

SYMMETRICAL ISOMERS OF *arachno*-5,5'-X-(6,9-C₂B₈H₁₃)₂
(X = O AND OSO₂O) COMPOUNDS

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Treatment of the [6,9-C₂B₈H₁₀]Na₂ salt with concentrated sulphuric acid produces two compounds of the general formula σ , ϱ '-5,5'-X-(6,9-C₂B₈H₁₃)₂, where X = O or OSO₂O, the constitution of which was established on the basis of their NMR data.

Recently^{1,2} we have reported a general reaction of the *nido*-[6,9-C₂B₈H₁₀]²⁻ dianion³ with anhydrous hydrogen halides giving high yields of 5-halogenated derivatives of the *arachno*-6,9-C₂B₈H₁₄ dicarborane⁴. The course of the reaction is best explained as a consequence of stereoselective addition of hydrogen halides to the B₍₅₎—C₍₆₎ bond within the framework of [6,9-C₂B₈H₁₀]²⁻. Slightly hydrated hydrogen fluoride was found to yield oxidoderivative 5,5'-O-(6,9-C₂B₈H₁₃)₂ as a result of the addition of water^{1,2}. We now report a more convenient preparative route to the latter species and discuss the structure of compounds with the 5,5'-linkage of two *arachno*-6,9-C₂B₈H₁₃ moieties (for numbering see Fig. 1).

Reaction of the [6,9-C₂B₈H₁₀]Na₂ salt (*I*) with concentrated sulphuric acid gives rise to two main products, 5,5'-O-(6,9-C₂B₈H₁₃)₂ (*II*) and 5,5'-OSO₂O-(6,9-C₂B₈H₁₃)₂ (*III*). Compound *II* is identical with the main product of the reaction of anion *I* with c. 97% hydrogen fluoride^{1,2} and the mass and NMR spectral data of *III* are clearly compatible with the B₍₅₎—OSO₂O—B_(5') linkage of two 6,9-C₂B₈H₁₃ subunits.

There are two possible modes of the linkage, the first one producing symmetrical σ , ϱ '-derivative (*A*), and the second one, leading to a (+) and (–) pair of σ , σ' - and ϱ , ϱ' -enantiomorphs (*B*) (the depicted basic orientation is that with open hexagonal faces turned downwards, B_(1–4) atoms are omitted for clarity, X = O and/or OSO₂O. Symbols σ and ϱ denote clockwise and anticlockwise numbering⁵, respectively).

The ¹¹B NMR spectra of both compounds *II* and *III*, consisting of one B₍₅₎ singlet and seven doublets of equal intensities, suggest the symmetrical alternative *A*. The

results of the recent X-ray diffraction study⁶ on compound *II* produced conclusive evidence in support of this constitution.

The only way how to achieve the found explicit formation of the σ , ρ' -derivatives *II* and *III* is the dehydration of two molecules of an unstable 5-HO-6,9-C₂B₈H₁₃ derivative^{1,2} by excess sulphuric acid. An alternative mechanism, such as stepwise reaction of water or sulphuric acid with two molecules of anion *I*, would also produce the asymmetrical derivative *B*.

EXPERIMENTAL

¹H (200 MHz) and ¹¹B (64.18 MHz) NMR spectra were obtained on a Varian XL-200 equipment in deuteriochloroform at 25°C. Chemical shifts are given in δ (ppm, referenced to tetramethyl-

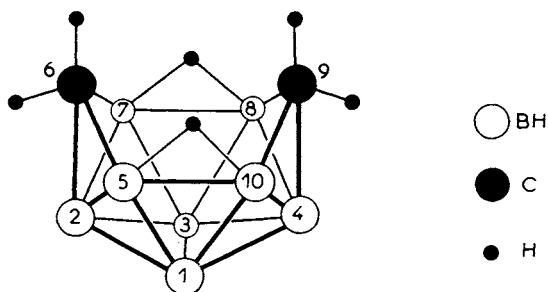


Fig. 1

Gross geometry and numbering system of *arachno*-6,9-C₂B₈H₁₄

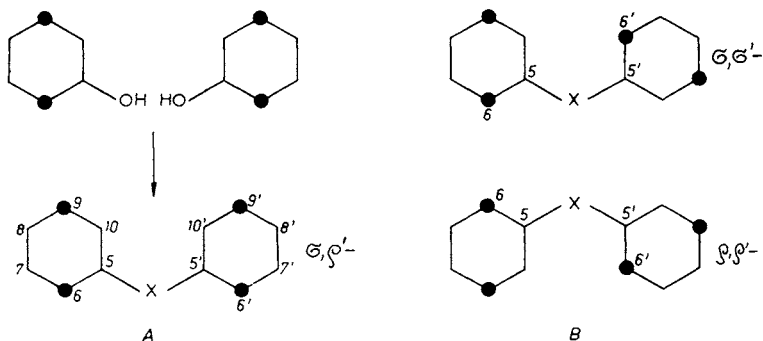


Fig. 2

Simplified representation of the two possible modes of the 5,5'-linkage of 6,9-C₂B₈H₁₃ subunits (X = O or OSO₂O, B (1-4) atoms omitted for clarity). Basic orientation is that with open hexagonal faces turned downwards, symbols σ and ρ denote clockwise and anticlockwise numbering⁶, respectively

silane and BF₃.O(C₂H₅)₂, positive values downfield). TLC was performed on Silufol sheets (silica gel on aluminium foil) in benzene. Melting points were determined in sealed capillaries and are uncorrected.

arachno-5,5'-O-(6,9-C₂B₈H₁₃)₂ (II) and 5,5'-OSO₂O-(6,9-C₂B₈H₁₃)₂ (III)

Concentrated sulphuric acid (5 ml) was added to a suspension of I (0.8 mmol) in benzene (50 ml) and the mixture was shaken for 3 h. The benzene layer was separated, a new portion of benzene (25 ml) was added and the mixture was stirred for additional 3 h. Combined benzene fractions were evaporated *in vacuo* to a volume of c. 15 ml and placed onto a column (2.5 × 30 cm) packed with silica gel. Benzene eluted two main fraction of R_F 0.48 and 0.20 (checked by TLC). The pure fractions were combined and evaporated *in vacuo* leaving two white products. The first one was crystallized from benzene-cyclohexane (1 : 1) to give 0.3 g (48%) of crystals the NMR spectra of which were identical with those of the recently prepared^{1,2} carborane II. The second product was crystallized in the same way to afford 0.2 g (24%) of III as crystals nonmelting up to 260°C; ¹H NMR spectrum: δ 1.24 (1 H, s, CH_(eq)), 1.05 (1 H, s, CH_(eq)), -0.15 (1 H, s, CH_(ax)), -0.32 (1 H, s, CH_(ax)), -2.66 (2 H, br s, μH); ¹¹B NMR spectrum: δ_B 4.92 (1 B, d, J_{B-H} c. 180, B_(2,2')), 1.63 (1 B, d, c. 170, B_(4,4')), -3.23 (1 B, s, 49, B_(5,5')), -16.99 (1 B, d, c. 160/45, B_(7,7')), -19.29 (1 B, d, B_(10,10')), -20.73 (1 B, d, B_(8,8')), -37.20 (1 B, d, 150, B_(1,1')), -39.40 (1 B, d, 150, B_(3,3')); m/z 346, corresponding to [C₄B₁₆H₂₆SO₄]⁺.

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