal with CH_4 and $\text{OCB}\equiv\text{BCO}$ is the acetylene equivalent, and the matrix-isolated $(\text{CH})_5\text{BCO}$ [10, 11] is isolobal with benzene. Further examples are monocyclic boron carbonyl compounds $(\text{BCO})_x^y$ with $4n+2$ delocalized π electrons, i.e., $(\text{BCO})_3^+$, $(\text{BCO})_4^{2+}$, $(\text{BCO})_5^-$, $(\text{BCO})_6$, and $(\text{BCO})_7^+$, which are isolobal with the corresponding aromatic hydrocarbon species C_3H_3^+ , $\text{C}_4\text{H}_4^{2+}$, C_5H_5^- , C_6H_6 , and C_7H_7^+ [12]. However, the isolobal $(\text{CH})_n$ and $(\text{BCO})_n$ polyhedral cages differ greatly in structure and stability [13]. For example, $(\text{BCO})_n$ cages are much less strained than their $(\text{CH})_n$ analogs, and the most stable $(\text{BCO})_n$ ($n \geq 10$) prefer to adopt structures with the largest number of three-membered rings, while $(\text{CH})_n$ prefers to form a cage with five- and six-membered rings. This isolobal relationship has also been applied to a new family of positively charged boron carbonyls: H_4BCO^+ is isolobal with CH_5^+ , $(\text{BCO})_2\text{H}^+$ is isolobal with the bridged vinyl cation C_2H_3^+ , $(\text{BCO})_2\text{C}_5\text{H}_9^+$ is isolobal with the 2-norbornyl cation, and $(\text{BCO})_5^+$ is isolobal with $(\text{CH})_5^+$ [14]. It was found that BCO analogs have geometries and electronic structures similar to those of their carbocation counterparts.

Pyrrole, furan, and thiophene are planar molecules with an aromatic cycle containing a heteroatom. As we all know, these species have significant aromaticities. Their geometric structures, electronic properties, and aromaticities have been extensively studied theoretically and experimentally [15, 16]. A nonequivalent resonance-stabilized pyrrole ring

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structure was determined as far back as 1939 [17], and was later reinvestigated using microwave spectroscopy [18, 19]. The geometric and vibrational properties of furan and pyrrole were calculated using ab initio methods at the MP2 level [20]. Cordell et al. [21] optimized the geometries of furan, pyrrole and thiophene by SCF ab initio computation. They found that extensive conjugation within the C–C–C–C portion of the ring occurs in all three compounds.

Due to the remarkable isolobal relationship of the $^4\Sigma^-CH$ excited state with the $^4\Sigma^-BCO$ ground state, a BCO group should be able to replace a CH group in all chemical compounds in principle. Hence, this isolobal relationship can be used to not only interpret known carbonyls but also conceive new boron carbonyls. Our earlier proposal for monocyclic boron carbonyls indicated that $(BCO)_6$ and other monocyclic boron carbonyl compounds with delocalized π electrons are aromatic [13]. Therefore, in the work described in the present paper, we predicted some new molecules through the stepwise substitution of the CH groups of pyrrole, furan, and thiophene with BCO.

We successively substituted BCO for CH in pyrrole, furan, and thiophene and investigated the structures, stabilities, and aromaticities of the substitution products: $(BCO)_n(CH)_{4-n}NH$ ($n=0-4$), $(BCO)_n(CH)_{4-n}O$ ($n=0-4$), and $(BCO)_n(CH)_{4-n}S$ ($n=0-4$). The results of this study are provided below, and the CO binding energies, changes in strain, and CO-stretching frequencies of the products are also discussed.

Computational details

All of the structures investigated here were optimized at the B3LYP/6-311++G** level of density functional theory, and frequency calculations performed at the same level were used to check that they were the minimum-energy structures. The frequency calculations also provided the zero-point energies (ZPEs). All of the relative energies were calculated at the B3LYP/6-311++G** level, and were corrected for the ZPE (scaled by an empirical factor of 0.99 at the B3LYP/6-311+G** level).

