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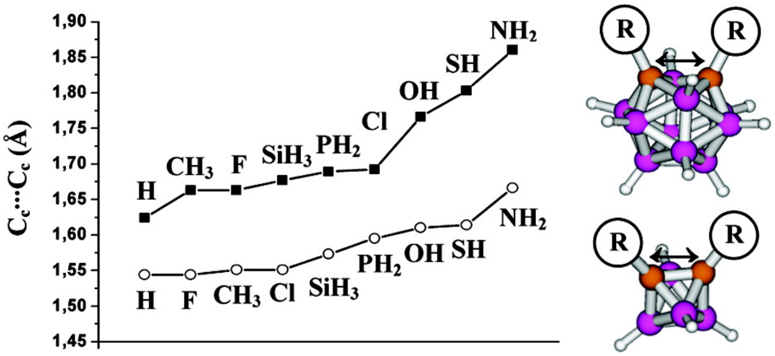

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Strikingly Long C⋯C Distances in 1,2-Disubstituted *ortho*-Carboranes and Their Dianions

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Abstract: Neutral and especially dianionic 6- and 12-vertex *closo ortho*-carboranes (*o*-carboranes) 1,2-R_2-1,2-$C_2B_nH_n$ (R = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, as well as e^-, CH_2^-, NH^-, O^-, SiH_2^-, PH^-, and S^-) exhibit extremely large variations (over 1 Å!) of the cage CC distances, from 1.626 to 2.638 Å, at the B3LYP/6-31G*//B3LYP/6-31G* DFT level. These CC "bond lengths," among the longest ever reported, generally are greater in the icosahedral than those in the corresponding octahedral systems and depend strongly on the substituents. While 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ has the longest $C_c\cdots C_c$ separation in neutral species (1.860 Å), $C_c\cdots C_c$ distances can be much larger in the corresponding dianions. These range from 1.823 Å ($R^- = e^-$) to 2.638 Å ($R^- = CH_2^-$) for 1,2-$(R^-)_2$-1,2-$C_2B_{10}H_{10}$ and from 1.626 Å ($R^- = SiH_2^-$) to 3.099 Å ($R^- = NH^-$) for 1,2-$(R^-)_2$-1,2-$C_2B_4H_4$. Remarkably, there is no abrupt discontinuity over the entire range of CC lengths. Consequently, the relationship between the gradual changes in the distances and the nature of the bonding was analyzed by means of the form of the Kohn−Sham orbitals, the Wiberg $C_c\cdots C_c$ bond indices, and Bader AIM method. Cluster carboranes, and possibly other heteroboranes, thus appear to offer unique opportunities for modulating $C_c\cdots C_c$ distances.

1. Introduction

Molecules with unusually long C−C bonds challenge bonding theories. The unusual coordination of their atoms also is relevant to the design of nonlinear optical materials[1] and homogeneous catalysts.[2] Unusually long C⋯C bonds have been found in a variety of organic molecules.[3] For example, 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobuta[*b*]naphthalene has one 1.729 Å C−C distance.[4] The lengthening of this "conventional" C−C single bond is attributed to through-bond interactions[5] of the favorably aligned benzene π-orbitals.[3] Exceptionally long C−C bonding interactions ranging from 1.6 Å to 3.5 Å are present in tetracyanoethylene (TCNE) anion dimers.[6−8] "Partial" C⋯C bonds, involving fewer than two electrons and varying to well over 2.2 Å in length, abound in nonclassical carbocations,[9] in transition states of organic reactions,[9] and in neutral homoaromatic systems.[10] What constitutes a "C−C bond" exactly? The definition is difficult. The very wide range of C⋯C separations in the systems studied here allows this question to be addressed.

Recent experimental and computational evidence of unusually long $C_c\cdots C_c$ separations (C_c denotes a carbon atom in the cluster) in 1,2-disubstituted *icosahedral o*-carboranes (1,2-R_2-1,2-$C_2B_{10}H_{10}$) and in metallacarboranes[11] suggests the possibility of *tuning* C⋯C distances in *o*-carborane systems.[12] Thus, experimental $C_c\cdots C_c$ lengths in various 1,2-R_2-1,2-$C_2B_{10}H_{10}$ derivatives, varying from 1.63 Å to 1.86 Å depending on the substituent (R), have been corroborated by density-functional theory (DFT) computations.[12,13] Interestingly, when R = H is replaced by R = SH in 1,2-R_2-1,2-$C_2B_{10}H_{10}$, the B3LYP/6-

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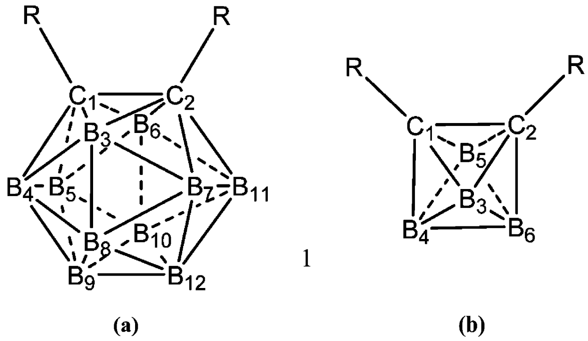
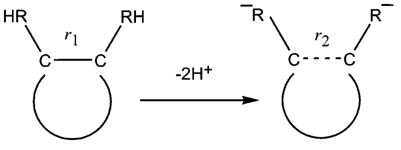
Scheme 1. Framework Structures and Atom Numbering of (a) the *Icosahedral* 1,2-R_2-1,2-$C_2B_{10}H_{10}$ and (b) the *Octahedral* 1,2-R_2-1,2-$C_2B_4H_4$ Carboranes[a]



[a] For clarity, boron-bound hydrogen atoms are not shown.

Scheme 2



31G* computed $C_c\cdots C_c$ distance increases from 1.624 Å to 1.803 Å.[12,13] Experimental substitution of H by a more bulky group, such as phenyl, also increases the $C_c\cdots C_c$ distance, but only to 1.764 Å.[14] Shorter $C_c\cdots C_c$ distances are also found in *o*-carboranes, such as in the icosahedral dehydro 1,2-dicarborane 1,2-$C_2B_{10}H_{10}$, which has a computed C=C distance of 1.378 Å at the B3LYP/6-31G* level, thus extending the range of C···C distances considerably.[15]

Thus the lengthening of the cage $C_c\cdots C_c$ bonds in *o*-carborane 1,2-derivatives must have electronic as well as steric origins.[16] These arise, for example, from back-donation[11,12] of lone pairs of the substituents to the σ^*(C−C) antibonding orbital, which serves as the cluster LUMO (lowest unoccupied molecular orbital). This increases the $C_c\cdots C_c$ distance. Hence, appropriate choices of the R substituents in 1,2-R_2-1,2-$C_2B_{10}H_{10}$ (Scheme 1), considering donor ability, steric effects, atomic orbital size matching, and electronegativity, might even result in continuous tuning of the $C_c\cdots C_c$ distance. The object of this paper is to explore this possibility computationally. The longest C···C separations, which might be achieved, would involve cage opening. Such structures can no longer be considered to be *closo* forms. At which C···C separation does this occur? In addition to the *icosahedral* 1,2-$C_2B_{10}H_{12}$ system, we also consider the smaller *octahedral* cluster, 1,2-$C_2B_4H_6$ (Scheme 1, with substituents on the carbons), to ascertain the dependence of the $C_c\cdots C_c$ bond lengthening on the cluster size. The back-donation model was tested by studying several substituents, R, with and without available lone pairs on the vicinal atom attached to the cluster carbon. These substituents include both first (R = {CH_3, NH_2, OH, F}) and second row elements (R = {SiH_3, PH_2, SH, Cl}). Dianions of the 1,2-$(R^-)_2$-1,2-$C_2B_nH_n$ type (Scheme 2), in which a proton is removed from each R substituent in the neutral species, enhanced the back-donation into antibonding orbitals and, as expected, were especially effective in extending the $C_c\cdots C_c$ distances.

Comparison[17] of the $C_2B_{10}H_{12}$, $C_2B_{10}H_{12}^-$ and $C_2B_{10}H_{12}^{2-}$ systems is particularly relevant, since electron addition has a striking effect on the molecular geometry. The icosahedral cage begins to open even in the singly charged anion *o*-$C_2B_{10}H_{12}^-$. The B4−B5 and B7−B11 distances (Scheme 1) are appreciably longer than those in the neutral cluster. The B4−B5, C1−B3, C1−B6, B5−B9, and B4−B9 distances increase substantially in the *o*-$C_2B_{10}H_{12}^{2-}$ dianion. Nevertheless, the $C_c\cdots C_c$ distance only varies modestly in the three species: 1.608 Å (neutral), 1.630 Å (monoanion), and 1.645 Å (dianion).

