Synthesis and Properties of Thia-*closo*-dodecaborane(11)

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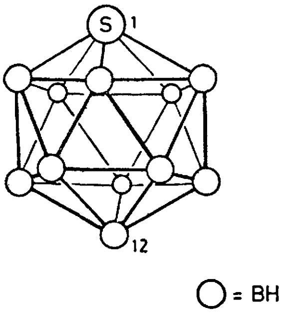
Summary The preparation of $SB_{11}H_{11}$ and its bromination to 12-Br-1-$SB_{11}H_{10}$ are described; the n.m.r. antipodal effect of the S(δ+) atom on the chemical shift of the opposite B(12) atom is shown.

ALTHOUGH 2-phenyl- and 2,4-diphenyl-1-thia-*closo*-dodecaboranes(11) have been synthesized since the discovery of thiaborane compounds,[1] the parent compound has not yet been described. We have now synthesised thia-*closo*-dodecaborane(11) (I) as in equation (1).

$$7\text{-}SB_{10}H_{12} + Et_3N{\cdot}BH_3 \xrightarrow{120\text{—}190^\circ} \underset{\text{(I) }38\%}{SB_{11}H_{11}} + \underset{\text{(II) } ca.\ 50\%}{SB_{10}H_{11}^{-}\overset{+}{N}HEt_3} + Et_3N \quad (1)$$

Compound (I) was isolated from the crude sublimate by column chromatography on silica gel with hexane as eluant, followed by sublimation at 90° and 10^{-2} Torr. From the triethylammonium salt (II) the starting compound can be recovered almost quantitatively.



The colourless camphor smelling 1-thia-*closo*-dodecaborane(11), sublimes (>240°) and is readily soluble in organic solvents. The chromatographic behaviour on silica gel† which parallels the dipole moment values of *closo*-derivatives[2] shows that (I) [R_F 0·40 (hexane), 0·60 (benzene–hexane 1:2)] has a much smaller dipole moment than 1,2-dicarba-*closo*-dodecaborane(12) [4·5 D; R_F 0·08 (hexane), 0·30 (benzene–hexane 1:2)] and is comparable with 1,7-dicarba-*closo*-dodecaborane(12) [2·8 D; R_F 0·41 (hexane), 0·60 (benzene–hexane 1:2)].

The mass spectrum of $^{32}S^{11}B_{11}{}^{1}H_{11}$ gives M^+ 164·16109 (calcd. 164·16 056). The i.r. spectrum is relatively simple and shows significant B–H$_t$ absorption bands at 2580 and 2620 cm^{-1}. The u.v. spectrum shows λ_1 216 nm (ϵ = 1095) and λ_2 219 nm (sh, ϵ = 967). The ^{11}B n.m.r. spectrum has three doublets of relative intensities 1:5:5, centred at −18·7; +3·7 and 5·7 p.p.m. (relative to $BF_3{\cdot}OEt_2$), and supports the proposed structure of (I). The values compare well with those of $2\text{-}PhB_{11}H_{10}S$ [−18·5(1), −8·3 (1, singlet); +3·9(8)].[1]

The bromination of (I) in methylene chloride in the presence of Al powder gave $12\text{-}Br\text{-}1\text{-}SB_{11}H_{10}$ (90%), m.p. 215—217°, M^+ 244. The position of the bromine atom follows from the ^{11}B n.m.r. spectrum which has a singlet of intensity 1 at −16·1‡ and two doublets, each of intensity 5 at +3·9 and +7·0 p.p.m. Bromination indicates that the B(12) atom is the most negative B atom in the molecule.

The occurence of the ^{11}B signal of the most negative B(12) atom in the lowest field of the n.m.r. spectrum is not surprising in the light of our finding that the ^{11}B chemical shift of a skeletal atom does not depend on its electron-density but is mainly influenced by the electron-density of the atom located on the opposite site of the molecule; the $\delta+$ charged atom shifts the signal of an antipodal atom to lower field while the $\delta-$ charged atom shifts it to higher field (compared with the non-charged atom).[3] This hypothesis is in accord with compound (I) where the B(12) atom is influenced significantly by the antipodal, positively charged S-atom and behaves as a least-shielded atom, the signal of which occurs in the lowest field of the spectrum. A similar, but a much more intense effect of the S($\delta+$) atom on the antipodal B(10) atom was observed with the $1\text{-}SB_9H_9$homologue ($\delta_{B(10)}$ = − 74·5 p.p.m.[4]). The rate of the antipodal effect thus depends not only on the electron-density but also on the shape of the *closo*-skeleton.

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† Precoated silica gel sheet Silufol, starch as binder (Kavalier n.p. Votice, Czechoslovakia); detection—I_2 vapour followed by $AgNO_3$ spray.

‡ In this case, the substitution of a single terminal hydrogen by the bromine atom causes, surprisingly, a shift to higher field.

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