As a simple and efficient measure of aromaticity, the nucleus-independent chemical shift (NICS) [22–24] (the negative of the computed absolute shielding at the center of the ring) was used to characterize the aromaticity of each monocyclic molecule. NICS values were computed at the B3LYP/6-311++G** level using the gauge-independent atomic orbital (GIAO) [25] method and the B3LYP/6-311++G** geometries. In addition to structures, stabilities, and aromaticities, we calculated CO-stretching frequencies to aid experimental investigations. All calculations were carried out with the Gaussian 03 program [26].

Results and discussion

Geometries and stabilities

The optimized $(BCO)_n(CH)_{4-n}NH$ ($n=0-4$), $(BCO)_n(CH)_{4-n}O$ ($n=0-4$), and $(BCO)_n(CH)_{4-n}S$ ($n=0-4$) clusters are shown in Figs. 1, 2, and 3. The charge populations of B and the heteroatoms in the rings are also included. The symmetries, relative energies, average charge populations, and correlative bond parameters of all isomers are listed in Table 1.

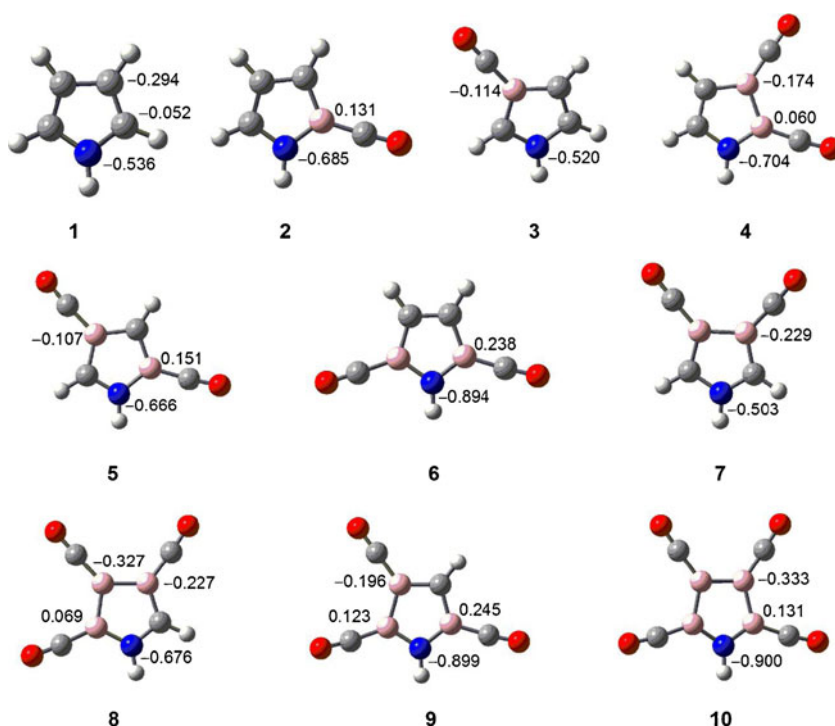
As shown in Fig. 1, $(CH)_4NH$ (**1**) was optimized with C_{2v} symmetry. The isomers of $(BCO)(CH)_3NH$ (**2** and **3**) both have C_s symmetry. Isomer **3** is 13.8 kcal/mol higher in energy than **2**, so the most stable $(BCO)(CH)_3NH$ isomer is **2**. Four isomers (**4**, **5**, **6**, and **7**) were found for $(BCO)_2(CH)_2NH$, and they were optimized with C_s , C_s , C_{2v} , and C_{2v} symmetries, respectively. The most stable isomer is **6**; **4**, **5**, and **7** are higher in energy by 13.9, 14.4, and 29.2 kcal/mol, respectively. There are two isomers for $(BCO)_3(CH)NH$ (**8** and **9**), both of which have C_s symmetry. Isomer **8** is 11.3 kcal/mol higher in energy than **9**, so **9** is more stable. The optimization of $(BCO)_4NH$ (**10**) yielded a structure with C_{2v} symmetry.

