

Modulation of the C–C distance in disubstituted 1,2- R_2 -*o*-carboranes. Crystal structure of *closo* 1,2-(SPh)₂-1,2- $C_2B_{10}H_{10}$

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Received 30 July 2001; accepted 6 June 2002

Abstract

1,2- C_c -substituted *o*-carboranes, where C_c represents the cluster carbon atoms, display a range of experimental/computed $C_c \cdots C_c$ distances from 1.629/1.624 Å for the unsubstituted parent compound 1,2- $C_2B_{10}H_{12}$ (**1**) to 1.798/1.818 Å for 1,2-(SPh)₂-1,2- $C_2B_{10}H_{10}$ (**5**)¹ or 1.858(5)/1.826(5) for 1,2- μ -SCH₂(CH₂OCH₂)₂CH₂S-1,2- $C_2B_{10}H_{10}$ (**7**). Different $C_c \cdots C_c$ distances can be achieved by modifying the substituents on the carbon of the cluster compound. The crystal structure of a new disubstituted *o*-carborane 1,2-(SPh)₂-1,2- $C_2B_{10}H_{10}$ (**5**) was elucidated by single crystal X-ray diffraction. Purely alkyl substituents alter the $C_c \cdots C_c$ distance of the parent compound very little, which implies that steric effects, although relevant, are not the major cause of the lengthening. In contrast, substituents with lone pairs alter the $C_c \cdots C_c$ distance substantially. Our calculations suggest that the cause of the elongation is the transfer of electron density from the available lone pairs on the substituents to the Ψ^* low-lying virtual orbitals mainly distributed around C_c , producing a decrease in the $C_c \cdots C_c$ bond order and, thereby, an increase in the $C_c \cdots C_c$ distance. A Bader analysis shows that the electron density at the bond-critical point, which is found at the mid-point of the $C_c \cdots C_c$ distance, decreases considerably with the presence of lone pairs of the sulfur atoms bound to the C_c atoms of the carborane cage. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bond-critical point; Bond modulation, *closo*-carboranes

1. Introduction

The single, double, and triple bond distances are well defined in conventional organic compounds although important exceptions exist. Relevant examples are cationic norbornenyl derivatives, on which extensive theoretical studies have been conducted to evaluate the existence of nonclassical bonding. As an example, in (C₅Me₅)₂Sm(O₂C₇Me₅), in which the seven carbon atoms in O₂C₇Me₅ adopt a norbornadiene structure, [1] the C7–C2 distance equals 1.876 Å much longer than two times the C single bond radii (1.53 Å) [2]. Besides

isolated cases, the possibility to tune up the C–C distance in conventional organic compounds is rare. Cluster boron chemistry, in particular the *o*-carboranes, provides the possibility to modulate the C–C distance in an almost continuous way within the same family of compounds. The $C_c \cdots C_c$ distance in metallacarborane cluster derivatives of [7,8- $C_2B_9H_{11}$]^{2–} can be regarded as highly plastic. Thus, examples of $C_c \cdots C_c$ elongation have been found with different metal ions, such as Ru(II), [3]; Rh(I), [4]; Rh(III), [5]; Mo (IV), [6] or Co(III) [7]. In conventional cluster terminology, species which experience a substantial $C_c \cdots C_c$ elongation are named pseudocloso [8]. Although steric effects of bulky substituents on C_c atoms have been described to be responsible for $C_c \cdots C_c$ elongation [9], other data from less bulky substituents [10] suggest that an electronic contribution may also be relevant. In a recent paper

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¹ A longer $C_c \cdots C_c$ computed distance has been found for 1,2-(SCH₃)₂-1,2- $C_2B_{10}H_{10}$ (**6**) but no experimental data are available.

concerning mixed sandwich pyrrolyl–dicarbollide cobalt complexes we have shown that electronic effects appear to be fundamental in $C_c \cdots C_c$ modulation.

The *closo* character of mixed sandwich pyrrolyl–dicarbollide complexes and the particularly equal $C_c \cdots C_c$ distance, 1.64 Å, in both the parent *closo* [3-Co(η^5 -NC₄H₄)-1,2-C₂B₉H₁₁] and *o*-carborane, led us to hypothesize that the same explanation concerning $C_c \cdots C_c$ modulation was valid for [3-Co(η^5 -NC₄H₄)-1,2-C₂B₉H₁₁] and *o*-carborane derivatives. To this aim, we decided to study the electronic influence of substituents on C_c atoms on the $C_c \cdots C_c$ distance in the latter. As with the mixed cobalt complexes, structural data from X-ray diffraction analysis were compared with calculated distances obtained with theoretical methods based on density functional theory. The good agreement between experimental and calculated $C_c \cdots C_c$ distances allowed us to explain the reasons of $C_c \cdots C_c$ elongation in terms of electronic effects based on theoretical calculations.