We expect our 1,2-$(R^-)_2$-1,2-$C_2B_nH_n$ dianions to behave differently. The back-donation from the substituents should be local and affect the $C_c\cdots C_c$ connectivity primarily, rather than the whole cluster. $C_c\cdots C_c$ bond breaking or substantial weakening in these dianions also is consistent with a simple electrostatic model. Assuming that a single negative charge is located on each R group, the reduction in Coulomb repulsion is, e.g., ∼50 kcal/mol on increasing the R···R distance from 1.8 Å to 2.5 Å! This is 60% of the energy of a single C−C bond.[18]

The work described here was presented at the 226th ACS National Meeting within the symposium *Contemporary Aspects of Chemical Bonding*.[19] During completion of our manuscript, a related study by Fox and co-workers[20] appeared reporting icosahedral cage distortions of *o*-carboranes 1-X-2-Ph-1,2-$C_2B_{10}H_{10}$ (X = F, O^-, OH, NH_2, NH^-, CH_2^-). Syntheses of related neutral and dianionic carboranes can be found in refs 21−23.

2. Methods

All computations used the Gaussian98 program.[24] We report data at the B3LYP/6-31G*//B3LYP/6-31G* DFT level, where all the geometries were energy minima with real vibrational frequencies. Reoptimization at MP2/6-31G* gave no significant differences (see Supporting Information), and calculations at the B3LYP/6-311++G** level revealed the same trends (the largest change in the $C_c\cdots C_c$ distance was 0.037 Å for 1,2-$(CH_2^-)_2$-1,2-$C_2B_{10}H_{10}$).

We studied the 1,2-R_2-1,2-$C_2B_nH_n$ icosahedral (n = 10) and octahedral (n = 4) *o*-carboranes with R = {H; CH_3, NH_2, OH, F; SiH_3, PH_2, SH, Cl}, as well as their corresponding dianions 1,2-$(R^-)_2$-1,2-$C_2B_nH_n$ (derived by formal proton removal from both R groups). For comparison, we include *syn*-*n*-butane, *syn*-1,2-diaminoethane, 1,2-*cis*-diaminoethene, and their corresponding dianions, e.g., $^-(CH_2)(CH_2)_2(CH_2)^-$.

3. Results

3.1. Neutral Icosahedral *o*-Carboranes. The carborane cages remain intact (see Supporting Information) in the optimized geometries of 1,2-R_2-1,2-$C_2B_{10}H_{10}$, with R = {H, CH_3, NH_2, OH, F} (Figure 1), but all the substituents elongate the

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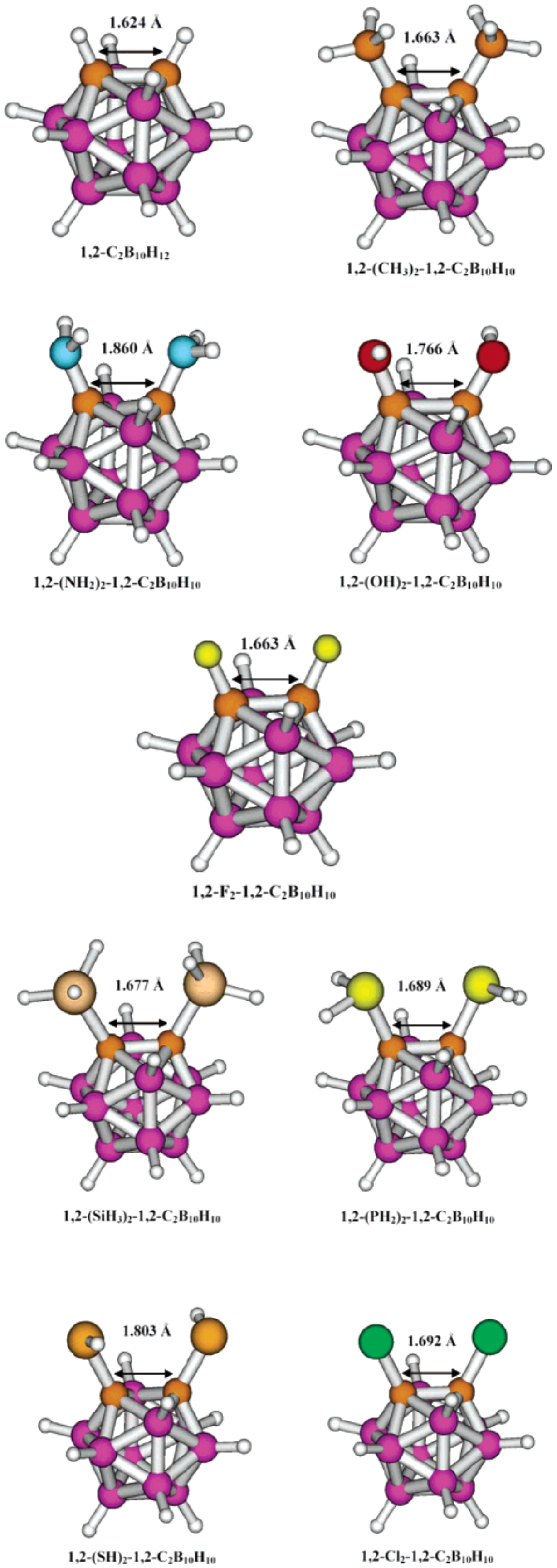

Figure 1. B3LYP/6-31G* optimized geometries and $C_c{\cdots}C_c$ distances (Å) of icosahedral *o*-carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl).

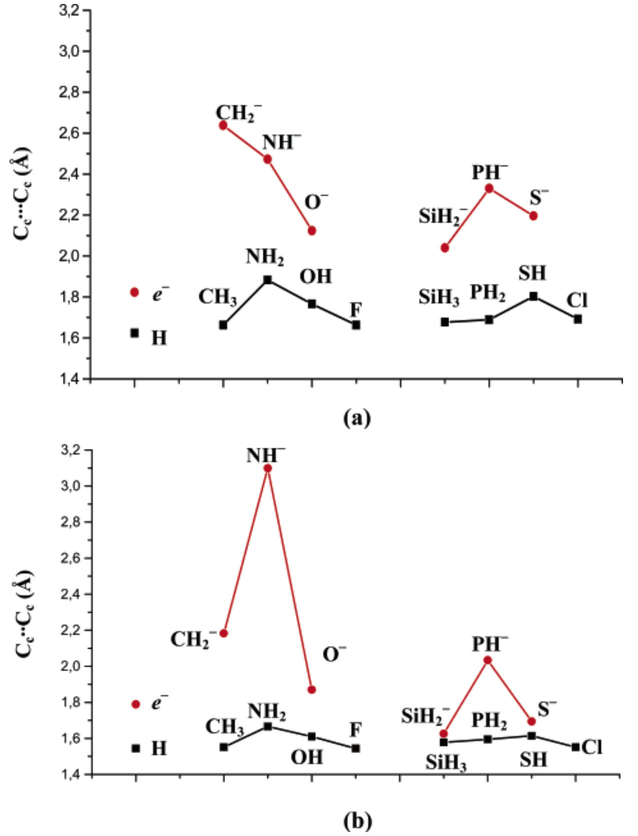

Figure 2. B3LYP/6-31G* $C_c{\cdots}C_c$ distances (Å) versus substituents R in (a) icosahedral *o*-carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = H; CH_3, NH_2, OH, F; SiH_3, PH_2, SH, Cl) (dark squares and dark solid lines), and the corresponding dianions (R = e^-; CH_2^-, NH^-, O^-; SiH_2^-, PH^-, S^-) (red circles and red solid lines), and (b) B3LYP/6-31G* $C_c{\cdots}C_c$ distances (Å) versus substituents R in octahedral *o*-carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_4H_4$ (R = H, CH_3, NH_2, OH, F; SiH_3, PH_2, SH, Cl) (dark squares and dark solid lines), and the corresponding dianions $1,2\text{-}(R^-)_2\text{-}1,2\text{-}C_2B_4H_4$ ($R^- = e^-$, CH_2^-, NH^-, O^-; SiH_2^-, PH^-, S^-) (red circles and red solid lines).

$C_c{\cdots}C_c$ distance. This lengthening is most pronounced for $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, where $C_c{\cdots}C_c = 1.860$ Å. The elongation trend (Figure 2a) is

$$[C_c{\cdots}C_c]^{NH_2} > [C_c{\cdots}C_c]^{OH} > [C_c{\cdots}C_c]^{F} \approx [C_c{\cdots}C_c]^{CH_3} > [C_c{\cdots}C_c]^{H} \quad (1)$$

The computed (1.624 Å, B3LYP/6-31G* computations as shown in Table 1; 1.620 Å, MP2/6-31G* computations in the Supporting Information) and experimental (1.629 Å[25]) $C_c{\cdots}C_c$ distances in the parent compound $1,2\text{-}C_2B_{10}H_{12}$ coincide very well within 0.005−0.009 Å. Lone pairs on the substituent atom attached to C_c are important. The vicinal amino groups in $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ have the largest effect, not only on the $C_c{\cdots}C_c$ distance, but also on the symmetry of the optimized structure. While $1,2\text{-}C_2B_{10}H_{12}$, $1,2\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and $1,2\text{-}F_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ adopt C_{2v} symmetry, C_s is favored by $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and C_2 symmetry, by $1,2\text{-}(OH)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$.

