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THE STRUCTURE OF A NEW ISOMER OF DICARBA-*nido*-UNDECABORANE(13)

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Summary

The intramolecular rearrangement involved in the electrophilic methylation of 7,8-$B_9C_2H_{11}^{2-}$ leads after protonation to the methyl derivative of a new isomer of dicarba-*nido*-undecaborane(13). By an X-ray structure analysis the latter compound is shown to be 11-methyl-2,7-dicarba-*nido*-undecaborane(12). It has the structure of an icosahedron with one missing vertex, with the carbon atoms adjacent, one in the open face of the polyhedron and the other in its closed part. The methyl group is attached to the boron atom of the open face bonded to both carbon atoms. The open face has two BHB-bridges which are symmetric relative to its carbon atom. The main interatomic distances are: av. B—B 1.794(8), av. B—C 1.685(7), C—C 1.606(6), B—Me 1.551(8), av. B—H (terminal) 1.08(3), av. B—H (bridging) 1.26(4), av. C—H 0.92(4) Å.

At present three isomers of dicarba-*nido*-undecaborane(13) are known. They are 7,8-, 7,9- and 2,9-$B_9C_2H_{13}$ *, formed by protonation of the corresponding $B_9C_2H_{12}^-$ anions produced by alkaline degradation of the *ortho*-, *meta*- and *para*-carboranes(12) respectively [2—4].

The alkylation of the 7,8-dicarba-*nido*-undecaborate dianion 7,8-$B_9C_2H_{11}^{2-}$, with alkyl halides in liquid ammonia gives the *B*-alkyldicarba-*nido*-undecaborate anion, *B*-$MeB_9C_2H_{11}^-$, differing by its structure and properties from the known isomers of the $B_9C_2H_{12}^-$ anion. This novel anion is reversibly protonated by diluted acids to yield a nonpolar compound, *B*-$MeB_9C_2H_{12}$ [5]. To elucidate the structure of this novel *nido*-carborane we undertook its X-ray study.

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* Atom numbering system as in ref. 1.

Experimental procedure and structure determination

The X-ray experiment was carried out with an automatic diffractometer Syntex $P2_1$ at —120°C. The crystals are rather unstable at room temperature and belong to the orthorhombic space group $P2_12_12_1$, a 6.58(2), b 10.30(3), c 13.74(4) Å, V 931(5) Å^3, M 148.2, D_m 1.04, D_c 1.06 g cm^{-3} for $Z = 4$.

The intensities of 878 independent reflections were measured by $\theta/2\theta$-scan (Mo-K_α radiation, graphite monochromator, $2\theta \leqslant 48°$), neglecting the absorption corrections. In subsequent calculations 689 reflections with $|F|^2 \geqslant 2\sigma$ were used. The structure was solved with the MULTAN technique using 139 normalized amplitudes $|E| \geqslant 1.4$. The E-series based on the best phase solution revealed all the non-hydrogen atoms. After isotropic refinement to $R = 0.144$ B and C atoms were identified unequivocally on the basis of temperature factors and interatomic distances. All 15 hydrogen atoms were then localized with the difference synthesis. The final aniso (B,C)—iso (H) full-matrix refinement led to $R = 0.049$ ($R_w = 0.032$).

Atomic coordinates and temperature factors are given in Tables 1 and 2, interatomic distances in Table 3. All calculations were carried out with XTL programmes on the Nova 1200 computer.

Structure description

The present structure analysis has shown the compound studied to be a new *nido*-carborane, 11-Me-2,7-$B_9C_2H_{12}$ (I). Its molecule has an *ortho*-carboranic icosahedral skeleton with one vertex missing see Fig. 1. Unlike the known 7,8-$B_9C_2H_{13}$ [2] where carbon atoms are also in the *ortho* position, the open face of molecule I includes only one carbon atom, C(7), and another, C(2), is situated in the closed part of the polyhedron. The methyl group is attached to the boron atom B(11) of the open face which is bonded to both carbon atoms. The boron atoms of the open face are connected pairwise by hydrogen bridges, B(8)—H(12)—B(9) and B(10)—H(13)—B(11). The molecular structure of I is notice-

(continued on p. 137)