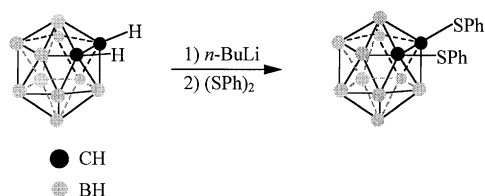
2. Results and discussion

In order to study the electronic influence of *exo*-cluster carbon substituents on the $C_c \cdots C_c$ distance, a series of disubstituted 1,2-R₂-1,2-C₂B₁₀H₁₀ (R = H, (1); Et, (2); Ph, (3); SH, (4); SPh, (5) and SMe, (6)) *o*-carborane derivatives was chosen.

The synthesis of 1,2-(SPh)₂-1,2-C₂B₁₀H₁₀ was successfully achieved by reacting *o*-carborane, *n*-butyllithium and phenyldisulphide in the ratio 1:2:2. Scheme 1 shows the synthesis reaction. This generated compound was characterized by elemental analysis and NMR spectroscopies and is in agreement with the proposed formula.

Good quality crystals for X-ray diffraction studies were grown by slow evaporation of a solution of **5** in CH₂Cl₂–C₆H₁₄ solutions. Crystallographic data and selected bond parameters for **5** are listed in Tables 1 and 2. Fig. 1 shows a drawing of the molecule with the labeling system in. The structure is formed of discrete molecules having crystallographic *C*₂ symmetry with the two fold axis going through the mid-points of C(1)–C(1)^a and B(6)–B(6)^a bonds (*a* = $-x+1, y, -z+1/2$).

The S–C bond lengths are equal within experimental errors and the angles around C(1) vary from 112.8(1) to 125.4(1)°. As a result the S atom is moved away from its



Scheme 1. Reaction proposed for the formation of **5**.

Table 1

Crystallographic data and structure refinement details for compound **5**

Chemical formula	C ₁₄ H ₂₀ B ₁₀ S ₂
Formula weight	360.52
Temperature (K)	294(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	20.0769(16)
<i>b</i> (Å)	8.7908(13)
<i>c</i> (Å)	11.7143(12)
β (°)	111.127(7)
Volume (Å ³)	1928.5(4)
<i>Z</i>	4
ρ (g cm ^{−3})	1.242
Absorption coefficient (mm ^{−1})	0.270
<i>F</i> (000)	744
Index ranges	$0 \leq h \leq 23, 0 \leq k \leq 10, -13 \leq l \leq 13$
Reflections collected/unique	1748/1697 [<i>R</i> _{int} = 0.014]
Reflections observed	1425
[<i>I</i> > 2σ(<i>I</i>)]	
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1697/0/159
Goodness-of-fit on <i>F</i> ²	1.060
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0851
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0447, <i>wR</i> ₂ = 0.0900
$\Delta\rho$ (e Å ^{−3})	0.206, −0.201

Table 2

Selected bond lengths (Å) and angles (°) for compound **5**

Bond lengths			
S–C(1)	1.776(2)	C(1)–B(2)	1.725(2)
S–C(7)	1.783(2)	C(1)–B(3)	1.700(2)
C(1)–C(1) ^a	1.799(3)	C(1)–B(4)	1.692(3)
Bond angles			
C(1)–S–C(7)	104.66(8)	S–C(1)–B(3)	119.7(1)
S–C(1)–C(1) ^a	118.09(5)	S–C(1)–B(4)	125.4(1)
S–C(1)–B(2)	121.4(1)	S–C(7)–C(8)	120.2(2)
S–C(1)–B(2) ^a	112.8(1)	S–C(7)–C(12)	119.5(2)
S–C(1)–C(1) ^a –S ^a	10.6(2)	C(1)–S–C(7)–C(12)	95.4(2)
C(1)–S–C(7)–C(8)	−89.5(2)	B(2) ^a –C(1)–S–C(7)	160.6(1)

^aEquivalent position $-x+1, y, -z+1/2$.

expected position towards the B(2)^a atom, thus decreasing the S–C(1)–B(2)^a angle and opening the S–C(1)–C(1)^a, S–C(1)–B(2) and S–C(1)–B(4) angles. This operation also increases the distance between the phenyl group and the carborane cage, and opens the S^a–C(1)^a–C(1)–S torsion angle to 10.6(2)°.

