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# COMMUNICATION

# A PENTUPLY-BRIDGING THIOCARBONYL GROUP: X-RAY CRYSTAL STRUCTURE OF A SALT OF THE 1-THIO-2-PHENYL-1,2-DICARBADODECABORATE (12) ANION, $[LH]^+[S(Ph)C_2B_{10}H_{10}]^-$ (L = 1,8-N,N,N$^1$,N$^1$-TETRAMETHYLNAPHTHALENE DIAMINE)

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**Abstract**—The carboranyl sulphide anion $[1,2\text{-}S(Ph)C_2B_{10}H_{10}]^-$, characterized as its salt $[C_{10}H_6(NMe_2)_2H]^+[S(Ph)C_2B_{10}H_{10}]^-$ (**1**), has been prepared from the carboranyl thiol and proton sponge and characterized by X-ray crystallography. The anion has a *nido*-shaped $[PhCB_{10}H_{10}]$ residue in which the $CB_4$ pentagonal face is capped by a $\mu_5$-thiocarbonyl unit [C—S distance 1.729(4) Å], attached by bonds of length C—C 1.835(5) Å [C(1) to C(2)], C—B 1.742(6), 1.695(5), 1.704(6) and 1.749(6) Å [C(1) to B(3), (4), (5) and (6)]. This slipped structure reflects delocalization of the anionic charge from the sulphur atom into the polyhedron, a delocalization supported by AM1 calculations and also reflected in $^{11}$B chemical shift data which show a pronounced antipodal effect.

Icosahedral carboranes, $C_2B_{10}H_{12}$, and their derivatives, $R_xC_2B_{10}H_{12-x}$, may be regarded as three-dimensional aromatic systems.[1–5] Many of their reactions resemble those of aromatic ring systems, and the electronic effect of substituents can be transmitted around the icosahedron in a way reminiscent of (though more complicated than) substituent effects on a benzene ring. To explore their capacity to conjugate to unsaturated substituents, and to tolerate multiple bonds to their skeletal atoms, we have prepared some model compounds for structural, spectroscopic and theoretical characterization. Here we describe a derivative where a formally anionic substituent sulphur atom, attached to a skeletal carbon atom in *ortho*-carborane, can delocalize some of its charge onto the cage atoms.

The thiol $1,2\text{-}HS(Ph)C_2B_{10}H_{10}$, prepared from $PhC_2B_{10}H_{11}$, sodium and sulphur in liquid ammonia,[6] when treated with an equimolar proportion of proton sponge [1,8-N,N,N$^1$,N$^1$-tetramethylnaphthalenediamine $C_{10}H_6(NMe_2)_2$] in hexane, gave a salt which crystallized from hot toluene as pale yellow crystals (m.p. 189–190°C), which analysed satisfactorily for $[C_{10}H_6(NMe_2)_2H]^+$ $[S(Ph)C_2B_{10}H_{10}]^-$ (**1**). The peak of highest $m/z$ in its mass spectrum was at 254, attributable to $^{12}C_8{}^1H_{16}{}^{11}B_{10}{}^{32}S$ accompanied by the usual carborane isotope distribution pattern, and a peak at $m/z$ 214 corresponded to $^{12}C_{14}{}^1H_{18}{}^{14}N_2$. Its $^1$H, $^{11}$B [in $(CD_3)_2SO$] and $^{13}$C (solid state) NMR spectra