As shown in Fig. 2, $(CH)_4O$ (**11**) was optimized with C_{2v} symmetry. The $(BCO)(CH)_3O$ isomers obtained (**12** and **13**) both have C_s symmetry. Isomer **13** is higher in energy by 23.3 kcal/mol than **12**, so the most stable $(BCO)(CH)_3O$ isomer is **12**. There are four isomers for $(BCO)_2(CH)_2O$: **14** and **15** with C_s symmetry, and **16** and **17** with C_{2v} symmetry. The most stable isomer is **16**; **14**, **15**, and **17** are higher in energy by 24.2, 26.2, and 51.3 kcal/mol, respectively. There are two isomers for $(BCO)_3(CH)O$ (**18** and **19**), both of which have C_s symmetry. Isomer **18** is 23.9 kcal/mol higher in energy than **19**, so **19** is more stable. Optimization of isomer **20** of $(BCO)_4O$ produced a structure with C_{2v} symmetry.

As shown in Fig. 3, isomer **21** of $(CH)_4S$ was optimized with C_{2v} symmetry. Two isomers (**22** and **23**) were found for $(BCO)(CH)_3S$, both with C_s symmetry. Isomer **23** is 13.0 kcal/mol higher in energy than **22**, so **22** is more stable. Four positional isomers were found for $(BCO)_2(CH)_2S$: **24** and **25** have C_s symmetry, while **26** and **27** have C_{2v} symmetry. Among these, **26** is more stable than the other three isomers **24**, **25**, and **27** by 15.0, 16.8, and 31.2 kcal/mol, respectively. The isomers of $(BCO)_3(CH)S$ obtained upon optimization (**28** and **29**) both have C_s symmetry. Isomer **28** is 14.7 kcal/mol higher in energy than **29**, so the most stable $(BCO)_3(CH)S$ isomer is **29**. Isomer **30** of $(BCO)_4S$ was optimized with C_{2v} symmetry.

It should be noted that the computed average B–B bond lengths range from 1.618 Å to 1.670 Å, meaning that they are longer than the formal B=B double bond (1.590 Å) in *trans*-OCBH=BHCO (isolobal with ethene). However, they are also shorter than the formal B–B single bond length of

Fig. 1 Optimized geometries of the $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$) species and the natural charges on the B and N atoms in them



1.820 Å (experimentally determined value: 1.78 Å [27]) in C_{2h} $\text{OCBH}_2\text{-BH}_2\text{CO}$ (isolobal with ethane). Their average B–C bond lengths (1.474–1.529 Å) are between those of typical B–C single (1.628 Å for $\text{OCBH}_2\text{-CH}_3$) and double (1.447 Å for OCBH=CH_2) bonds; all average C–C bond lengths (1.360–1.400 Å) are between those of the corresponding single (1.531 Å for $\text{H}_3\text{C-CH}_3$) and double (1.324 Å for $\text{H}_2\text{C=CH}_2$) bonds.

It was found that the most stable isomers are those with the largest number of α -BCO substitutions. This was particularly true of furan-like isomers with the most electronegative atom, O, in their structures. An electron-deficient group such as BCO is more stable when it is located close to the most electronegative groups. For $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=1-4$) and $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=1-4$), it was found that the BCO groups prefer to occupy the vertices with the

Fig. 2 Optimized geometries of the $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$) species and the natural charges on the B and O atoms in them