The S $\cdots$ S^a distance of 3.483(1) Å is only ca. 0.12 Å shorter than the sum of the corresponding van der Waals radii, [11] and the free electron pairs of the S atoms are orientated away from each other to minimize repulsions.

Comparison of **5** with 1,2-dithia-1,2-dicarba-*closo*-dodecaboranes incorporating a macrocyclic fragment chain between the S atoms, 1,2-(1',10'-dithia-4',7'-diox-

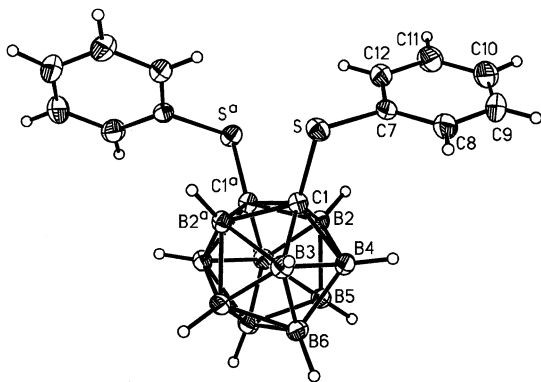


Fig. 1. ORTEP plot of 1,2-(SPh)₂-1,2-C₂B₁₀H₁₀ (**5**) and the atomic numbering scheme. Displacement ellipsoids are shown at 30% probability levels, except for H atoms which are drawn as small circles of arbitrary radii.

adecane-1',10'-diyl)-1,2-dicarba-*closo*-dodecaborane (**7**) [12] and 1,2-(1',7'-dithia-4'-oxaheptane-1',7'-diyl)-1,2-dicarba-*closo*-dodecaborane (**8**) [13] reveals some minor differences. The C(1)–C(1)^a or C_c···C_c distance in **5** is quite short, 1.799(3) Å, being significantly shorter than those in the two non-equivalent molecules of 1,2-(1',10'-dithia-4',7'-dioxadecane-1',10'-diyl)-1,2-dicarba-*closo*-dodecaborane (1.858(5) and 1.826(5) Å). The value of the C_c···C_c bond in 1,2-(1',7'-dithia-4'-oxaheptane-1',7'-diyl)-1,2-dicarba-*closo*-dodecaborane is 1.816 (6) Å and, although longer than in **5**, the difference is not as significant. In 2-methyl-1-sulfido-1,2-dicarba-*closo*-dodecaborane anion [14] the distance is 1.792(5) Å. Therefore, the contribution of methyl and sulfido substituents to the lengthening of C_c···C_c bond is comparable to that of two SPh groups.

The computed and experimental C_c···C_c distances of compounds **1–6** are displayed in Table 3. As it is shown there, binding of ethyl groups to C_c does not change significantly the C_c···C_c distance. The presence of an electron-withdrawing and bulkier group, such as phenyl in **3** does increase this distance more. Theory and experiment does deviate about 0.03 Å in giving the C_c···C_c distance. However, the most striking results

from Table 3 are the large C_c···C_c distances in thio-C_c-substituted *o*-carboranes **4–6**. Moreover, the phenyl group in **5** produces a similar effect on the C_c···C_c distance to that of the simple thiol. Another result to be discussed is the longer C_c···C_c distance in **6** than in **5**: a methyl group bound to sulfur provides a longer C_c···C_c distance than a phenyl group. As we will show below, not only steric but electronic effects must be taken into account in order to understand these results. Leaving aside the packing forces, we consider that three factors may influence the C_c···C_c distance: (i) steric (repulsive) effects due to substituting one or both of the contiguous carbon atoms with those containing bulky groups or those containing lone pairs, (ii) an electronic effect due to the electronegativity differences between hydrogen atoms and substituting groups and (iii) a π -electronic back-donation from the substituting groups into Ψ^* orbitals of the cluster, mostly sited on the C_c···C_c region. Steric crowding would produce repulsive forces that would tend to move the contiguous carbon atoms apart; an enhanced electronegativity of the substituent would deplete electron density between C_c(1) and C_c(2) and would lengthen the distance, and π -electronic back-donation to the LUMO (Ψ^*) orbital, mostly sited on the two carbon atoms, would weaken the C_c···C_c bond order. It is then apparent that although influential, the steric crowding or lone pair–lone pair repulsive forces is not sufficient to explain the C_c···C_c lengthening in **4–6**. As a consequence, electronic factors should be also considered, as we pointed out earlier [10] when it was proposed that the C_c···C_c distances could be estimated with the empirical equation: $d = d_0 + \sum a_i + \sum S_i$, where d is the C_c···C_c distance in the *o*-carborane derivative, d_0 the C_c···C_c distance in the *o*-carborane, a_i the summed electronic contributions and S_i the summed steric contributions.

