

SYNTHESIS AND STRUCTURE OF ISO-C₄B₁₈H₂₂

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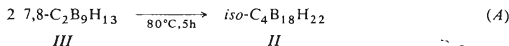
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Iso-C₄B₁₈H₂₂ isolated earlier as a minor by-product in the H₂CrO₄ oxidation of the C₂B₉H₁₂⁽⁻⁾ anion was prepared in 10% yield by thermolysis of 7,8-C₂B₉H₁₃. The originally suggested structure, 3-(8'-*nido*-5,6-C₂B₈H₁₁)-1,2-C₂B₁₀H₁₁, is confirmed by the ¹¹B NMR spectra.

In the preparation of the *n*-C₄B₁₈H₂₂ carborane (*I*), performed by the oxidation of the 7,8-C₂B₉H₁₂⁽⁻⁾ anion with chromic acid, a minor neutral species *II* of an identical molecular cut-off in the mass spectrum was isolated in less than 1% yield¹.

We report herein a more convenient preparation of the *iso*-C₄B₁₈H₂₂ carborane (*II*) which can now be obtained in reasonable yields (about 10%) by heating the 7,8-C₂B₉H₁₃ carborane (*III*) in benzene or toluene (Eq. (*A*)).



Mass spectra of isomeric *I* and *II* (Fig. 1) indicate differences in structure of both carboranes. The presence of a very intense pattern with the cut-off at *m/z* 122 in the spectrum of *II* shows that its molecule contains the skeleton of the *nido*-C₂B₈H₁₂ carborane while the less intense pattern with the cut-off at 146 indicates the presence of the C₂B₁₀H₁₂ skeleton. The presence of *nido*-C₂B₈H₁₂ moiety in the skeleton of carborane *II* is suggested by the acidity of compound *II* (p*K*_a 6.18). This suggestion was confirmed by the ¹H NMR spectrum of carborane *II* which exhibits three broad signals of skeletal CH groups of intensities 1 : 1 : 2 centred at δ 6.54, 5.04 and 3.55 ppm. The chemical shifts of the former two signals are very close to those of 5,6-C₂B₈H₁₂ (*III*) (δ 6.47, 4.98 ppm) and the signal of intensity two is practically identical with the CH absorption of 1,2-C₂B₁₀H₁₂ (*IV*) (δ 3.55 ppm). The fact that the signal of intensity two at 3.55 ppm is uniform indicates that the 1,2-dicarbadodecaborane(12) is substituted either in the B(3) or B(8) positions which preserves the ¹H NMR-identity of both CH vertices.

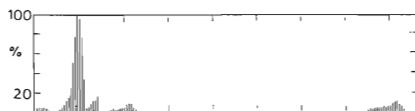
The above facts are in agreement with the ¹¹B NMR spectra which show features of both 5,6-dicarba-*nido*-dodecaborane(12) and 1,2-dicarba-*closo*-dodecaborane(12). Analysis of our decoupled and line-narrowed spectra (according to²), a simulation of

TABLE I

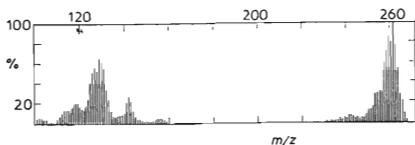
¹¹B Chemical shifts of *iso*-C₄B₁₈H₂₂ (*II*) and their correspondence to the spectra of parent 5,6-C₂B₈H₁₂ (*III*) and 1,2-C₂B₁₀H₁₂ (*IV*); referred to BF₃·O(C₂H₅)₂ with + signals in the lower magnetic field from the standard, $\Delta = \delta_{11} - \delta_{\text{parent skeleton}}$

δ	<i>II</i>		<i>III</i> δ^a	<i>IV</i> δ^b
	assignment	Δ		
+ 8.5 ± 0.3 ^c	8'	+5.2	+ 3.3	—
+ 6.9	7'	+0.4	+ 6.5	—
+ 5.3	1'	+0.3	+ 5.0	—
- 2.4	9'	+1.3	- 3.7	—
- 2.7	3'	-0.1	- 2.6	—
	9 = 12	+0.6	—	- 3.3
- 7.9	10'	+2.1	-10.0	—
- 8.8	8 or 10	+1.4	—	-10.2
-11.6 ± 0.3 ^d	3	+4.1	—	-15.7
-13.1	4 = 11	+1.5	—	-14.6
-13.6	5 = 7	+1.0	—	-14.6
-14.6	6	+1.1	—	-15.7
-27.0	2'	+0.2	-27.2	—
-37.4	4'	+1.7	-39.1	—

^a Signals in parent skeleton *III* corresponding to the primed B atoms; ^b signals in parent skeleton *IV* corresponding to the nonprimed B atoms; ^c very broad singlet; ^d singlet hidden in the overlapped signals.