The conformation of $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with the lone pairs on nitrogen facing one another (C_{2v} symmetry) has a local minimum, only 1.8 kcal mol^{-1} higher in energy than the

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Table 1. Neutral Icosahedral and Octahedral Carboranes: Computed (B3LYP/6-31G*) $C_c\cdots C_c$ Distances (Å), Wiberg $C_c\cdots C_c$ Bond Indices (WBI), Bader Bond Order *n*, and Topological Properties of the Density at Bond Critical Points along $C_c\cdots C_c$ − Density $\rho(r_c)$ (e Å^{-3}) and $L(r_c) = -\nabla^2\rho(r_c)$ (e Å^{-5})[a]

icosahedral	$C_c\cdots C_c$	WBI	n	$\rho(r_c)$	$L(r_c)$	octahedral	$C_c\cdots C_c$	WBI	*n*	$\rho(r_c)$	$L(r_c)$
R = H	1.624	0.74	0.66	1.26	4.80	R = H	1.544	0.86	0.80	1.47	6.41
R = CH_3	1.663	0.71	0.61	1.18	3.78	R = CH_3	1.551	0.85	0.80	1.46	6.24
R = NH_2	1.860	0.44	0.44	0.83	−0.65	R = NH_2	1.666	0.64	0.61	1.18	1.78
R = OH	1.766	0.53	0.51	0.99	1.23	R = OH	1.610	0.71	0.70	1.32	3.95
R = F	1.663	0.65	0.63	1.22	4.36	R = F	1.544	0.81	0.84	1.52	7.40
R = SiH_3	1.677	0.70	0.57	1.12	2.84	R = SiH_3	1.573	0.84	0.73	1.38	4.77
R = PH_2	1.689	0.68	0.57	1.11	2.80	R = PH_2	1.595	0.79	0.71	1.34	4.17
R = SH	1.803	0.51	0.47	0.90	0.19	R = SH	1.614	0.72	0.67	1.28	3.30
R = Cl	1.692	0.64	0.57	1.12	2.96	R = Cl	1.551	0.82	0.80	1.46	6.27

molecule	$C_c\cdots C_c$	WBI	*n*	$\rho(r_c)$	$L(r_c)$
ethane	1.530	1.04	0.93	1.63	13.2
syn-n-butane	1.538	1.01	0.94	1.64	13.2
syn-1,2-diaminoethane	1.531	1.01	0.99	1.69	14.3

[a] Ethane, *syn-n*-butane, and *syn*-1,2-diaminoethane data are included for comparison.

conformer in Figure 1, but is still effective in increasing the $C_c\cdots C_c$ distance to 1.883 Å. The short C−N bond length in 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$, $r_{CN} = 1.393$ Å,[26] is consistent with the elongation of the $C_c\cdots C_c$ distance: both features result from π-electron back-donation from the nitrogen lone pairs to the CC cage antibonding orbital. The trends shown in (1) are consistent with this reasoning: the largest $C_c\cdots C_c$ separations, in 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ and 1,2-$(OH)_2$-1,2-$C_2B_{10}H_{10}$, are found with the best π donors. The fluorine lone pairs in 1,2-F_2-1,2-$C_2B_{10}H_{10}$ donate electron density poorly, and the $C_c\cdots C_c$ bond elongation (0.04 Å compared to 1,2-$C_2B_{10}H_{12}$) is small. Methyl groups result in the same lengthening in 1,2-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$, evidently due to steric effects.

Figure 3 displays Kohn−Sham frontier and other molecular orbitals (MOs) of the same neutral set. Since H, CH_3, and F substituents do not interact significantly with the cage, common patterns are exhibited by 1,2-$C_2B_{10}H_{12}$, 1,2-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$, and 1,2-F_2-1,2-$C_2B_{10}H_{10}$. But the appreciable interaction among the OH and NH_2 lone pairs and the $C_c\cdots C_c$ orbitals is apparent in 1,2-$(OH)_2$-1,2-$C_2B_{10}H_{10}$ and especially in the diamino derivative, 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ (see the HOMO in particular). The appearance of the MOs of the dihydroxy derivative 1,2-$(OH)_2$-1,2-$C_2B_{10}H_{10}$ MOs is intermediate between those of 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ and the other molecules in Figure 3.

The Kohn−Sham orbitals considered here (for consistency with the molecular geometries) are not expected to show any noticeable differences with the corresponding Hartree−Fock orbitals for these systems (see, e.g., ref 27). Formally, Kohn−Sham orbitals relate to a "model" noninteracting system, constrained by a potential that depends on the choice of exchange-correlation function. Thus, strictly, we examine the electron density of the model system in these DFT calculations.

The trend in $C_c\cdots C_c$ distances (Figure 1 and Figure 2a) for the second row substituents (2) is different from the first row (1):

$$[C_c\cdots C_c]^{SH} > [C_c\cdots C_c]^{Cl} \approx [C_c\cdots C_c]^{PH_2} \approx [C_c\cdots C_c]^{SiH_3} \quad (2)$$

The optimized geometries of the second row series, shown in Figure 1, all have C_2 symmetry. The dichloro derivative (1,2-Cl_2-1,2-$C_2B_{10}H_{10}$, C_{2v}) is an exception. The $C_c\cdots C_c$ distance in 1,2-$(SiH_3)_2$-1,2-$C_2B_{10}H_{10}$ is slightly larger (0.013 Å) than that in the methyl analogue 1,2-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$, presumably due to the bulkier second-row SiH_3 groups. Pyramidal (as opposed to fixed planar) PH_2 substituents are known to function relatively poorly as π-donors.[28] Thus, the 1.689 Å $C_c\cdots C_c$ separation of the PH_2 derivative 1,2-$(PH_2)_2$-1,2-$C_2B_{10}H_{10}$, while longer than the 1.624 Å of its 1,2-$C_2B_{10}H_{12}$ parent, is considerably shorter than the 1.860 Å for its NH_2 analogue, 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$. Comparison between computed ($C_c\cdots C_c = 1.689$ Å at B3LYP/6-31G* level, Table 1, 1.668 Å at MP2/6-31G* level; see Supporting Information) and experimental $C_c\cdots C_c$ distances for R = PH_2 is available for the related compound 1,2-$(P\,{}^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$,[16b] with $(C_c\cdots C_c)_{exp} = 1.719$ Å (the bulkier ${}^iPr$ groups give a slightly longer experimental $C_c\cdots C_c$ distance). The largest $C_c\cdots C_c$ distance (1.803 Å) in this second row series is for 1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$, which compares very well to the experimental $C_c\cdots C_c$ distance (1.798 Å) in 1,2-$(SPh)_2$-1,2-$C_2B_{10}H_{10}$.[12,29] In contrast, the maximum separation for the first row substituents is not for the OH analogue but for R = NH_2. Replacing O by S increases the $C_c\cdots C_c$ length from 1.766 Å to 1.803 Å, but it decreases when N is replaced by P. The poor p-π overlap associated with pyramidal PH_2 is not a problem with SH because the lower coordination results in the availability of a p-lone pair. The $C_c\cdots C_c$ distance in 1,2-Cl_2-1,2-$C_2B_{10}H_{10}$ is slightly larger than that in 1,2-F_2-1,2-$C_2B_{10}H_{10}$. Thus, electronegativity, size, and the ease of lone pair donation all influence the $C_c\cdots C_c$ distance.

In sharp contrast to the $C_c\cdots C_c$ behavior, the maximum variation in the cage B−C_c and B−B distances is only ±0.017 Å for all our first- and second-row 1,2-disubstituted icosahedral *o*-carboranes (see Supporting Information). Clearly, the rest of the icosahedral cage remains intact in all the neutral systems.

3.2. Neutral Octahedral *o*-Carboranes. Figure 2b also shows the $C_c\cdots C_c$ distance trends for 1,2-substituted octahedral *o*-carboranes (see Figure 4 for the optimized geometries of 1,2-R_2-1,2-$C_2B_4H_4$ with R = {H, CH_3, NH_2, OH, F}). While the variations in $C_c\cdots C_c$ distances in the icosahedral and octahedral *o*-carboranes follow the same trend (see (1)), the changes are smaller for the latter set. Comparing Figure 2a with 2b shows this clearly: for each substituent, the $C_c\cdots C_c$ separations in the octahedral cage are shorter than those in the corresponding icosahedral cage. The longest $C_c\cdots C_c$ distance is 1.661 Å when

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(26) Computed CN distances are $H_3C{-}NH_2$ (1.464 Å) and $H_2C{=}NH$ (1.270 Å) at B3LYP/6-31G* level.