The –SMe and –SPh substituents were selected as suitable probes to determine the major factors influencing the C_c···C_c lengthening. In fact, since –SPh is larger than –SMe it should facilitate C_c···C_c elongation for reasons of steric crowding. Furthermore, –SPh is

Table 3

Experimental (where available), B3LYP/6-31G^a computed C_c···C_c distances (Å) in ethane and compounds **1–6**, and electron density ($e \text{ Å}^{-3}$) at the BCP at the mid-point between the carbon atoms of the cluster, also computed at the B3LYP/6-31G^a level of theory for compounds ethane, **1** and **6**

Compound	Experimental C _c –C _c distance	Computed C _c –C _c distance	$\rho(r_{\text{BCP}})$
CH ₃ –CH ₃	1.525 [20]	1.530	1.64
1,2-C ₂ B ₁₀ H ₁₂ (1)	1.629 [21]	1.624	1.26
1,2-Et ₂ -1,2-C ₂ B ₁₀ H ₁₀ (2)		1.687	
1,2-Ph ₂ -1,2-C ₂ B ₁₀ H ₁₀ (3)	1.733(4)/1.720(4) ^a [22]	1.764	
1,2-(SH) ₂ -1,2-C ₂ B ₁₀ H ₁₀ (4)		1.803	
1,2-(SPh) ₂ -1,2-C ₂ B ₁₀ H ₁₀ (5)	1.798(3)	1.818	
1,2-(SMe) ₂ -1,2-C ₂ B ₁₀ H ₁₀ (6)		1.836	0.85
1,2- μ -SCH ₂ (CH ₂ OCH ₂) ₂ CH ₂ S-1,2-C ₂ B ₁₀ H ₁₀ (7)	1.858(5)/1.826(5) ^a [12]	1.900	

^a Two molecules in the asymmetric unit.

also more electron-withdrawing than $-\text{SMe}$, therefore, its stronger capability for electron polarization or greater electron-depletion in the $\text{C}_c \cdots \text{C}_c$ connectivity should promote $\text{C}_c \cdots \text{C}_c$ elongation.

If we restrict our discussion to the structural data obtained by X-ray diffraction we observe that the thioether species **5** (see Table 3) have a long $\text{C}_c \cdots \text{C}_c$ distance, almost 20% longer than that of a single $\text{C}-\text{C}$ bond. This raises some doubts about whether a significant degree of bonding exists at all. However, as seen in Table 3, a continuous range of $\text{C}_c \cdots \text{C}_c$ distances is observed, ranging from 1.62 to 1.84 Å, indicating that a smooth elongation and not an abrupt break takes place. This implies that the $\text{C}_c \cdots \text{C}_c$ is a bond of gradually decreasing strength. As noted above, our interpretation is that steric crowding, or lone pair–lone pair repulsion, although partly responsible for the elongation, are not the major factor responsible for the weakening of the bond. Electronic effects are very relevant, too. We go on, now, to discuss on electronic effects of the H/H (**4**), SPh/SPh (**5**) and Sme/SMe (**6**) substituents on the $\text{C}_c \cdots \text{C}_c$ distance. The Pauling electronegativity of sulfur (2.5) is identical with that of carbon. However, the inductive character can be modulated by substituents on S. The methyl group will make the sulfur atom less electron-withdrawing than the phenyl group. If electronegativity, or electron polarization towards sulfur, was the reason for the $\text{C}_c \cdots \text{C}_c$ elongation, the SPh/SPh substituents should produce the longer $\text{C}_c \cdots \text{C}_c$ distance, due to electron density depletion. This conclusion is in contradiction with our calculations, since the longer distance is found with Sme/SMe (**6**). In earlier work, the $\text{C}_c \cdots \text{C}_c$ elongation produced by phosphorus in 1-PPh₂-2-Me-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ was interpreted in terms of overlap of the tangential *p* orbitals in the cluster with *p* or *d*-orbitals on the phosphorus [15]. At that time, we did not pursue this explanation. Our interpretation of the $\text{C}_c \cdots \text{C}_c$ distance in the present series of 1,2- C_c -substituted *o*-carboranes is that π -back donation from an occupied orbital on sulfur, the lone pair, is partially transferred to the LUMO (Ψ^*) on the cluster with important orbital contributions for the carbon atoms C_c . Thus the LUMO antibonding orbital on the carbon atoms is partially filled, decreasing the $\text{C}_c \cdots \text{C}_c$ bond order. This hypothesis is supported by our calculations performed on compounds **1–6**. Fig. 2 shows the HOMO of compound (**1**) calculated at the B3LYP/6-31G* level of theory. As can be seen, no nodes exist in the $\text{S}-\text{C}_c$ connectivity, although there is one between the two C_c 's. This can be interpreted considering the interaction of two orbitals coming from different fragments: the HOMO on the S,S fragment that combines with the LUMO on the unsubstituted *o*-carborane (**1**) to form two new molecular orbitals (see Fig. 3). One of them, the occupied one corresponding to the HOMO in **5** has an important original LUMO contribution, that is $\text{C}-\text{C}$