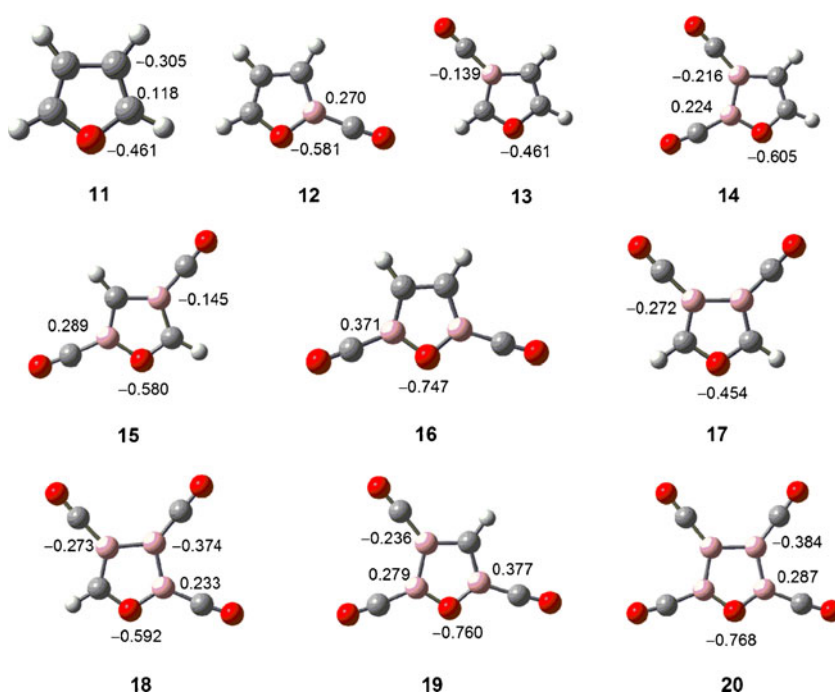
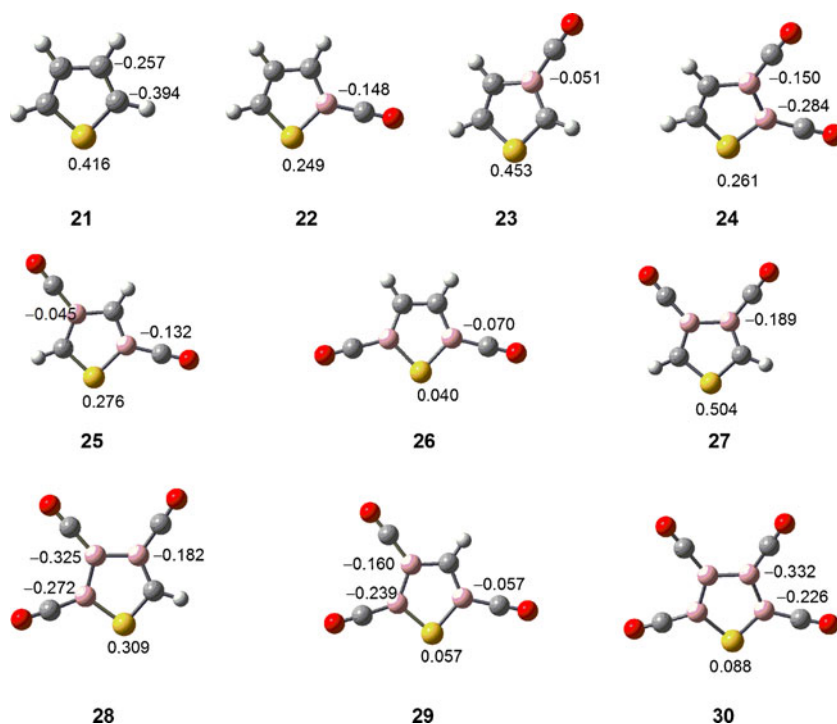
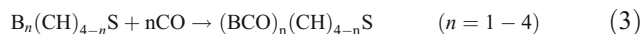
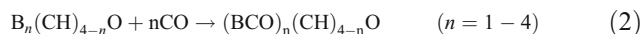
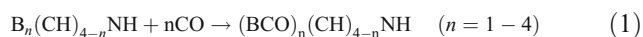


Fig. 3 Optimized geometries of the $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=0-4$) species and the natural charges on the B and S atoms in them



largest positive charge compared to the neighboring nuclei resulting in relative stability of all positional isomers. However, the BCO groups prefer to occupy the vertices with the largest negative charge compared to the neighboring nuclei for $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=1-4$). In any case, the BCO groups of the most stable isomers are always α -substituted.

In order to explore the stability of individual molecules, we computed the CO binding energies of the most stable $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=1-4$), $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=1-4$), and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=1-4$) clusters. Equations 1–3 were used to evaluate the respective CO binding energies. All of the values computed are listed in Table 2.