a



b

FIG. 1

Mass spectra of *iso*-C₄B₁₈H₂₂ (*a*) and of *n*-C₄B₁₈H₂₂ (*b*)

particular parts by a curve resolver, and the PRFT study (according to³) confirmed the presence of one broad singlet at $c. 8.5 \pm 0.3$ ppm and indicated a presence of the second singlet, (hidden in the multiplet of intensity nine) centred at -11.6 ± 0.3 ppm. Both signals are the widest ones in the spectrum, similar to most signals in B-B linked borane skeletons³⁻⁶, and are practically missing in the ¹¹B line-narrowed spectra. Changes in the ¹¹B chemical shift brought by the B-substitution have been found to amount to 7 ± 5 ppm for the substituted B-atom and to -2 ± 1 ppm for adjacent B-atoms, being negligible for more distant atoms³⁻⁶. These observations together with the complete assignment⁷ of all signals in 5,6-C₂B₈H₁₂ allow to assign the former singlet to the B(8') atom ($\Delta = 5.2$ ppm) in the *nido*-part and the latter one to the B(3) atom ($\Delta = 4.1$ ppm) in the *closo*- part of iso-C₄B₁₈H₂₂. The relevance of individual signals in the composed carborane *II* to the appropriate signals in the parent *nido*-carborane *III* and *closo*-carborane *IV* is shown in Table I and is in agreement with the above discussed changes brought by the B-substitution. For further comments see Table I.

The iso-C₄B₁₈H₂₂ carborane (*II*) represents the first known example of an uncharged species, composed of *nido*- and *closo*-carborane. As mentioned formerly⁸ this conjuncto-species is very likely formed by a boron transfer from one C₂B₉ skeleton to the missing vertex of the other C₂B₉ skeleton in some reaction step. The transferred boron atom then forms the B(3) atom of the *ortho*-carborane framework and remains simultaneously attached to the B(8) atom of the *nido*-moiety. The pro-

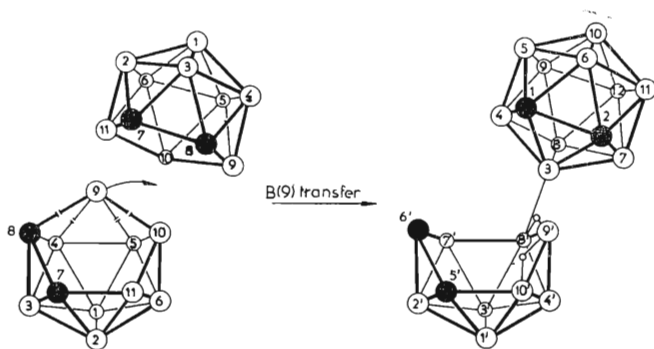


FIG. 2

Probable formation of iso-C₄B₁₈H₂₂ from C₂B₉ skeletons and numbering of both units
 O BH, ● CH, ○ H

posed reaction scheme shown in Fig. 2 rendered now, on the basis of the above ¹¹B NMR and the recent X-ray diffraction study⁹, to be probable reaction path explaining the formation of *II*.

EXPERIMENTAL

¹H and ¹¹B NMR spectra were measured using a Varian XL-200 spectrometer. The mass spectra were recorded with a GC/MS HP 5985 instrument at 70 eV. Electronic spectra were measured on a Beckman Acta M IV device and IR spectra on a Beckman IR-20 A Spectrometer. TLC was carried out on Sulifol sheets (silica gel on aluminium foil, starch as a binder; Kavalier, Votice, Czechoslovakia).

Preparation of Carborane *II*

Conc. sulfuric acid (10 ml) was added to a suspension of 7,8-C₂B₉H₁₂N(CH₃)₄ (6.3 g; 0.03 mol) in benzene (30 ml). The solution was stirred at ambient temperature for 0.5 h, the benzene layer was separated and heated at 80°C for further 5 h. The mixture was cooled to *c.* 20°C, mixed with water (50 ml) and neutralized by stepwise addition of crystalline K₂CO₃ (6 g). After shaking, the benzene layer was separated, poured onto a silica gel column (50 g) and eluted till the distinctly yellow zone reached the bottom of the column. The eluate was evaporated, the residue was dissolved in 15 ml of benzene-n-hexane mixture (1:2) and chromatographed on a silica gel column. Portions containing (according to TLC) the pure carborane *II* were combined and evaporated. Recrystallization of the residue from n-hexane yielded crystals (0.4 g; 10%) of carborane *II*; m.p. 148–149°C (sealed capillary, uncorrected); *R_F* rel. 35 (n-hexane, *R_F* 5,6-C₂B₈H₁₂ 0.20 = 100); *pK_a* (50% ethanol) 6.8; ¹H NMR (200 MHz, CDCl₃) δ 6.54 (1 H, s, CH_(5' or 6')), 5.04 (1 H, s, CH_(5' or 6')), 3.55 (2 H, s, CH_(1,2)) ppm; relative to tetramethylsilane. IR spectrum (CH₂Cl₂): 3 065 (s, CH carborane), 2 580 (vs, BH terminal), 1 865 (w, BH bridge), 1 552 (ms) 1 443 (s) cm⁻¹. UV spectrum λ_{max} (CH₂Cl₂): 276 nm. (ε 5 350) ¹¹B NMR spectra: see Table I.

The IR and electronic spectra were recorded by Drs F. Hanousek and F. Haruda, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež and the mass spectra were measured by Z. Weidenhoffer. These colleagues are thanked for their assistance.

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