

THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAMETHYL-AMMONIUM 1-DIMETHYLAMINO-1-CARBA-UNDECAHYDRO-*closo*-DODECABORATE

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The title compound crystallizes in the trigonal system and in the $P\bar{3}$ space group. The unit cell parameters are $a = b = 2\,717.1(8)$ pm, $c = 1\,222.5(3)$ pm, $V = 7\,816.10^6$ pm³. $Z = 18$, density calculated $D_c = 0.995$ Mg m⁻³. Radiation used CuK α , $\lambda = 154.18$ pm, intensities measured at room temperature. $M_r = 260.34$, linear absorption coefficient $\mu = 0.342$ mm⁻¹, $F(000) = 2\,520$. Final $R = 0.077$ for 3 096 observed independent reflections. There is an unusual number of six isomers in the asymmetric unit. The structure is built up from $CB_{11}H_{11}.N(CH_3)_2$ anions and $N(CH_3)_4$ cations. The dimethylamino group attached to the carbon atom of the carbaborane icosahedron is not planar (as usual in aromatic compounds), but has an almost tetrahedral form, which reveals the presence of the sp^3 hybridization of the orbitals of the nitrogen atom. The C-N-C bond angles are $117.6(3)^\circ$, $112.7(3)^\circ$ and $111.8(3)^\circ$ on average. The comparison of the monocarbaborane $CB_{11}H_{11}$ with the $B_{12}H_{12}$ framework showed an overall contraction of the first one — the averaged C-B bond lengths are shorter by 6 pm and the B-B bond lengths by up to 3 pm than the B-B bond lengths in $B_{12}H_{12}$. Cartesian coordinates of the averaged framework are given. The mutual arrangement of the ions simulates fairly well the space group $R\bar{3}$, but the symmetry is reduced to $P\bar{3}$ due to the presence of the orientational (but not positional) disorder of the anions and of the cations. The centroids of the anions form a nearly perfect primitive cubic point lattice. The cations are positioned in the proximity of the center of the cube formed by the anions and consequently, their central nitrogen atoms simulate the same cubic point lattice. The arrangement of the building units resembles the $B2$ structure type with one exception: the positions on the 3-fold axes (two vertices of each cube) are vacant.

The present study reports the result of the X-ray investigation of the title compound, previously prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences¹. It deals with the first known example of a compound, where the dimethylamino group attached to the apical carbon atom of the carbaborane skeleton shows a non-planar but a nearly tetrahedral arrangement. This work forms a part of our continuing study of the structure of boranes and heteroboranes in collaboration with the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences.

EXPERIMENTAL

Determination of Crystallographic Symmetry, Unit Cell and Possible Space Groups

The title compound was prepared^{1,2} in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences. For data collection a colourless needle-like sample of dimensions approximately $0.15 \times 0.15 \times 0.75$ mm was used. Preliminary oscillation and Weissenberg photographs revealed the presence of a mirror plane perpendicular to the needle direction and the presence of a 3-fold axis perpendicular to the mirror. The $hk0$ as well as the $hk1$ layer Weissenberg photographs showed no absence for reflections with $-h + k + l \neq 3n$ nor with $h - k + l \neq 3n$ (obverse or reverse setting of the rhombohedral unit cell). Thus the crystal system is trigonal non centered one, i.e. the unit cell is not rhombohedral. The unit cell parameters (with e.s.d.'s) were calculated and refined by least squares methods³ from 23 reflections measured with a Syntex P2₁ diffractometer. The intensities of 5 399 symmetrically independent reflections were measured, using a graphite monochromator, with the same apparatus by a $\theta/2\theta$ scan up to $\theta = 50.11^\circ$ for $h = 0 \div 27$, $k = -22 \div 0$ and $l = -12 \div +12$.