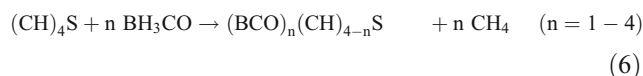
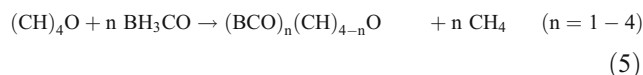
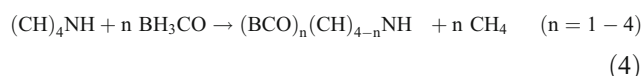


It was found that all calculated CO binding energies are exothermic, suggesting that the corresponding species are stable. The CO binding energies increase as the number of CO ligands increases. For comparison, we also calculated the binding energies per CO group (Table 2), which were found to range from -49.5 kcal/mol (**29**) to -85.1 kcal/mol (**2**), indicating that the CO groups can come from a large and various organic CO donors. It is helpful for chemists to choose corresponding CO donors in organic syntheses. Among these species, the CO binding energy per CO group of isomer **2** is

the largest among those of the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$; it is largest for **12** among the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$; and it is largest for **22** among the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$. Note that the CO binding energies per CO group of the monosubstituted isomers (**2**, **12**, and **22**) are the largest among all of the $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$, $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$, and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ species.

Strain energy

In addition to the stabilities of the individual species, we also computed the differences in strain energy between the BCO-substituted species investigated here and their corresponding hydrocarbons using the equations provided below. The computed reaction energies are summarized in Table 2.



The reaction energies calculated via Eqs. 4–6 represent the differences in strain energy between the BCO-substituted

Table 1 Relative energies (E_{rel} , in kcal/mol), average charge populations, correlative bond parameters (in Å), and NICS values (in ppm) of all isomers investigated here

Species	Symm.	E_{rel}	q_{B}	q_{N}	$r_{\text{B-B}}$	$r_{\text{B-C}}$	$r_{\text{C-C}}$	NICS (0)	NICS (1)	NICS (0) _{zz}	NICS (1) _{zz}
1	C_{2v}	0.00		-0.536			1.391	-13.9	-10.3	-16.7	1.2
2	C_s	0.00	0.131	-0.685		1.505	1.400	-10.0	-8.0	-16.8	-2.1
3	C_s	13.76	-0.114	-0.520		1.519	1.360	-10.8	-8.0	-11.3	-1.4
4	C_s	13.88	-0.057	-0.704	1.640	1.520	1.370	-9.1	-7.1	-15.8	-2.7
5	C_s	14.44	0.022	-0.666		1.506		-7.4	-6.4	-21.4	-4.3
6	C_{2v}	0.00	0.238	-0.894		1.525	1.385	-7.7	-6.5	-13.5	-1.6
7	C_{2v}	29.21	-0.229	-0.503	1.670	1.489		-9.9	-7.2	-21.8	-1.9
8	C_s	11.30	-0.162	-0.676	1.643	1.502		-7.9	-6.4	-19.8	-4.5
9	C_s	0.00	0.057	-0.899	1.658	1.508		-6.7	-6.1	-6.6	-0.7
10	C_{2v}	0.00	-0.101	-0.900	1.643			-6.6	-5.8	-16.7	-3.1
11	C_{2v}	0.00		-0.461			1.384	-11.9	-9.4	-17.8	1.7
12	C_s	0.00	0.270	-0.581		1.484	1.399	-8.7	-7.7	-16.7	0.1
13	C_s	23.25	-0.139	-0.461		1.510	1.351	-9.7	-7.8	-10.7	-3.2
14	C_s	24.18	0.004	-0.605	1.618	1.529	1.364	-8.0	-6.9	-5.6	-2.0
15	C_s	26.23	0.072	-0.580		1.500		-6.5	-6.5	-8.4	-3.6
16	C_{2v}	0.00	0.371	-0.747		1.509	1.396	-6.6	-6.4	-13.8	-0.5
17	C_{2v}	51.28	-0.272	-0.454	1.666	1.474		-8.8	-7.3	-24.3	-2.2
18	C_s	23.88	-0.138	-0.592	1.636	1.486		-6.6	-6.3	-7.1	-3.6
19	C_s	0.00	0.14	-0.760	1.642	1.502		-5.8	-5.9	-6.3	-2.3
20	C_{2v}	0.00	-0.049	-0.768	1.636			-5.4	-5.5	-19.2	-2.8
21	C_{2v}	0.00		0.416			1.387	-12.9	-10.3	-20.5	-2.8
22	C_s	0.00	-0.148	0.249		1.486	1.396	-10.4	-8.9	-8.7	-0.7
23	C_s	13.04	-0.051	0.453		1.509	1.360	-10.0	-8.3	-14.2	-2.1
24	C_s	15.02	-0.217	0.261	1.620	1.523	1.367	-8.8	-7.6	-8.4	-0.7
25	C_s	16.83	-0.089	0.276		1.498		-7.6	-7.3	-11.5	-2.3
26	C_{2v}	0.00	-0.070	0.040		1.503	1.393	-8.6	-7.8	-17.1	-4.2
27	C_{2v}	31.24	-0.189	0.504	1.662	1.481		-8.7	-7.5	-24.4	-5.0
28	C_s	14.66	-0.260	0.309	1.636	1.486		-7.0	-6.76	-9.4	-2.5
29	C_s	0.00	0.152	0.057	1.634	1.498		-7.0	-6.84	-6.9	-1.0
30	C_{2v}	0.00	-0.279	0.088	1.632			-5.7	-6.1	-20.0	-5.6