(27) Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414−3420.

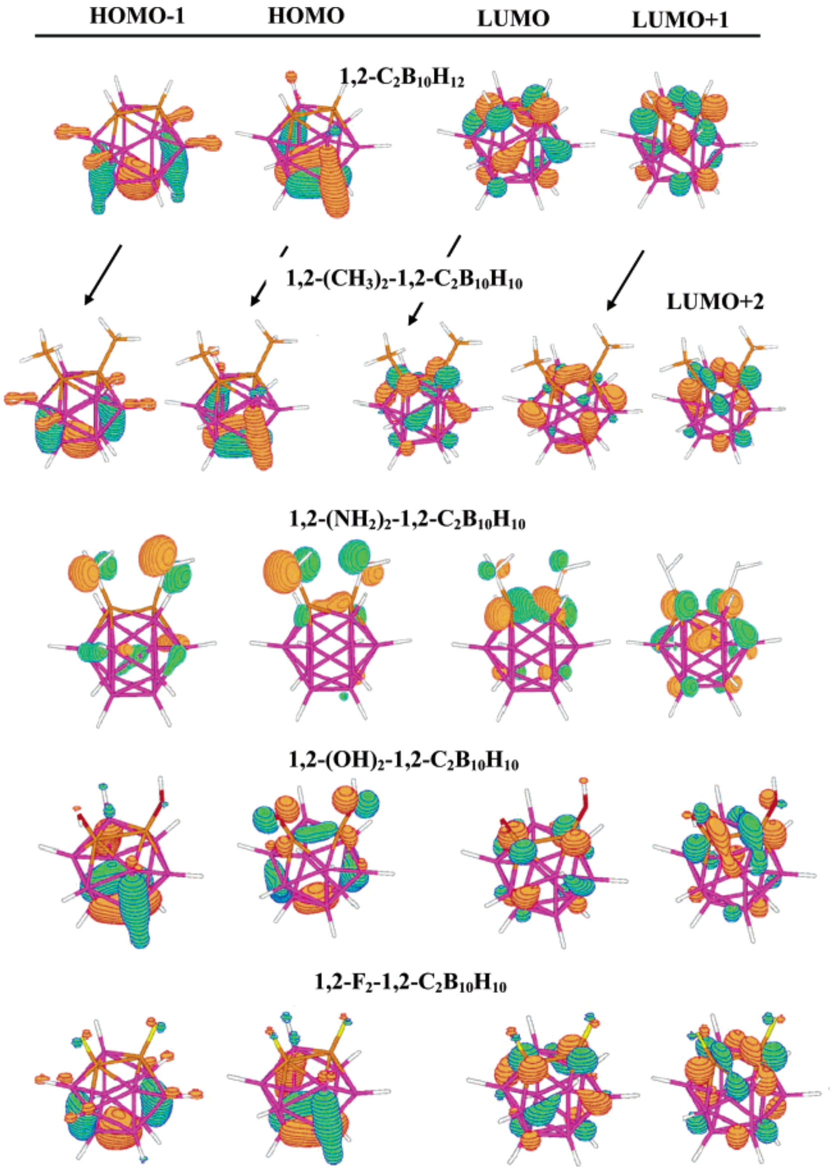

Figure 3. Frontier Kohn−Sham molecular orbitals and further orbitals close in energy (MOs, B3LYP/6-31G*) in icosahedral *o*-carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ ($R = H, CH_3, NH_2, OH, F$). For $R = CH_3$, the LUMO+2 is also shown.

$R = NH_2$, $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_4H_4$, but this is 0.211 Å shorter than that of the icosahedral analogue $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. Similarly substituted icosahedral and octahedral compounds adopt the same point group symmetries. Changes in geometry other than the $C_c\cdots C_c$ length are small and resemble those of the icosahedral analogues (see Supporting Information).

The B3LYP/6-31G* C−C distance in ethane, 1.530 Å, is somewhat shorter than the lengths in $1,2\text{-}C_2B_4H_6$ (1.544 Å) and $1,2\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_4H_4$ (1.551 Å). The NH_2 groups in $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_4H_4$ are oriented face-to-face. Since the *exo*-CN lengths in $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_4H_4$ (1.394 Å) and $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (1.407 Å and 1.395 Å) are equivalent, the icosahedral cage must play a substantial role in the much greater $C_c\cdots C_c$ elongation in $1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$.

The trends of the optimized geometries of $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_4H_4$, $R = \{SiH_3, PH_2, SH, Cl\}$ (Figure 4) and those of the corresponding icosahedral molecules in Figure 1 are nearly the same (see (2)). However, the variations are smaller for the octahedral carboranes.

3.3. Dianions of Icosahedral *o*-Carboranes. As expected, the dianions formed by formal proton abstraction from each R group in icosahedral ($n = 10$) and octahedral ($n = 4$) neutral carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_nH_n$ (Scheme 2) exhibit much larger effects (Figure 5). It is even possible to "tune" the $C_c\cdots C_c$ connectivity locally without affecting the rest of the cluster!

The trend in the $C_c\cdots C_c$ distances (Figure 2a) for the parent $(1,2\text{-}C_2B_{10}H_{10})^{2-}$ and first-row substituted dianions $1,2\text{-}(CH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, $1,2\text{-}(NH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and $1,2\text{-}(O^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ is

$$[C_c\cdots C_c]^{CH_2^-} > [C_c\cdots C_c]^{NH^-} > [C_c\cdots C_c]^{O^-} > [C_c\cdots C_c]^{e^-} \tag{3}$$

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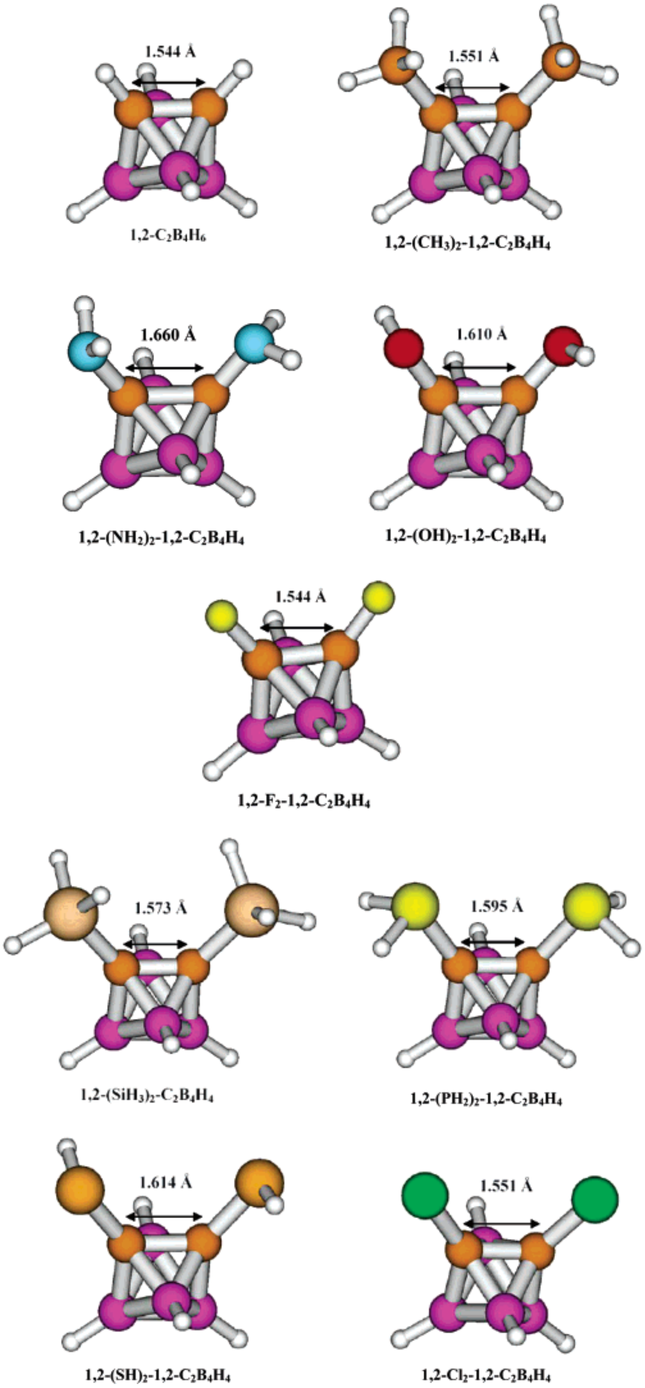
(28) Dransfeld, A.; Nyulaszi, L.; Schleyer, P. v R. *Inorg. Chem.* **1998**, *37*, 4413−4420.

(29) We are not aware of an experimental crystal structure for $1,2\text{-}(SH)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. An experimental and computational study on the $1,2\text{-}(SPH)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ compound was carried out in ref 12 above.