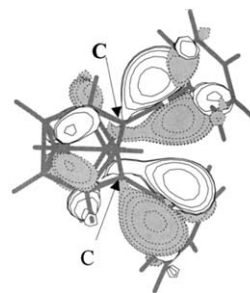


Fig. 2. HOMO of compound **1** calculated at the B3LYP/6-31G* level of theory.

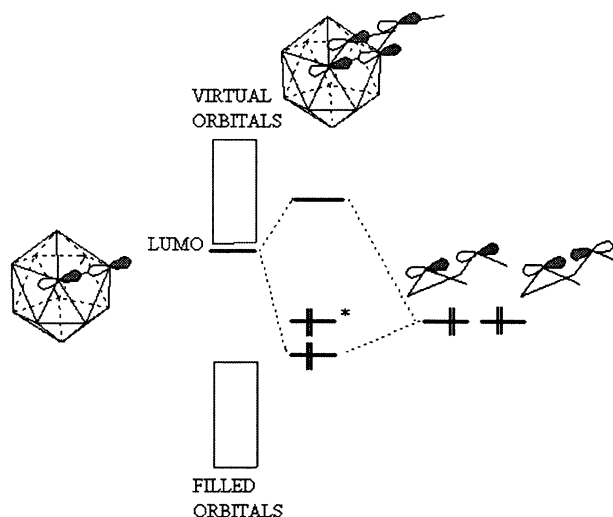


Fig. 3. Schematic energy level diagram for combination of LUMO of compound **1** and HOMO of SR groups in **4–6**.

antibonding (Fig. 4). This transfer of electronic density into the Ψ^* orbitals on $\text{C}_c(1)$ and $\text{C}_c(2)$ is one of the causes of bond lengthening when hydrogen atoms are replaced by groups with lone pairs. The HOMO is then the result of mixing one filled orbital with one empty one, the LUMO, and the global result of this HOMO is a partial transfer of electron density into the $\text{C}-\text{C}$ antibonding orbital fragment [16]. As mentioned above, the extent of $\text{C}_c \cdots \text{C}_c$ bonding at the distances exhibited by the compounds studied in this work is not clear. A

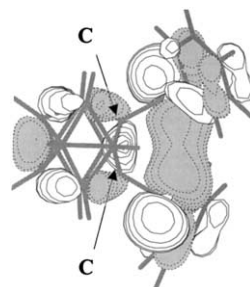


Fig. 4. NHOMO of compound **5** calculated at the B3LYP/6-31G* level of theory showing that $\text{S}-\text{S}$ orbitals overlap.

Bader analysis [17] shows that there is a bond critical point (BCP) at the mid-point of $C_c \cdots C_c$ in all compounds. At the BCP, the electron density is a maximum in the plane defined by the two vectors of negative curvature of the density, and a minimum along the axis of positive curvature—in this case the $C_c \cdots C_c$ axis. Fig. 5 shows a contour map of electron density for compounds **1** and **6** in the plane perpendicular to the $C_c \cdots C_c$ line. The BCP passes through at the mid-point of this line, where the maximum of the density is depicted as the core of the contour density circles at the mid-left site of the contour maps.