structures and their corresponding hydrocarbon clusters. The reaction energies are all exothermic, indicating that the $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=1-4$), $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=1-4$), and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=1-4$) structures are less strained than their corresponding hydrocarbon clusters $(\text{CH})_4\text{NH}$, $(\text{CH})_4\text{O}$, and $(\text{CH})_4\text{S}$. This phenomenon was also observed for $(\text{BCO})_n$ and $(\text{CH})_n$ cage clusters [14]. It was found that the strain energy decreases as the number of BCO groups increases, and among all of the substituted clusters, the $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=1-4$) clusters exhibited the largest strain energy differences from their corresponding hydrocarbons.

CO-stretching frequency and aromaticity

To further aid experimental investigations, we computed the CO-stretching frequencies for all of the $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$

($n=1-4$), $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=1-4$), and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=1-4$) isomers. However, in this discussion, we will present only the infrared-active CO-stretching frequencies with the largest IR intensities for the most stable isomers in Table 2. It should be noted that all of the most stable isomers have C–O stretching frequencies lower than $2,143\text{ cm}^{-1}$, the value for free CO [28, 29].

Note also that the electron deficiency of the boron atom and the presence of an electron-withdrawing group weaken the Coulomb attraction, as do the dense charge populations on such small rings, ultimately leading to rather low CO-stretching frequencies. In addition, the presence of an electron-withdrawing group results in greater B→CO π backdonation and Coulomb repulsion, which causes these isomers to have lower CO-stretching frequencies than $2,143\text{ cm}^{-1}$, as shown in Table 2.

Table 2 CO binding energies (DE, in kcal/mol), CO binding energies per CO group (DE/n), differences in strain energy between BCO-substituted clusters and their corresponding hydrocarbons, and CO-stretching frequencies of the most stable isomers

Species	Symm.	DE	DE/n	Strain	ν_{CO}^a
2	C_s	-85.1	-85.1	-20.7	2122.2
6	C_{2v}	-104.8	-52.4	-42.9	2077.8
9	C_s	-149.1	-49.7	-50.1	2107.3
10	C_{2v}	-202.3	-50.6	-61.8	2096.9
12	C_s	-81.6	-81.6	-27.8	2145.6
16	C_{2v}	-111.7	-55.9	-59.6	2091.9
19	C_s	-155.8	-51.9	-66.1	2119.3
20	C_{2v}	-204.3	-51.1	-76.2	2111.8
22	C_s	-76.7	-76.7	-20.0	2143.3
26	C_{2v}	-114.4	-57.2	-44.1	2100.4
29	C_s	-148.5	-49.5	-51.5	2121.0
30	C_{2v}	-199.3	-49.8	-61.6	2112.4

^a Scaled by the factor (0.970) as the ratio between the computed and experimental detected CO frequency

To characterize the aromaticities of these systems, we used the computed NICS values at the center of and 1 Å above the ring. All of the computed NICS values at the center of the ring (NICS (0)) and 1 Å above the ring (NICS (1)), as well as the corresponding NICS (0) *zz* and NICS (1) *zz* values, are given in Table 1.