$1,2\text{-}C_2B_4H_6$ $1,2\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_4H_4$

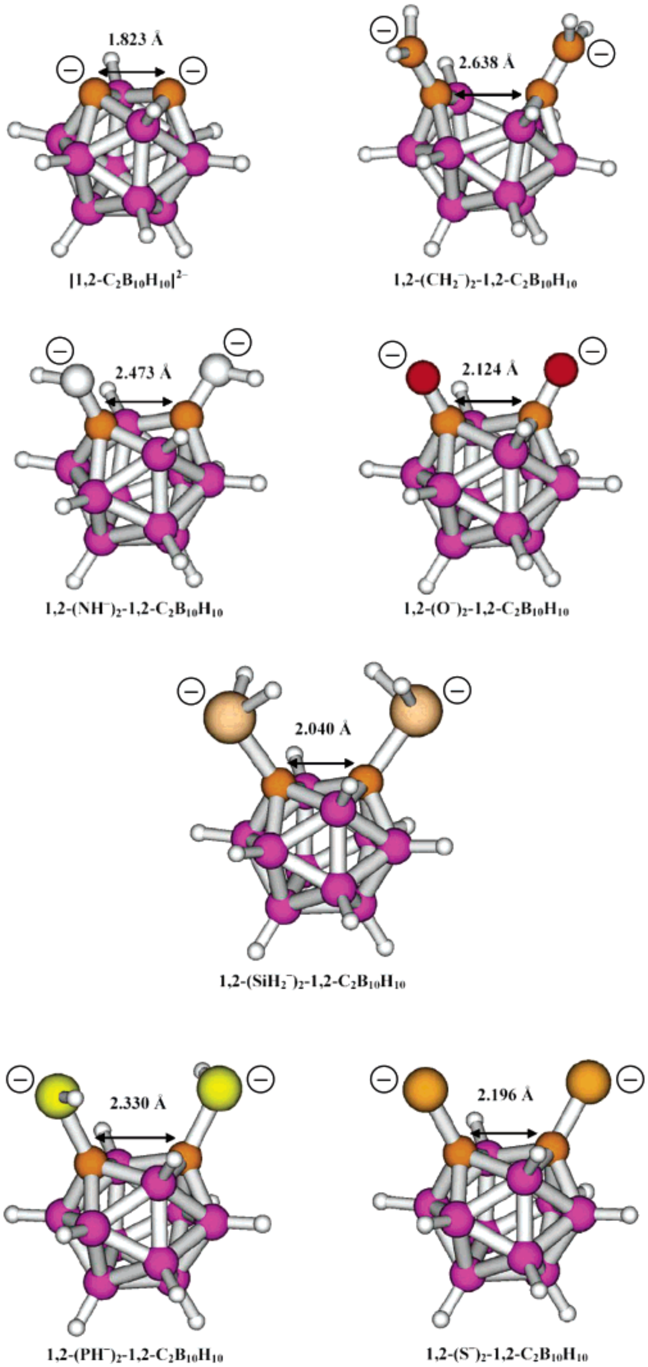
$1,2\text{-}(NH_2)_2\text{-}1,2\text{-}C_2B_4H_4$ $1,2\text{-}(OH)_2\text{-}1,2\text{-}C_2B_4H_4$

$1,2\text{-}F_2\text{-}1,2\text{-}C_2B_4H_4$

$1,2\text{-}(SiH_3)_2\text{-}C_2B_4H_4$ $1,2\text{-}(PH_2)_2\text{-}1,2\text{-}C_2B_4H_4$

$1,2\text{-}(SH)_2\text{-}1,2\text{-}C_2B_4H_4$ $1,2\text{-}Cl_2\text{-}1,2\text{-}C_2B_4H_4$

Figure 4. B3LYP/6-31G* optimized geometries and $C_c \cdots C_c$ distances (Å) of octahedral *o*-carboranes $1,2\text{-}R_2\text{-}1,2\text{-}C_2B_4H_4$ (R = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl).



$[1,2\text{-}C_2B_{10}H_{10}]^{2-}$ $1,2\text{-}(CH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

$1,2\text{-}(NH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ $1,2\text{-}(O^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

$1,2\text{-}(SiH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

$1,2\text{-}(PH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ $1,2\text{-}(S^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

Figure 5. B3LYP/6-31G* optimized geometries and $C_c \cdots C_c$ distances (Å) of dianions obtained by formal proton abstraction from each R group in icosahedral *o*-carboranes $1,2\text{-}(R^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = e^-, CH_2^-, NH^-, O^-, SiH_2^-, PH^-, S^-).

The $C_c \cdots C_c$ separations are much larger than those in the neutral species. The dianions exhibit large local distortions and partial opening of the cages. The $C_c \cdots C_c$ distance is 1.823 Å in the parent dianion $(1,2\text{-}C_2B_{10}H_{10})^{2-}$. This is a special case since no back-donation from α-substituents is possible. The $C_c \cdots C_c$ distance is even longer (well over 2.1 Å) when α-substituents are present, as in $1,2\text{-}(CH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, $1,2\text{-}(NH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and $1,2\text{-}(O^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$.

Despite the substantial increase in the $C_c \cdots C_c$ separation, much of the cage structure is largely unaltered (see Supporting Information). However, in $1,2\text{-}(CH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $1,2\text{-}(NH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, which have the longest $C_c \cdots C_c$ distances, the $C_1{-}B_3$ and $C_1{-}B_6$ lengths increase considerably, by 0.715 Å and 0.500 Å, respectively, relative to $1,2\text{-}C_2B_{10}H_{12}$. The cages of these two icosahedral carborane dianions are opened substantially (see Figure 5). Differences in the other $B{-}C_c$ distances and the B—B bond lengths are smaller (see SI), varying from −0.138 Å to 0.111 Å. $1,2\text{-}(CH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ possesses well-defined essentially planar sp^2 $C_c{=}CH_2^{(-)}$ groups: the 1.373 Å $C_c \cdots CH_2^-$ distances and 121° HCH^- angles are very similar to the ethylene values (1.331 Å and 122° at B3LYP/6-31G*).

The $C_c \cdots C_c$ separations in the optimized geometries of the second-row $1,2\text{-}(SiH_2^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, $1,2\text{-}(PH^-)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and 1,2-$(S^-)_2$-1,2-$C_2B_{10}H_{10}$ dianions (Figure 5) also are elongated compared to the corresponding neutral systems:

$$[C_c\cdots C_c]^{PH^-} > [C_c\cdots C_c]^{S^-} > [C_c\cdots C_c]^{SiH_2^-} \tag{4}$$

The 1,2-$(SiH_2^-)_2$-1,2-$C_2B_{10}H_{10}$ (C_{2v}), 1,2-$(PH^-)_2$-1,2-$C_2B_{10}H_{10}$ (C_2), and 1,2-$(S^-)_2$-1,2-$C_2B_{10}H_{10}$ (C_{2v}) dianions preserve the icosahedral cage geometries. The pyramidal, inward-pointing conformations of the SiH_2 groups in 1,2-$(SiH_2^-)_2$-1,2-$C_2B_{10}H_{10}$ (Figure 5) differ from those of the CH_2's in 1,2-$(CH_2^-)_2$-1,2-$C_2B_{10}H_{10}$. The optimized 1,2-$(PH^-)_2$-1,2-$C_2B_{10}H_{10}$ and 1,2-$(S^-)_2$-1,2-$C_2B_{10}H_{10}$ geometries are similar to those of their first-row analogues, 1,2-$(NH^-)_2$-1,2-$C_2B_{10}H_{10}$, and 1,2-$(O^-)_2$-1,2-$C_2B_{10}H_{10}$. Whereas SH results in the largest $C_c\cdots C_c$ separation of all neutral second row substituents, this occurs with PH^- in the dianions. PH^-, with its dicoordinate P and perpendicular lone pair, is a much better π-donor than pyramidal PH_2. Variations in the C_c—B and B—B cage bond lengths are small, differing from 1,2-$C_2B_{10}H_{12}$ by −0.047 Å to +0.065 Å (see Supporting Information).