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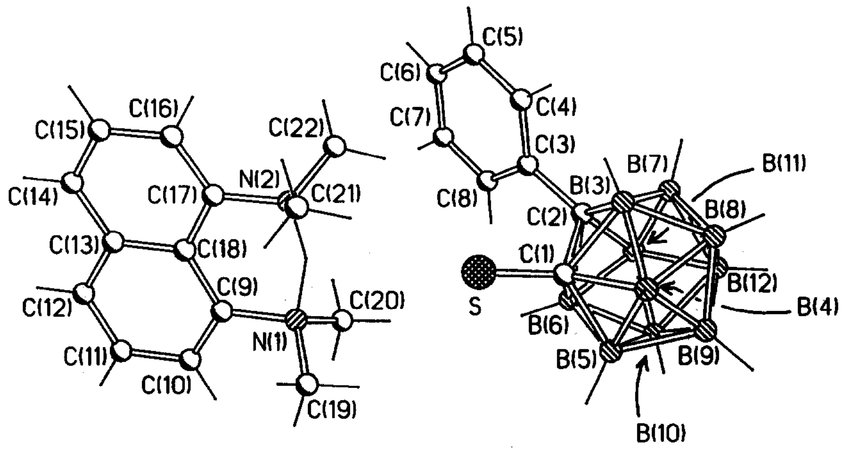

Fig. 1. Structure of compound **1**.

supported the proposed structure which was confirmed by X-ray crystallography (Fig. 1).†

We have previously reported[7] the preparation and structural characterization of the oxygen analogue $[1,2\text{-}O(Ph)C_2B_{10}H_{10}]^-[C_{10}H_6(NMe_2)_2H]^+$ (**2**) and a comparison can now be drawn between the effects of oxygen and sulphur as substituents on a skeletal carbon atom.

Interatomic distances around the C—S unit are shown in Fig. 2 for the anion of the title compound (**1**) with distances for the oxygen anion for comparison. The C—S distance in the anion, 1.729(4) Å, is significantly shorter than a normal C—S single bond distance which is typically 1.80–1.84 Å, depending on the number and nature of the substituents;[11] in particular, the closely-related carboranyl disulphide and trisulphide, $(1,2PhC_2B_{10}H_{10})_2S_{2\,\text{or}\,3}$, have C—S (single bond) distances of 1.79–1.80 Å and 1.78–1.79 Å respectively.[12] Full carbon–sulphur double bonds can be as short as 1.56 (in $CS_2$) or 1.61 Å (in $F_2CS$), whereas compounds with C—S bond orders of *ca* 1.5 (thiophen, thiourea, thioacetamide) have C—S distances of *ca* 1.71 Å.[11]

This indicates that although there is some delocalization of electronic charge from the sulphur atom into the cage, it is not as marked as that seen in the oxygen analogue. [In the anion of **2** the C—O bond length of 1.245(3) Å is in the region typical of a double bond in ketones.] Hence, in valence bond terms, the sulphur anion is best represented, as shown in Fig. 3, as a hybrid of (**a**) and (**b**), whereas the oxygen anion is best represented by (**b**) alone.

These conclusions are supported by calculations carried out using the MNDO-AM1 method in the MOPAC 5.0 package,[13] with AM1 parameters for sulphur substituted for the older less accurate MNDO sulphur parameters.[14] The calculated bond order for the *exo*-C—S bond is 1.22 compared with 0.98 for the parent thiol, while for the oxygen anion the *exo*-C—O bond order is 1.69.

The C—C, C—B and B—B distances and calculated bond orders in Fig. 2 show how the *exo*-C$\overset{\cdots}{\text{—}}$S multiple bonding affects the bonding between the CS unit and the *nido*-shaped $PhCB_{10}H_{10}$ residue. There is a significant slip distortion of the CS unit away from C(2) towards B(4) and B(5), as the primary source of its bonding to the $CB_4$ pentagonal face is the $5e_1(y)$ frontier orbital to which C(2) does not contribute.[7,15,16] This results in a lengthening of the skeletal C(1)—C(2) bond to 1.835 Å (bond order 0.39), whereas the neutral trisulphide $(1,2PhC_2B_{10}H_{10})_2S_3$, with *exo*-C—S single bonds, by contrast has a skeletal C(1)—C(2) distance of 1.74 Å (bond order 0.58).[12] The analogous oxygen anion has a C(1)—C(2) bond length of 2.001(3) Å and bond order of 0.17.