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC TEMPERATURE FACTORS
$T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
B(1)	—1903(8)	2413(5)	1244(4)	19(2)	19(3)	20(3)	2(2)	—3(2)	—1(2)
B(3)	—87(9)	1884(5)	2115(3)	15(2)	21(3)	18(2)	3(2)	0(3)	—2(2)
B(4)	—2660(8)	1999(5)	2444(4)	16(2)	20(2)	15(2)	3(2)	0(2)	—5(2)
B(5)	—4093(8)	1500(5)	1407(4)	11(2)	22(3)	25(3)	1(2)	—1(2)	—2(2)
B(6)	—2368(8)	1054(5)	454(4)	14(2)	19(2)	19(2)	—2(2)	—1(2)	0(2)
B(8)	—1253(9)	593(5)	2800(4)	22(3)	19(3)	13(2)	—2(2)	—1(2)	1(2)
B(9)	—3944(9)	478(6)	2418(4)	14(2)	23(3)	17(3)	—1(2)	2(2)	2(2)
B(10)	—3747(9)	—137(6)	1102(4)	19(3)	23(3)	17(2)	—5(2)	—3(2)	—1(2)
B(11)	—970(8)	—356(5)	926(4)	18(2)	18(3)	19(2)	0(2)	0(2)	2(2)
C(2)	—122(7)	1296(4)	977(3)	14(2)	22(2)	20(2)	—1(2)	8(2)	4(2)
C(7)	211(8)	277(4)	1847(3)	13(2)	18(2)	16(2)	4(2)	—2(2)	4(2)
C(11′)	38(9)	—1341(5)	220(4)	29(2)	22(2)	21(2)	10(2)	0(2)	—1(2)

TABLE 2

COORDINATES ($\times 10^3$) AND B_{iso} ($\times 10$, Å^2) OF HYDROGEN ATOMS[a]

Atom	x	y	z	B_{iso}
H(1)	−171(5)	338(4)	97(3)	9(8)
H(2)	94(7)	153(4)	56(3)	28(12)
H(3)	126(5)	247(3)	240(2)	10(8)
H(4)	−313(6)	277(4)	291(3)	16(10)
H(5)	−552(5)	192(3)	127(2)	6(7)
H(6)	−264(5)	122(3)	−39(2)	5(7)
H(7)	146(5)	−6(3)	198(2)	6(7)
H(8)	−65(5)	39(3)	353(2)	11(8)
H(9)	−505(7)	37(5)	293(3)	38(12)
H(10)	−479(6)	−66(3)	70(2)	10(8)
H(11)	120(7)	−104(5)	−6(4)	49(16)
H(11′)	−86(10)	−146(6)	−45(5)	59(21)
H(11″)	23(9)	−211(5)	45(4)	45(16)
H(12)	−269(7)	−30(4)	269(3)	29(11)
H(13)	−269(7)	−98(4)	147(3)	42(12)

[a] Terminal hydrogens have the same numbers as corresponding B and C atoms, primed numbers refer to the Me group, H(12) and H(13) are bridging hydrogens.

TABLE 3

INTERATOMIC DISTANCES d (Å)

B(1)—H(1)	1.07(4)	C(2)—H(2)	0.94(4)
B(3)—H(3)	1.14(3)	C(7)—H(7)	0.91(3)
B(4)—H(4)	1.06(4)	Av.	0.92(4)
B(5)—H(5)	1.05(3)	C(11)—H(11)	0.91(5)
B(6)—H(6)	1.18(3)	C(11)—H(11)	1.10(6)
B(8)—H(8)	1.09(3)	C(11)—H(11)	0.87(5)
B(10)—H(10)	1.03(3)		
Av. 1.08(3)			

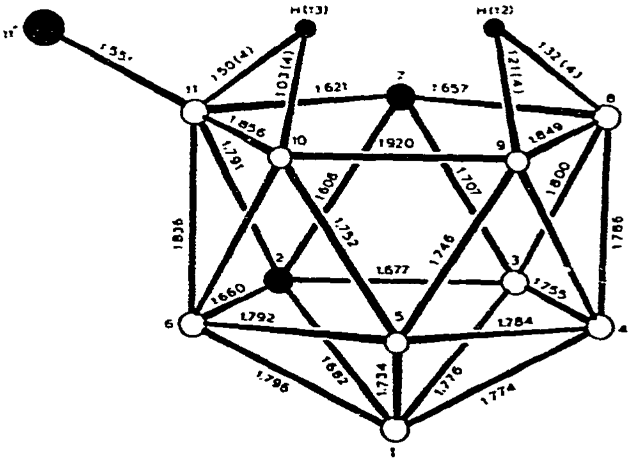

Fig. 1. Molecular of 11-methyl-2,7-dicarba-*nido*-undecaborane(13). Terminal and Me group hydrogens are not shown; s.d. B—B, B—C and C—C bonds 0.006—0.008 Å.