All of the isomers were calculated to have negative NICS (0), NICS (1), and NICS (0) *zz* values. The NICS (1) *zz* values are also negative, except for the isomers **1**, **11**, and **12**, indicating that their aromaticities 1 Å above the ring are mainly due to σ orbitals. The negative NICS values at the center of and 1 Å above the ring indicate that these isomers are aromatic. Based on their NICS values, they are only slightly less aromatic than their corresponding hydrocarbon counterparts. Meanwhile, the NICS value gradually increases as the number of BCO groups increases. For example, the NICS values at the center of (1 Å above) the ring in $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$) are -10.0 (-8.0 ppm), -7.7 (-6.5 ppm), -6.7 (-6.1 ppm), and -6.6 (-5.8 ppm) for $(\text{CH})_4\text{NH}$, $(\text{BCO})(\text{CH})_3\text{NH}$, $(\text{BCO})_2(\text{CH})_2\text{NH}$, $(\text{BCO})_3(\text{CH})\text{NH}$, and $(\text{BCO})_4\text{NH}$, respectively. According to the results of previous studies, pyrrole is more aromatic than furan [16]. The same was found for the corresponding BCO-substituted analogs. For example, the NICS values at the center of (1 Å above) the ring in $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$) are -8.7 (-7.7 ppm), -6.6 (-6.4 ppm), -5.8 (-5.9 ppm), and -5.4 (-5.5 ppm) for $(\text{CH})_4\text{O}$, $(\text{BCO})(\text{CH})_3\text{O}$, $(\text{BCO})_2(\text{CH})_2\text{O}$, $(\text{BCO})_3(\text{CH})\text{O}$, and $(\text{BCO})_4\text{O}$, respectively. These are lower than the corresponding NICS values for $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$) mentioned above.

It should be noted that the stability of these isomers could be due to either favorable electrostatic interactions

or aromaticity. The NICS values calculated here show that the most stable isomers are not those of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$) and $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$) with the most negative NICS values. There is no direct correlation between the relative stability and the aromaticity for these two systems. It is likely that isomers **2**, **6**, and **9** of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ and **12**, **16**, and **19** of $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ are more stable than the other isomers just because of stronger electrostatic interactions. On the other hand, we also found that the most stable isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=0-4$) are those with the most negative NICS (1) values. For example, the NICS (1) value of **22** is -8.9, which is lower than that of isomer **23**, so **22** is more stable. The stability of these isomers could therefore be due to their aromaticities.

Conclusions

The structures, stabilities, and aromaticities of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$ ($n=0-4$), $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$), and $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$ ($n=0-4$) clusters, which are isolobal with $(\text{CH})_4\text{NH}$, $(\text{CH})_4\text{O}$, and $(\text{CH})_4\text{S}$, respectively, have been investigated by performing calculations at the B3LYP/6-311++G** level of theory. The most stable positional isomers of individual clusters were obtained. Their average B–B, B–C, and C–C bond lengths were found to lie between those of the corresponding typical single and double bonds.

Calculations of the CO binding energies of the most stable clusters showed that they are all exothermic, further indicating that these BCO-substituted species are stable. It should be noted that the CO binding energy per CO group for isomer **2** is the largest among those of the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{NH}$, the CO binding energy per CO group for isomer **12** is the largest among those of the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$, and the CO binding energy per CO group for isomer **22** is the largest among those of the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{S}$.

Calculated differences in strain energy between the BCO-substituted structures and their corresponding hydrocarbon clusters were all found to be exothermic, indicating that the BCO-substituted structures are less strained. It was noted that the strain energy decreases as the number of BCO groups increases, and among all of the substituted clusters, the isomers of $(\text{BCO})_n(\text{CH})_{4-n}\text{O}$ ($n=0-4$) showed the largest strain energy differences from their corresponding hydrocarbons.

The computed NICS values were all negative, indicating that these BCO-substituted clusters are aromatic compounds, in good agreement with the aromaticities of the corresponding hydrocarbon species. To further aid experimental investigations, CO-stretching frequencies were also computed.

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