The pentagonal face C(2)B(3–6) shows the slight "envelope" folding about the B(3)—B(6) axis away

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† Crystal data for $[C_{14}H_{19}N_2][C_8H_{15}B_{10}S]$: $M = 466.7$, monoclinic, $a = 20.103(6)$, $b = 9.611(3)$, $c = 26.370(8)$ Å, $\beta = 90.17(3)°$, $U = 5094.9$ Å$^3$, $Z = 8$, space group $I2/a$ (alternative setting of $C2/c$). The structure was determined from 2114 unique observed reflections measured at 125 K on a Stoe–Siemens diffractometer equipped with an Oxford Crysostream cooler,[8,9] and refined on $F$ to a final $R = 0.0477$, $R' = 0.0503$ with anisotropic thermal parameters and constrained isotropic hydrogen atoms.[10] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

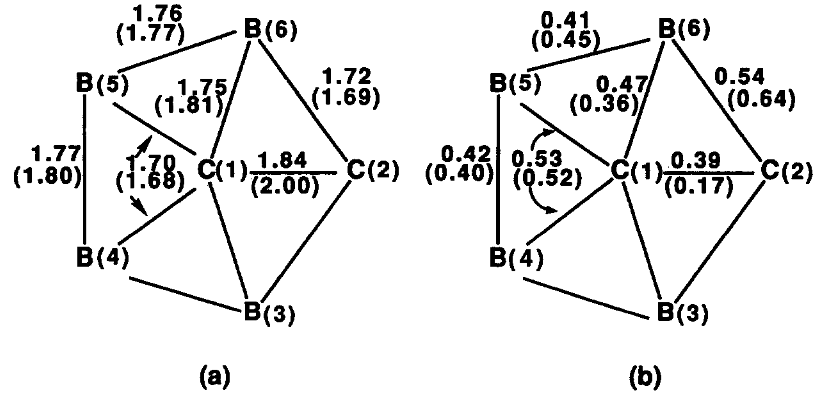


Fig. 2. (a) Interatomic distances (Å) and (b) calculated bond orders for anions $[X(Ph)C_2B_{10}H_{10}]^-$; $X = S$ (O).

from the CS unit that normally accompanies a slip distortion, with C(2) folded away from C(1), some 0.110 Å out of the mean plane through boron atoms B(3–6).

For both anions $[S(Ph)C_2B_{10}H_{10}]^-$ and $[O(Ph)C_2B_{10}H_{10}]^-$ the pattern of bonding of the CX unit to the $CB_4$ pentagonal face of the *nido*-shaped $[PhCB_{10}H_{10}]$ residue is the same. Bond orders increase in the order C(1)—C(2) < C(1)—B(3,6) < C(1)—B(4,5) as a result of the slip distortion already referred to, which is greater when $X = O$ than when $X = S$. Bond orders around the pentagonal face decrease in the order

C(2)—B(3,6) > B(3,6)—B(4,5) > B(4)—B(5)

for $X = O$, whereas the facial boron–boron bonds in the sulphide have similar bond orders. Figure 4 shows the changes in atomic charges and bond orders on going from the parent thiol to the anion. A similar pattern emerges. Negative charge is transferred to the facial atoms on deprotonation, the effect of which is to weaken the bonds to the CS unit but strengthen those around the pentagonal face.

The data in Fig. 2 show that there is more charge-transfer from the *exo* atom X into the polyhedron when $X = O$ than when $X = S$ (even though oxygen is more electronegative than sulphur), presumably because a carbon–oxygen bond gains much more in bond energy than a carbon–sulphur bond with an increase in bond order, offsetting better the loss in skeletal bond energy.