TABLE 4

ANGLES ω (degrees)

Angle	Number of angles	Interval of ω	Av. ω	Angle	Number of angles	Interval of ω	Av. ω	Angle	Number of angles	Interval of ω	Av. ω
Ortho-angles [a]				*Meta-angles* [a]				*Exo-angles*			
BCB	4	63,8(3)–65,0(3)	64,4(3)	BCB	5	112,5(4)–120,2(4)	116,3(4)	HCC	2	121(2)	121(2)
CCB	4	56,7(3)–67,4(3)	61,9(3)	CCB	3	110,2(4)–112,4(4)	111,6(4)	HCB	7	115(2)–119(3)	117(2)
BBB	27	56,6(3)–66,6(3)	60,0(3)	BBB	24	102,9(4)–113,5(4)	108,0(4)	HBB	32	115(3)–131(3)	122(3)
BBC	8	54,5(3)–61,4(3)	58,8(3)	BBC	13	100,7(3)–110,0(4)	104,3(4)	HBC	5	118(2)–122(2)	120(2)
CBC	2	55,9(3)–56,6(2)	56,2(2)	Av.			110,0(4)	Av.			120(2)
Av.			60,0(3)								
								HCB [b]	3	111(3)–116(4)	113(3)
								HCH [b]	3	98(5)–110(57)	105(5)
								Av.			109(4)

[a] *Ortho*-angles in the triangular faces, *meta*-angles in the pentagons including the open face. [b] Angles in the Me group.

ably distorted from the true icosahedral due to the presence of two carbon atoms in the *ortho* position. Molecule I is "squeezed" in the direction C(2)—C(7) showing distortion of both *endo* and *exo* angles * (see Table 4).

The average values of external σ-bond lengths. B—H (terminal), 1.08(3) Å and C—H 0.92(4) Å, are quite usual for carboranes [6—8]. The B(11)—Me bond length (1.551(8) Å) is almost the same as that in the *closo*-carborane compound studied by us, 1,2,3,6-Me_4-1,2-$B_{10}C_2H_8$ (1.556(9) Å) [9]. There are some regularities observed in the interatomic distances of I, e.g. 1.606(6) Å C—C distance is intermediate between those values found in *closo*- and *nido*-carboranes, e.g. 1.65 Å in 1,2-$B_{10}C_2H_{12}$ [10] and 1.55 Å in 1,2-Me_2-1,2-$B_7C_2H_9$ [6]. This effect could be explained as follows. The carbon atoms of 1.2-carborane(12) undergo mutual repulsion due to the partial positive charge on both of them and their interatomic distance is increased in comparison with that of *nido*-carboranes with carbon atoms in the *ortho* position in the open face, where this charge is largely compensated by the negative charge of the face. In the present case the position of the carbon atoms is characteristic for both *closo*, C(2), and *nido*, C(7), carboranes, and therefore the C—C distance has an intermediate value. An electron-withdrawing influence of the carbon atoms on their boron neighbours is also proved by the increase of the corresponding B—B distances to an average of 1.802(8) Å, in comparison with the average of 1.767(8) Å between the rest of the boron atoms except those in the open face. A similar effect is characteristic for other carborane systems [10,11].

The most interesting fragment of molecule I is its open face C(7)B(8)B(9)B(10)B(11). The corresponding root-mean-square plane is parallel to the plane C(2)B(3)B(4)B(5)B(6) (Table 5). The *endo*-angles of the open face are not equal (Table 6). The angle at C(7) is 9° greater than those at the boron atoms. The *exo*-angles BBMe are close to the value of 121.7° which is as expected for icosahedral *closo*-carboranes.