In order to estimate the ‘degree’ of bonding in these compounds we chose ethane as a model for a single C–C bond, and compounds **1**, **2** and **6** for comparative purposes. Table 3 shows in the last column the electron density at the BCP sited at the mid-point of $C_c \cdots C_c$ in

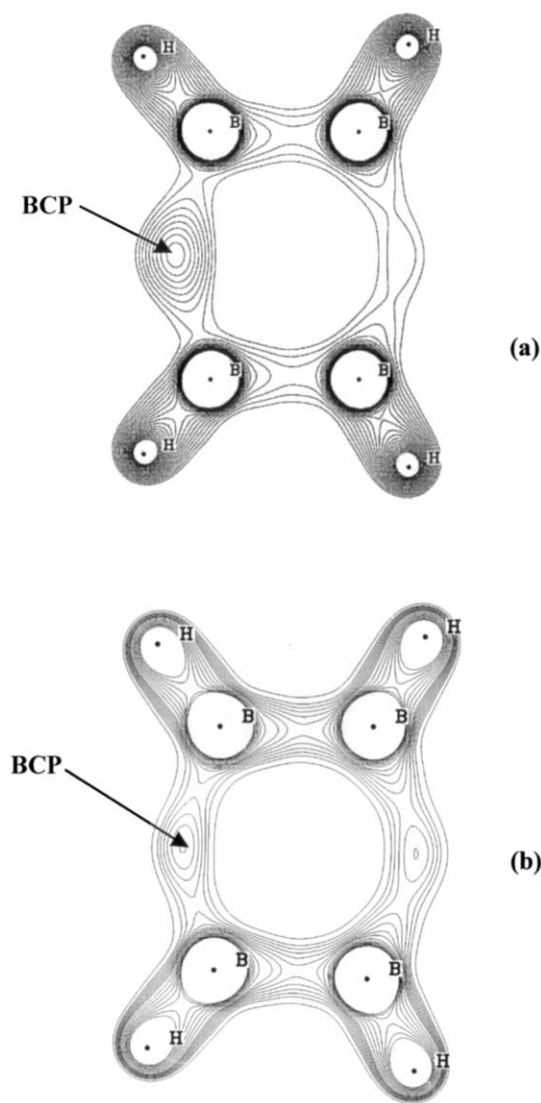


Fig. 5. Contour map of the electron density for compounds **1** (a) and **6** (b) in the plane perpendicular to the $C_c \cdots C_c$ line and containing the BCP at the midpoint between the two carbon atoms.

ethane and compounds **1**, **2** and **6**. According to these results the density at the BCP is 76 and 52% smaller, respectively, in compounds **1** and **6** as compared with ethane. Nevertheless, the density at the BCP is not zero, and therefore, certain extent of $C_c \cdots C_c$ bonding is predicted, depending on the density at the BCP.

3. Conclusion

To summarize, and as it has been shown by the above results, the $C_c \cdots C_c$ distance in 1,2- C_c -substituted *o*-carboranes can be modeled as function of the substituents. Purely alkyl substituents do not substantially alter the $C_c \cdots C_c$ distance of the parent compound, implying that steric effects, although relevant, are not the major cause of the lengthening. In contrast, substituents with lone pairs alter the $C_c \cdots C_c$ distance substantially. This cannot be explained by lone pair–lone pair repulsion or by the effect of electron-polarizing groups. The more plausible explanation is the transfer of electron density from the available lone pairs on the carbon substituents to the Ψ^* orbitals, producing a decrease in the $C_c \cdots C_c$ bond order and, thereby, an increase in the $C_c \cdots C_c$ distance.

4. Experimental

4.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Nicolet 710 FT spectrophotometer, 1H - and $^1H\{^{11}B\}$ -NMR (300.13 MHz), $^{13}C\{^1H\}$ -NMR (75.47 MHz) and ^{11}B -NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B -NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and those for 1H , $^1H\{^{11}B\}$ - and $^{13}C\{^1H\}$ -NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hz.

4.2. Materials

Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. Diethyl ether was distilled from sodium benzophenone prior to use and the rest of the solvents were of reagent grade quality and were used without further purification. Commercial *o*-carborane was sublimed under high vacuum prior use. A 1.4 M solution of *n*-butyllithium in hexane (Fluka), phenylsul-

fide, KCl and MgSO₄ purchased from commercial sources and used as received.