3.4. Dianions of Octahedral *o*-Carboranes. The optimized geometries of the first-row $(1,2\text{-}C_2B_4H_4)^{2-}$, 1,2-$(CH_2^-)_2$-1,2-$C_2B_4H_4$, 1,2-$(NH^-)_2$-1,2-$C_2B_4H_4$, and 1,2-$(O^-)_2$-1,2-$C_2B_4H_4$ dianions (Figure 6) show trends in $C_c\cdots C_c$ distances such as that in Figure 2b:

$$[C_c\cdots C_c]^{NH^-} \gg [C_c\cdots C_c]^{CH_2^-} > [C_c\cdots C_c]^{O^-} > [C_c\cdots C_c]^{e^-} \tag{5}$$

The remarkably long $C_c\cdots C_c$ distance (3.099 Å) in 1,2-$(NH^-)_2$-1,2-$C_2B_4H_4$ characterizes the opened cage; there are other large distortions (Figure 6 and Supporting Information). Except for this NH^- dianion, the changes in the $C_c\cdots C_c$ distances of the octahedral species are all smaller than those in the corresponding icosahedral cases. The nonplanarity of the CH_2^- group in the 1,2-$(CH_2^-)_2$-1,2-$C_2B_4H_4$ dianion (Figure 6) differs from the icosahedral analogue 1,2-$(CH_2^-)_2$-1,2-$C_2B_{10}H_{10}$ (Figure 5). The $C_c\cdots CH_2$ distance in 1,2-$(CH_2^-)_2$-1,2-$C_2B_4H_4$, 1.410 Å, is slightly longer than that in the corresponding icosahedral dianion 1,2-$(CH_2^-)_2$-1,2-$C_2B_{10}H_{10}$. The opening of the cage in 1,2-$(NH^-)_2$-1,2-$C_2B_4H_4$ increases the C_1—B_3 distance by 1.072 Å as compared to the parent dianion $(1,2\text{-}C_2B_4H_4)^{2-}$.

The optimized geometries of 1,2-$(R^-)_2$-1,2-$C_2B_4H_4$, $R^- = \{SiH_2^-, PH^-, S^-\}$ (Figure 6) mirror the trend of the $C_c\cdots C_c$ distances in the dianions with second-row substituents (Figure 2b):

$$[C_c\cdots C_c]^{PH^-} > [C_c\cdots C_c]^{S^-} > [C_c\cdots C_c]^{SiH_2^-} \tag{6}$$

For a given substituent, the elongations are shorter than those for the icosahedral analogues.

In general, substituent effects on the $C_c\cdots C_c$ lengths are almost always larger in the icosahedral than in the octahedral systems. The icosahedral unit is larger than the octahedral and better able to accommodate larger distortions. The Mulliken populations of nitrogen and carbon indicate a smaller degree of back-donation in 1,2-$(NH_2)_2$-1,2-$C_2B_4H_4$ than in 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$.

3.5. Neutrals and Dianions of *syn-n*-Butane, *syn*-1,2-Diaminoethane, and 1,2-*cis*-Diaminoethene. The computed central CC distances in syn-*n*-butane, *syn*-1,2-diaminoethane, 1,2-*cis*-diaminoethene, and their corresponding terminal dianions do not mimic the behavior of the carborane cages (Tables 1 and 2). The substituent effects in these acyclic analogues are quite small and the central C⋯C distances in the neutrals are shorter than those in the icosahedral and octahedral *o*-carborane analogues 1,2-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$, 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ and 1,2-$(CH_3)_2$-1,2-$C_2B_4H_4$, 1,2-$(NH_2)_2$-1,2-$C_2B_4H_4$.

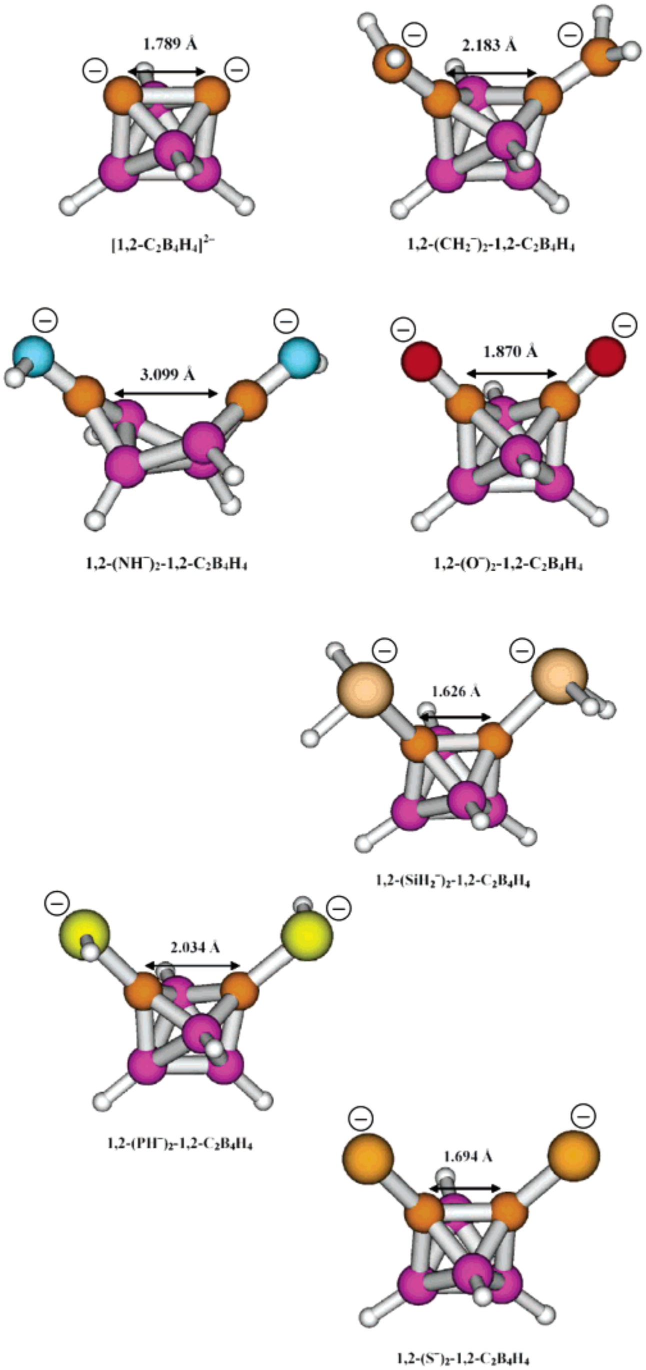


Figure 6. B3LYP/6-31G* optimized geometries and $C_c\cdots C_c$ distances (Å) of dianions obtained by formal proton abstraction from each R group in octahedral *o*-carboranes 1,2-$(R^-)_2$-1,2-$C_2B_4H_4$ ($R^- = e^-$, CH_2^-, NH^-, O^-, SiH_2^-, PH^-, S^-).

There also are only small increases in the central C⋯C distances of syn-*n*-butandiyl, *syn*-1,2-diaminoethane, and 1,2-*cis*-diaminoethene dianions with 1,4- and (*N*,*N*′)-proton abstraction (0.02 Å, 0.07 Å, and 0.05 Å, respectively). The central

Table 2. Icosahedral and Octahedral Carborane Dianions: Computed (B3LYP/6-31G*) $C_c \cdots C_c$ Distances (Å), Nature of the Critical Point (CP) between C_c's (BCP, Bond Critical Point; RCP, Ring Critical Point), Wiberg $C_c \cdots C_c$ Bond Indices (WBI), and Topological Properties of the Density at Bond Critical Points along $C_c \cdots C_c$ − Density $\rho(r_c)$ (e Å^{-3}) and $L(r_c) = -\nabla^2\rho(r_c)$ (e Å^{-5})[c]

icosahedral	$C_c \cdots C_c$	CP	WBI	$\rho(r_c)$	$L(r_c)$	octahedral	$C_c \cdots C_c$	CP	WBI	$\rho(r_c)$	$L(r_c)$
$R^- = e^-$	1.823	BCP	0.59	0.85	−0.72	$R^- = e^-$	1.789	BCP	0.67	0.95	−0.96
$R^- = CH_2^-$	2.638	RCP	0.02	0.19	−2.41	$R^- = CH_2^-$	2.183	RCP	0.12	0.53	−5.45
$R^- = NH^-$	2.473	RCP	0.05	0.27	−2.89	$R^- = NH^-$	3.099		0.02		
$R^- = O^-$	2.124	RCP	0.21	0.52	−2.89	$R^- = O^-$	1.870	BCP	0.40	0.79	−2.60
$R^- = SiH_2^-$	2.040	RCP	0.34	0.59	−2.70	$R^- = SiH_2^-$	1.626	BCP	0.79	1.26	3.01
$R^- = PH^-$	2.330	RCP	0.09	0.43	−3.59	$R^- = PH^-$	2.034	RCP	0.27	0.63	−4.68
$R^- = S^-$	2.196	RCP	0.18	0.48	−3.28	$R^- = S^-$	1.694	BCP	0.64	1.09	0.82

dianion	$C_c \cdots C_c$	CP	WBI	$\rho(r_c)$	$L(r_c)$
(a)	1.556	BCP	1.00	1.60	12.55
(b)	1.611	BCP	0.92	1.47	10.28

[a] (*syn-n*-Butane − $2H^+)^{2-}$. [b] (*syn*-1,2-diaminoethane − $2H^+)^{2-}$. [c] Data for the *syn-n*-butane, *syn*-1,2-diaminoethane, and 1,2-*cis*-diaminoethene dianions are included for comparison.