Of these, 2 303 reflections were classified as unobserved using the criterion $I < 1.96\sigma(I)$. The Lorentz and polarization corrections were applied. The effects of absorption and extinction are negligible and the measured intensities were not corrected for them. The unobserved reflections and their e.s.d.'s were estimated in 16 regions of $\sin \theta/\lambda$ as the average of the values for the centric and acentric case⁴ by $F_{\text{unobs}} = (7/12) F_{\text{min}}$ and $\sigma(F_{\text{unobs}}) = (5/72)^{1/2} F_{\text{min}}$.

Checking the intensities showed the extinction symbol to be $P---$. The possible space groups⁵ are $P3$ (No. 143), $P\bar{3}$ (No. 147), $P312$ (No. 149), $P321$ (No. 150), $P\bar{3}m1$ (No. 156), $P\bar{3}m1$ (No. 164), $P31m$ (No. 157) and $P\bar{3}1m$ (No. 162). To decide about the Laue class some strong reflections were chosen and checked against additionally measured equivalent reflections, corresponding to them in the $\bar{3}m$ class. Significant differences of the compared values excluded the presence of this point symmetry. Thus, the Laue class is $\bar{3}$ and the possible space groups are $P3$ or $P\bar{3}$.

Structure Determination and Refinement

The structure of $[\text{CB}_{11}\text{H}_{11}.\text{N}(\text{CH}_3)_2]^- [\text{N}(\text{CH}_3)_4]^+$ was solved with the use of MULTAN 80 program⁶. A first — unsuccessful — attempt was made with the centrosymmetric space group $P\bar{3}$. With the space group $P3$ recognizable fragments of each of the six symmetrically independent monocarbaborane frameworks (icosahedra, "cages") were found and the six central nitrogen atoms of the cations too. But at the same time, in contradiction to the fact that the space group $P3$ is noncentrosymmetric, the $N(z)$ cumulative probability distribution showed strong indication of centricity and even of hypercentricity. By application of Fourier methods, all remaining non-hydrogen atoms of the carbaborane cages, the nitrogen atoms of the dimethylamino groups, and the nitrogen atoms of the cations were revealed. At this stage it became apparent that: (i) the orientation (not the position) of the cations and of the dimethylamino groups is disordered, (ii) the crystal structure exhibits a nearly rhombohedral arrangement.

The first fact came out when inspecting the values of the isotropic temperature factors of the carbon atoms of the methyl groups: they were significantly greater than the average of other non-hydrogen atoms. Thus, the hydrogen atoms of the methyl groups of the cations could not be included in the computations. The second fact became visible by inspecting the positions of the centroids of the carbaborane cages, which very closely simulate a rhombohedral point lattice. A test was carried out to compare the average value of the structure factors whose indexes obey the "rhombohedral" condition for the reverse setting, $h - k + l = 3n$, with the average value

of the "non-rhombohedral" structure factors. Their ratio is 1.96. This confirms the quasi-rhombohedral character of the structure of $[\text{CB}_{11}\text{H}_{11}\cdot\text{N}(\text{CH}_3)_2]^- [\text{N}(\text{CH}_3)_4]^+$ and explains the centric $N(z)$ cumulative probability distribution.

The Fourier and least squares computations were carried out by local programs⁷ in two parallel ways:

(i) By refining the positional and thermal parameters of individual atoms.

(ii) By refining the position and the orientation of the anions and of the cations as rigid bodies.

In both cases the minimized function was $\sum w\Delta^2$ with $\Delta = ||F_o| - |F_c||$ and $w = 1/(\sigma^2(|F_o|) + (0.03 F_o)^2)$. The atomic scattering factors were taken from International Tables⁸.

In the case (i) the thermal parameters of non-hydrogen atoms were refined isotropically in the initial refinement cycles and anisotropically in the later stages. The hydrogen atoms were given the optimal calculated positional parameters and fixed values of isotropic temperature factor $B = 6.5$. Non-hydrogen atoms were refined until all parameter shifts were lower than 0.14 of the corresponding estimated standard deviation.

In the case (ii) isotropic thermal parameters of the individual non-hydrogen atoms were applied. But the minimized function did not converge well and this way was abandoned.