4.3. Synthesis of *closo* 1,2-(SPh)₂-1,2-C₂B₁₀H₁₀ (**5**)

A solution containing diethyl ether (30 ml) and 1,2-dicarba-*closo*-dodecaborane (0.500 g, 3.467 mmol) was cooled to 0 °C during the addition (10 min, dropwise) of *n*-buthyllithium (4.9 ml, 6.9 mmol). After stirring for 30 min at 0 °C, the mixture was left to stand at room temperature (r.t.) for 30 min, then cooled again to 0 °C before adding an diethyl ether solution (10 ml) of phenyldisulphide (1.51 g, 3.47 mmol). The ice-bath was removed and the mixture stirred 30 min at r.t. The ether mixture was washed twice with a solution of KCl in water (50 ml). The organic layer was dried (anhydrous MgSO₄, 24 h), and evaporated to yield the analytically pure white solid, yield 0.95 g (76%). Recrystallization from dichloromethane–*n*-hexane (1/1) gave pale yellow microcrystals. Anal. Calc. for C₁₄H₂₀B₁₀S₂: C, 46.64; H, 5.59; S, 17.79. Found: C, 46.45; H, 5.67; S, 17.50%. IR: ν (cm⁻¹) = 3066 (ν C_{aryl}–H), 2631, 2619, 2590, 2581, 2563 (ν B–H), 1470, 1439, 746, 725, 705, 685, 496 (δ C_{aryl}–H). ¹H-NMR (CDCl₃, 25 °C): δ = 7.76–7.41 (m, H_{aryl}), 3.6–0.5 (br, B–H). ¹H{¹¹B}-NMR (CD₂Cl₂, 25 °C): δ = 7.76–7.41 (m, H_{aryl}, 10H), 2.45 (br s, B–H, 2H), 2.38 (br s, B–H, 4H), 2.02 (br s, B–H, 2H) and 1.80 (br s, B–H, 2H). ¹³C{¹H}-NMR (CDCl₃, 25 °C): δ = 137.4, 131.3, 130.3, 129.4 (C_{aryl}), 91.7 (B–C). ¹¹B-NMR (CDCl₃, 25 °C): δ = –3.6 (d, ¹J(B, H) = 147, 2B), –8.9 (4B), –9.9 (2B), –11.7 (2B).

4.4. X-ray crystallographic study

The unit cell parameters for 1,2-(SPh)₂-1,2-C₂B₁₀H₁₀ were calculated by least-squares refinement of 25 well-centered reflections and the data were collected by ω –2 θ scan mode on a Rigaku AFC-5S diffractometer. Intensities of three reflections monitored periodically during the data collection exhibited no significant variation. The data were corrected for Lorentz and polarization effects, and for extinction. Also an empirical absorption correction was performed (Ψ scans). The structure was solved and refined according to routine procedure using the SHELX-97 program package [18]. Approximate non-hydrogen positions were obtained by direct methods, and after refinement of non-hydrogen atoms, all hydrogen atom positions were picked from subsequent Fourier map. In final refinement, the non-hydrogen atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters.

4.5. Computational approach

All calculations in this work were performed with the GAUSSIAN-98 suite of programs [19] using the B3LYP/6-31G* model, which is based on density functional theory and uses a double- ζ basis set, with an additional set of polarization functions on all atoms except hydrogen. The molecular geometries were all optimized at the same level of theory and the energy minima were checked through frequency calculations in compounds **1**, **2**, **4** and **6**. The molecular geometries of compounds **3** and **6** were optimized starting from the X-ray geometry, obtaining null forces on nuclei. No frequency calculations were performed on these molecules due to the size of the system.

5. Supporting information available

Crystallographic data for **5** have been deposited with the Cambridge Crystallographic Data Centre in. cif format, ref. No. CCDC No 136786.

Acknowledgements

This work was supported by CICYT (Project MAT98-0921), Generalitat de Catalunya (Grant 1998F1 00724), and the Academy of Finland (project 41519, RK).

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- [16] As a reviewer has suggested the NHOMO may well be the non-bonding orbital (*) shown in Fig. 3. The graphical representation displayed in Fig. 4 seems to support this possibility. This lowering in energy with regard to the HOMO can be the result of symmetry allowed orbital mixing with filled and empty orbitals on the original cluster. We thank the reviewer for his comments.
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