Further indications of the effect of delocalization of the anionic charge into the polyhedron have been provided by our NMR studies. Using $^{11}B$—$^{11}B$ COSY studies to establish peak assignments on the parent hydroxide and thiol and their products of deprotonation, compounds **1** and **2**, we find a consistent pattern (see Table 1). Resonances shift to lower field for boron nuclei in sites 3, 6, 7 and 11, and to higher field for the remainder; the most pronounced change being shown by the upfield shift of the resonance due to the antipodal boron atom,

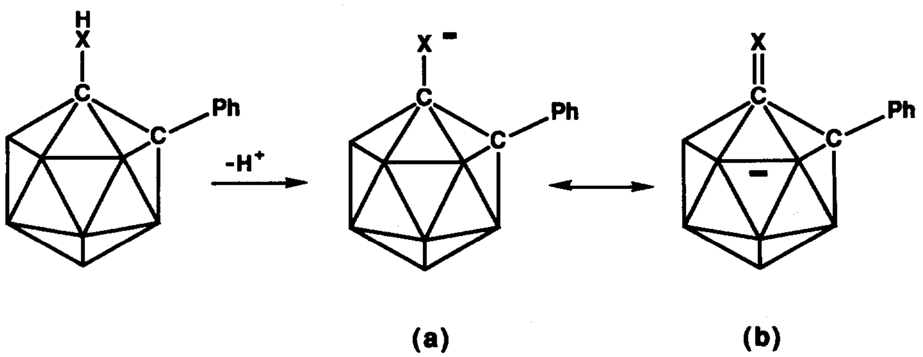
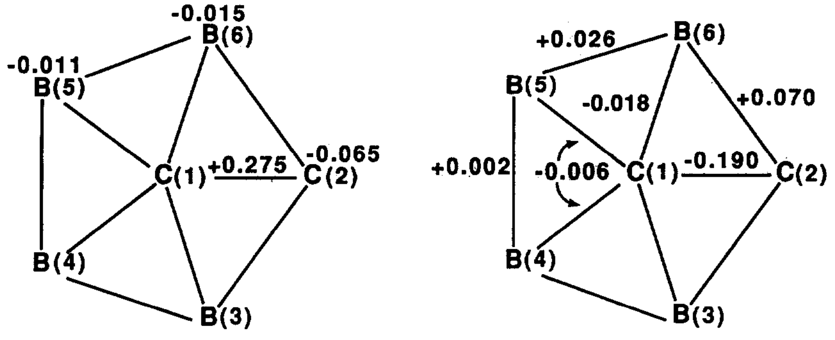


Fig. 3. Resonance forms of the anion of **1**.



(a) (b)

Fig. 4. Calculated changes in (a) atomic charges and (b) bond orders on deprotonation of $HS(Ph)C_2B_{10}H_{10}$.

Table 1. $^{11}B$ NMR chemical shift data for (i) 1-HX-2-Ph—$C_2B_{10}H_{10}$ and (ii) [1-X-2-Ph—$C_2B_{10}H_{10}$]

| | X = S | | | X = O | | |
|---|---|---|---|---|---|---|
| | (i) | (ii) | Δ*[a] | (i) | (ii) | Δ* |
| B(3,6) | −8.87 | −4.30 | +4.57 | −11.40 | −5.43 | +5.97 |
| B(4.5) | −8.87 | −9.65 | −0.78 | −11.40 | −14.04 | −2.64 |
| B(7,11) | −8.87 | −5.95 | +2.92 | −11.40 | −11.12 | +0.28 |
| B(8,10) | −6.85 | −11.99 | −5.14 | −13.78 | −16.97 | −3.19 |
| B(9) | −1.31 | −5.95 | −4.65 | −5.02 | −6.51 | −1.49 |
| B(12) | −2.53 | −11.99 | −9.46 | −11.40 | −21.06 | −9.66 |

[a] Δ* = The chemical shift change on deprotonation.

Spectra were recorded at 115.552 MHz using solutions in $C_6D_6$ for (i) (X = S,O) and $(CD_3)_2SO$ for (ii) (X = S,O), referenced to $BF_3Et_2O$ at 0.00 ppm.

B(12), opposite the site of deprotonation, a shift intelligible in that although most remote from the site of deprotonation the antipodal boron atom uniquely has its tangential *p*-orbitals aligned parallel to those on the carbon atom opposite, i.e. those involved in C$\overset{...}{-}$X multiple bonding.[17]

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