CC distances in the three acyclic dianions are much shorter than those in the icosahedral and octahedral carborane dianions. Thus, comparison of the dianion of *syn-n*-butane with 1,2-$(CH_2^-)_2$-1,2-$C_2B_{10}H_{10}$ and 1,2-$(CH_2^-)_2$-1,2-$C_2B_4H_4$ show a lengthening of 1.09 Å and 0.63 Å from hydrocarbon to icosahedral and octahedral *o*-carborane dianions, respectively.

3.6. Atoms-in-Molecules Description of the C−C Bonding. The $C_c \cdots C_c$ distances of many octahedral and icosahedral *o*-carboranes vary considerably depending on the α-substituent. We examine the bonding in this unusual "long CC bond" series further by computing the topological properties of the electron density using Bader's "atoms in molecules" theory (AIM).[30]

Saddle points associated with the total electron density ρ are known as "critical points." These are distinguished according to the signs of the eigenvalues of the Hessian of ρ. A *bond* critical point (BCP) is characterized by two negative eigenvalues (λ_1, λ_2) and one positive eigenvalue (λ_3) of the Hessian and is often denoted (3,−1). The values of $\rho(r)$ at the bond critical points of carbon−carbon bonds parallel the bond strengths and have been used to determine bond orders.[31] A *ring* critical point (RCP), denoted (3,+1), has two positive eigenvalues and one negative eigenvalue (see ref 32 for a concise introduction). The sign of the Laplacian, $\nabla^2\rho(r)$, indicates whether the charge density is locally depleted [$L(r) = -\nabla^2\rho(r) < 0$] or locally concentrated [$L(r) = -\nabla^2\rho(r) > 0$]; its value at a bond critical point characterizes the type of interaction ('closed shell' or 'shared' respectively).[30,32]

Table 1 gathers together the densities and Laplacians at the BCPs found between the two C_c atoms in the neutral species computed at B3LYP/6-31G*//B3LYP/6-31G* (results with the 6-311++G** basis set are very similar and show the same trends).

Bond critical points exist between the C_c atoms in all the neutral icosahedral carboranes. As shown by the almost linear relationship in Figure 7, longer $C_c \cdots C_c$ distances are associated with lower electron densities at the BCPs. Very similar plots have been reported for C−C bonds in other molecules, such as linearly annelated arenes,[33] where, of course, the bond length range was much smaller. All neutral icosahedral molecules (except 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$) have positive $L(r)$ values, indicating that $\rho(r_c)$ is locally concentrated, as it is with a wide range of C−C bonds in organic molecules.[31] The exception, 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$, with the longest $C_c \cdots C_c$ (1.860 Å) of all the neutrals, has $L(r) < 0$ at the BCP. Here the density is locally depleted at r_c, which together with the magnitude of $L(r)$ suggests a so-called "intermediate interaction", as in F_2 or in BeH.[32] $C_c \cdots C_c$ BCPs with positive $L(r)$ exist in all the neutral octahedral carboranes; the electron densities at these BCPs lie on the same correlation line in Figure 7 as that for the icosahedral molecules.

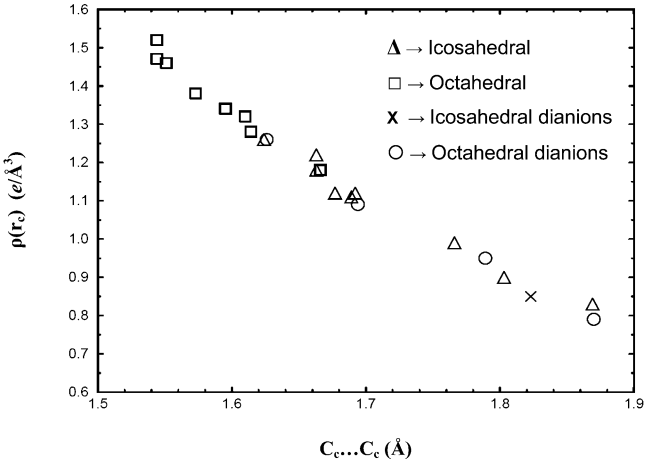


Figure 7. Density at the bond critical point $\rho(r_c)$ (e Å^3) versus $C_c \cdots C_c$ distances (Å) for the neutral icosahedral and octahedral *o*-carboranes included in this work.

The topological properties of the dianion electron densities are collected in Table 2: $C_c \cdots C_c$ distances, $\rho(r_c)$ and $L(r)$. *Only one* of the icosahedral dianions has a $C_c \cdots C_c$ BCP (the parent 1,2-$C_2B_{10}H_{10}^{2-}$, which has the shortest $C_c \cdots C_c$ distance). The *octahedral* dianions with BCPs are $(1,2\text{-}C_2B_4H_4)^{2-}$, 1,2-$(O^-)_2$-1,2-$C_2B_4H_4$, 1,2-$(SiH_2^-)_2$-1,2-$C_2B_4H_4$, and 1,2-$(S^-)_2$-1,2-$C_2B_4H_4$. Only those systems where $C_c \cdots C_c < 1.9$ Å have a bond critical point between the carbon atoms. It is striking that the electron densities at these BCPs lie on the same line as that for the neutrals (Figure 7). The values of $L(r)$ in Tables 1 and 2 taken together indicate that $L(r)$ changes sign when $C_c \cdots C_c > \sim 1.77$ Å, suggesting some change in the character of the bond at this separation.

We investigated the critical points in the carboranes in more detail. Where BCPs exist we have also found two (3,+1) RCPs

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(30) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

(31) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

(32) For a short introduction, see: Popelier, P. *Atoms in Molecules: An Introduction*; Prentice Hall: Harlow, U.K., 2000.

(33) Wiberg, K. B. *J. Org. Chem.* **1997**, *62*, 5720.

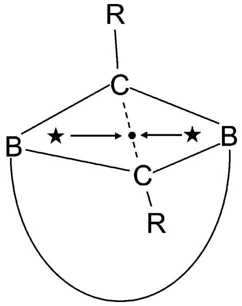

Figure 8. Schematic plot of the bond and ring critical points in the *o*-carboranes (see text). The stars indicate ring critical points (RCP), and the dot denotes the bond critical point (BCP) between the C_c's.

(rather than (3,−1) BCPs) located in the B−C−C rings on a line perpendicular to the C−C bond, as shown by the two stars in Figure 8. Where BCPs exist and substituent changes increase the $C_c \cdots C_c$ separation, these RCPs move toward the BCP as shown by the arrows in Figure 8. The carbon−carbon bonds in these long bond molecules have large ellipticities ϵ ($\epsilon = (\lambda_1/\lambda_2) - 1)$); high values of ϵ have been associated with the susceptibility of a bond to rupture, as in the propellanes.[31]

All the systems with $C_c \cdots C_c > 1.9$ Å lack bond critical points (BCPs) between the two cage carbon atoms C_c's. Instead, there is a *single* (3,+1) ring critical point (RCP) lying between the two carbon atoms C_c's, suggesting a change in the nature of the $C_c \cdots C_c$ interaction at this distance, which characterizes the resulting opened or partially opened four-membered C−B−C−B ring (cf. the topological analysis of *closo*-1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3, H[34]). No such C−B−C−B RCP was located in 1,2-$(NH^-)_2$-1,2-$C_2B_4H_4$; instead, as suggested by the structure of this "open" molecule (with the largest $C_c \cdots C_c$, Figure 6), there are two equivalent RCPs associated with the two C−B−B−B rings.

4. Discussion

Chemists use various operational criteria to discuss the nature of a CC bond. They note that covalent bonds involving carbon not only bind other elements with significantly large energies but also have directional character. Chemists visualize this as arising from the favorable overlap of the orbitals of the constituent atoms, which implies that these orbitals must point toward each other to a significant extent. CC distances alone need not be decisive. For example, the 2.0 Å separation of the 1,3-carbons in cyclobutane and the 1.8 Å interbridgehead carbon distance in bicyclo[1.1.1]pentane are relatively short, but do not imply "bonds" as no "free valences" are present. The attractive 2.5 Å CC separations in branched hydrocarbons, which contribute to their greater stability than *n*-alkanes, also do not constitute "CC bonds". Such van der Waals attractive CC interactions at longer distances are not considered to be "bonds", since their energies are quite small and pronounced directional character is lacking. It seems reasonable to expect that "long CC bonds" would have appreciable bond energies arbitrarily chosen to be, e.g., in the 20 to 25 kcal/mol range, so that the fragments do not separate readily at room temperature.