RESULTS AND DISCUSSION

The final values of the reliability factors for the 3 096 observed reflections are:

$$R = \sum \Delta / \sum |F_o| = 0.077 \quad \text{and} \quad R_w = (\sum w\Delta^2 / \sum |F_o|^2)^{1/2} = 0.087,$$

where Δ and w as above. For all 5 399 reflections the corresponding values are $R_z = 0.114$ and $R_{wz} = 0.102$. The final difference map gave no significant features. The absolute value of the positive and negative residual peak heights was in the limit of $0.44 \cdot 10^{-6} \text{ e pm}^{-3}$ which is adequate in view of the presence of the orientational disorder of the cations and of the fact that methyl hydrogens were not included in the computations.

One formula unit, consisting of the $[\text{CB}_{11}\text{H}_{11}\cdot\text{N}(\text{CH}_3)_2]^-$ anion and the $[\text{N}(\text{CH}_3)_4]^+$ cation is shown in Fig. 1 together with the numbering scheme of atoms. Six formula units constitute the asymmetric unit of the $P3$ space-group, giving rise to wreath-like formations around each of the 3-fold axes of the unit cell, as shown in Fig. 2.

Table I gives the fractional coordinates and the equivalent isotropic thermal parameters⁹ B_{eq} of the non-hydrogen atoms, Table II the average, minimal and maximal C—B, B—B and C—N bond lengths in the $\text{CB}_{11}\text{H}_{11}$ framework and the $[\text{N}(\text{CH}_3)_4]^+$ cations. The bond lengths are in very good agreement with the values found in similar structures¹⁰⁻³². Table III gives the coordinates of the centroids of the monocarbaborane icosahedra and Table IV the distances between the representative points of the ions (the centroids and the central nitrogen atoms of the cations).

The nitrogen atom attached to the apical carbon atom of the carbaborane cage shows a nearly tetrahedral arrangement, i.e. an sp^3 hybridization of the nitrogen orbitals. This contrasts with the practically planar arrangement of dimethylamino groups in aromatic compounds. The now found sp^3 hybridization at the nitrogen in dimethylamino group makes the $p-\pi$ (skeletal) interaction difficult. This arrangement documents much weaker N-cage interaction than is the classical $\pi-\pi$ conjugation of dimethylamino group with an aromatic ring. This fact indicates either a strong influencing of the $(\text{CH}_3)_2\text{N}^-$ arrangement by packing forces in the "wreaths" or a generally weak interaction between the p electron pair on the nitrogen atom and the borane cage. For solving this problem further dimethylamino-substituted boron cages should be studied.

Table V gives the bond lengths and angles of the 6 dimethylamino groups of the asymmetric unit and their mean, minimal and maximal values. In the compound studied the mean bond C(1)—N(1) is distinctly longer — 145.2 pm — than the corresponding one in the planar conformation³³, which is 140.4 pm. The bond lengths of the two methyl C atoms in the planar conformation³³ are both equal to 147.5 pm, here they are different: N(1)—C(2) = 141.3 and N(1)—C(3) = 149.8 pm. The shorter bond includes a greater angle with the bond of the N atom to the C(1) atom of the cage: C(1)—N(1)—C(2) = 117.6°. The corresponding angle of the