In the open face, interatomic distances are significantly different from those in the closed part of the polyhedral skeleton. The average B—C distance 1.639(7) Å in this face is shorter than the others (average 1.703(7) Å) due to the smaller coordination number of C(7) and its smaller excessive positive charge [12.13]. On the other hand, the B—B distances in the open face are longer than those in the closed part of the molecule (average 1.875(8) and 1.767(8) Å, respectively). Similar regularities were also found in other *nido*-carboranes and their derivatives, e.g. $(Me_4N)^+[PhCHB_{10}H_{10}CPh]^-$ [7], $(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4B_9C_2H_{11})$ [8] and $Me_2AlB_9C_2H_{12}$ [14].

The dihedral angles between the open face and the planes of the hydrogen bridges B(8)H(12)B(9) and B(10)H(13)B(11) are 79 and 73°, respectively.

This orientation of the hydrogen shows that the atomic orbitals of the corresponding boron atoms are directed towards the missing vertex of the icosahedral molecule which confirms the view of Hawthorne et al. on the structure of the open face in dicarbollide ions [15].

The direction of the B—H(bridge) apparently represents the direction of the corresponding atomic orbital of the boron atom. Therefore the RBH(bridge)

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* *Endo* angles are the angles in pentagonal fragments of the polyhedral molecule, and *exo* angles are the angles between the polyhedron edges and the external σ-bonds

TABLE 5

EQUATIONS $Ax + By + Cz = D$ OF PLANAR MOLECULAR FRAGMENTS AND DEVIATIONS OF THE ATOMS Δ (Å) FROM THESE PLANES

Plane	A	B	C	D	Atom and Δ	
I	−0.08	9.39	−3.43	8.06	C(2)	−0.013(4)
					B(3)	0.018(5)
					B(4)	−0.012(5)
					B(5)	0.002(5)
					B(6)	0.011(6)
II	−0.06	9.37	−3.50	−6.97	C(7)	0.076(4)
					B(8)	−0.071(6)
					B(9)	0.010(6)
					B(10)	0.049(6)
					B(11)	−0.088(5)
III	2.90	−1.48	−9.45	−9.66	B(8)	
					B(9)	
					H(12)	
IV	−1.78	−5.99	−7.81	−6.59	B(10)	
					B(11)	
					H(13)	

[a] Dihedral angles: I/II 0°, II/III 79°, II/IV 73°, III/IV 39°.

angle (R = H or CH_3) should be a valence angle and can be a measure of hybridization of the boron atom involved. The observed values of angle H(terminal)BH(bridge), 102(3)—103(3)°, and C(11')B(11)H(bridge), 111(2)°, correspond to the sp^3-hybridization of the boron atoms of the open face that was previously supposed [13,15,17].

The hydrogen bridges seem to be asymmetric. At least the distance H(13)—B(11) 1.50(4) Å e.g. to the boron atom bearing the Me-group is markedly longer than the other distance H(13)—B(10) 1.03(4) Å of the same bridging hydrogen, and the latter distance is close to those for ordinary B—H σ-bonds (average 1.08(3) Å). An asymmetry of hydrogen bridges testifies to polarization of the

TABLE 6

ANGLES ω (degrees) AT ATOMS OF THE OPEN FACE

Angle	ω	Angle	ω
C(7)B(8)B(9)	108.6(4)	H(12)B(8)B(9)	41(2)
B(8)B(9)B(10)	102.9(4)	H(12)B(9)B(8)	45(2)
B(9)B(10)B(11)	103.3(4)	H(13)B(10)B(11)	54(2)
B(10)B(11)C(7)	108.7(4)	H(13)B(11)B(10)	41(2)
Av.	105.9(4)	Av.	45(2)
B(8)C(7)B(11)	114.7(4)	B(8)H(12)B(9)	94(3)
		B(10)H(13)B(11)	85(3)
C(11')B(11)B(6)	120.7(4)	Av.	90(3)
C(11')B(11)B(10)	125.6(4)		
C(11)B(11)C(2)	120.8(4)		
C(11)B(11)C(7)	123.1(4)		
Av.	122.6(4)		

three centre BHB bonds with positive charges on the B(10) and possibly B(9) atoms.

Thus the electron density of these atoms should be lower than those of B(8) and B(11) notwithstanding their proximity to the carbon atom.

In conclusion it may be noted that the main geometrical features of the polyhedral skeleton in the molecule studied are caused by the presence of two differently positioned neighbouring carbon atoms and by steric repulsion of the bridging hydrogen atoms in the open face.

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