However, this working definition does not solve the problem, since the "long CC" distances discussed in this paper are present in "supported" systems, i.e., in which other parts of the molecule (the cage) help to hold the separated carbon atoms together and decrease the entropy loss on bond dissociation. The determination of the "CC bond energy" is especially difficult in such cases. Instead, recourse is usually made to theoretical methods which give "bond orders" or "bond indices," such as those by Pauling, Wiberg, Bader, and Fulton. But there is no agreement for benzene, where these methods give CC bond orders ranging from about 1.4 to 1.7! These methods have neither been devised for nor systematically tested in "long bond" situations. Thus, the CC distance−bond order relationship of Pauling cannot be used reliably in long CC bond systems, where a 2.0 Å separation might be antibonding (as in cyclobutane) or bonding (as in the molecules we are considering, see below).

We have shown that the CC bond lengths in icosahedral and octahedral *o*-carboranes vary substantially with the nature of the carbon substituents. NH_2 and SH disubstituted icosahedral and octahedral *o*-carboranes have the longest $C_c \cdots C_c$ distances for neutral, first-row and second-row substituents, respectively. In the corresponding dianions, the elongation is even more pronounced. To what extent does the carbon−carbon bond break? To what extent is the closo cage transformed into a partially opened nido system? The simple Pauling bond-order relationship,[35] based only on the carbon−carbon distance, gives an appreciable $C_c \cdots C_c$ bond order of 0.62 for 1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$ ($R = 1.860$ Å); even for 1,2-$(NH^-)_2$-1,2-$C_2B_{10}H_{10}$ ($R = 2.473$ Å), the Pauling bond order is 0.26.[36]

Another crude way of estimating bond orders of partial CC bonds can be based on the energy curve for the dissociation of ethane into two methyl radicals (Scheme 1 and Table 1, Stahl et al.[10]). Stretching ethane to a 1.9 Å CC distance decreases the bond energy by only 21.9 kcal/mol, corresponding to an energy-based "bond order" of 0.76. Even at a CC separation of 2.5 Å, the energy-based "bond order" (0.25; almost identical with the Pauling value!) is still significant and corresponds to a residual bond energy of 22.5 kcal mol^{-1}.

The smallest $C_c \cdots C_c$ Wiberg bond indexes (WBI)[37] for the neutrals (Table 1) are exhibited by R = NH_2 for both the icosahedral (0.44) and octahedral (0.64) cages; these correspond to the long $C_c \cdots C_c$ distances. In keeping with their shorter carbon−carbon distances, the $C_c \cdots C_c$ WBIs of octahedral cages are larger than in their icosahedral analogues. Some dianion cages are open or almost open (Figures 5 and 6; Table 2); this is reflected in the negligible WBIs for $R^- = \{CH_2^-, NH^-, PH^-\}$ in icosahedral and $R^- = \{NH^-, CH_2^-\}$ in octahedral carboranes.

AIM theory defines a bond order in terms of the electron density at the bond critical point (BCP).[30] These Bader indices, computed as in ref 31 for those systems with a BCP, are also listed in Tables 1 and 2. Calculated Wiberg and Bader bond indices for the neutral molecules are compared in Figure 9, plotted as a function of the CC bond length. In general, the values of Wiberg and Bader indices are close; some of the second row substituents show the largest differences. Nevertheless the topological analysis in the previous section suggests a significant change in the $C_c \cdots C_c$ interaction at distances greater than ~1.9 Å, which corresponds to Wiberg indices below ~0.4.

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(34) Subramanian, G.; Schleyer, P. v. R.; Dransfeld, A. *Organometallics* **1998**, *17*, 1634.

(35) Pauling, L. *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960

(36) $\exp\{-(d - d_0)/\alpha\}$, with $\alpha = 0.70$ Å and $d_0 = 1.530$ Å, the computed C−C distance in ethane (B3LYP/6-31G*); d is the $C_c \cdots C_c$ distance in the carboranes (//B3LYP/6-31G*).

(37) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1090.

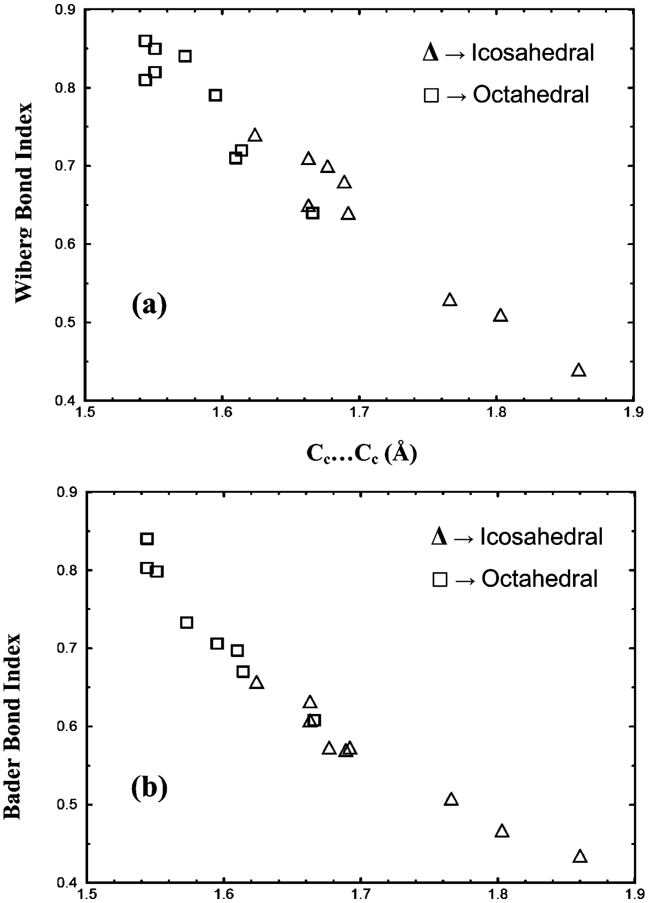

Figure 9. (a) Wiberg and (b) Bader bond indices versus $C_c\cdots C_c$ distances (Å) for the neutral icosahedral and octahedral *o*-carboranes considered in this work.

It is worth noting that the computed WBIs of the acyclic ethane and *syn*-1,2-diaminoethane (Table 1; see section 3.5) lie near above an extrapolated correlation line for the carboranes, as do the calculated BCP densities,[38] and thus provide CC single bond "anchors" for the large variation in carbon−carbon separations examined.

5. Conclusions

The CC bond lengths in icosahedral and octahedral *o*-carboranes vary substantially with the nature of the carbon substituents. NH_2 and SH disubstituted icosahedral and octahedral *o*-carboranes have the longest $C_c\cdots C_c$ distances for neutral, first-row, and second-row substituents, respectively. The elongations are even more pronounced in the corresponding dianions. The $C_c\cdots C_c$ distances can be "tuned" over a wide range, often without affecting the geometry of the remainder of the cluster significantly.

We have discussed the $C_c\cdots C_c$ bonding in these systems using a variety of bond indices and also by topological analyses. Bond critical points are found in all the *o*-carboranes and dianions with $C_c\cdots C_c$'s less than ~1.9 Å. This distance corresponds to a Wiberg bond index of about 0.4. It is clear that the nature of the carbon−carbon interactions here needs further examination, and this should also help in the development of new bond order measures specifically for such long-bond situations.

The range in CC bond lengths arises from the weakening of the cross bond of a bicyclobutane-type BCBC ring system due to the influence of the substituents. The deltahedral bicyclobutane system converts into a monocyclic four membered ring with a relatively short cross-ring distance. In the most extreme species we have described, the C$\cdots$C distance is extended even further by a more extensive cage opening. As the CC distance increases gradually, the point at which the CC bond can be said to "break" depends on the metric used to define "bonding".

New opportunities afforded by exohedral multiple bonding in boranes have also recently been highlighted by Balakrishnarajan and Hoffmann[39] who examined structural changes in closo borane cages B_n ($n = 6,7,10,12$) with exo NH_2, S^-, and O^- units (thus with available lone pairs). They have drawn interesting comparisons with aromatic ring redox chemistry. We hope that our study will stimulate experimental work on related carborane chemistry, shed further light into the rich chemistry of these systems, and further enhance interest in long CC bonds in molecules.

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Supporting Information Available: Symmetry-unique $C_c\cdots C_c$, C_c-B, and $B-B$ distance differences (Å) for all carboranes relative to the parent compounds 1,2-$C_2B_nH_n$ ($n = 10$ and $n = 4$ for icosahedral and octahedral *o*-carboranes, respectively) for all *o*-carboranes (neutrals and dianions) included in this work computed at the B3LYP/6-31G*//B3LYP/6-31G* level of theory. Also included are the $C_c\cdots C_c$ distances (Å) and topological properties of the density at bond critical points: $\rho(r_c)$ (e Å^{-3}) and the Laplacians of the density $L(r_c) = -\nabla^2\rho(r_c)$ (e Å^{-5}) computed at the MP2/6-31G*//MP2/6-31G* level of theory; all neutral and dianions were also optimized at the MP2/6-31G*//MP2/6-31G* level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Not shown in Figures 9 and 7, respectively.
(39) Balakrishnarajan, M. M.; Hoffmann, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 3777; **2004**, *43*, 27.