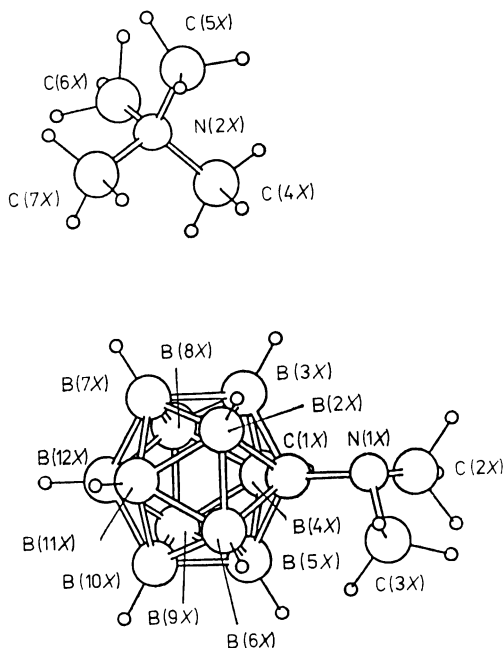


FIG. 1

The formula unit $[\text{CB}_{11}\text{H}_{11}.\text{N}(\text{CH}_3)_2]^- [\text{N}(\text{CH}_3)_4]^+$ and the numbering scheme. Here X stands for A, B, C, D, E, F respectively

longer bond is smaller: $C(1)-N(1)-C(3) = 112.7^\circ$. The angle $C(2)-N(1)-C(3)$ of the two methyl $C-N$ bonds is 111.8° . These last two angles are much nearer to the tetrahedral angle 109.47° than to the angle of approximately 120° of the planar case.

Cartesian coordinates and bond lengths of the averaged $CB_{11}H_{11}$ framework are given in Table VI. The comparison with the $B-B$ bond length 178.3 pm of the $B_{12}H_{12}$ framework³⁴ shows that all bonds of the $CB_{11}H_{11}$ framework are more or less contracted. For the $C-B$ bonds the contraction is 6 pm on average, for the $B-B$ bonds in the central part it is $1.3-3$ pm and for the bonds of $B(12)$ it is 1.4 pm. The height of all pentagonal pyramids in the framework of $B_{12}H_{12}$ is 94.74 pm, whereas in the framework of $CB_{11}H_{11}$ the heights differ. The distance of

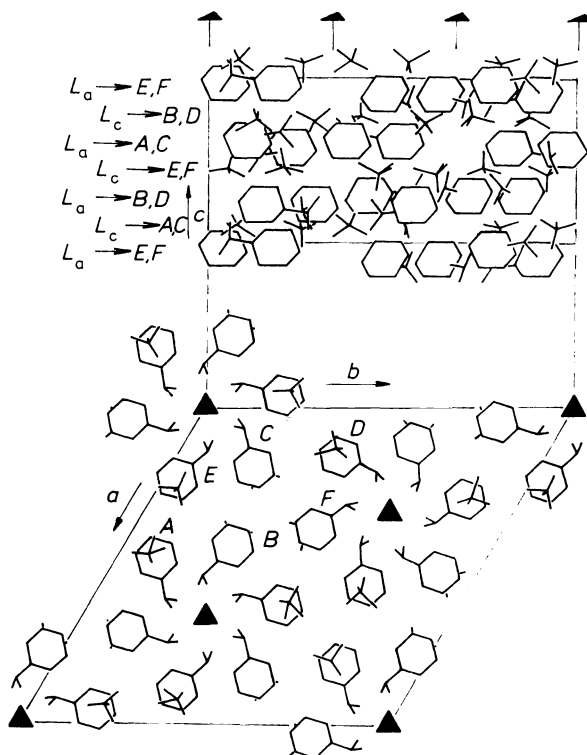


FIG. 2

The projections $a \cdot b$ (along c) and $b \cdot c$ (along a) of the content of the elementary cell. The hexagons stand for the anions $[CB_{11}H_{11}.N(CH_3)_2]^-$, the four-pointed stars for the cations $[N(CH_3)_4]^+$. The six isomers of the asymmetric unit are marked by A, B, C, D, E, F . The "wreaths" of anions and cations around the 3-fold axes are visible in the $a \cdot b$ projection. The layers of anions (L_a) and of cations (L_c) are indicated by arrows in the $b \cdot c$ projection

TABLE I

Final positional parameters with their estimated standard deviations ($\cdot 10^4$) and B_{eq} values ($\cdot 10^{-4} \text{ pm}^2$) of the non-hydrogen atoms

Atoms	x/a	y/b	z/c	B_{eq}
Molecule <i>A</i>				
C(1 <i>A</i>)	5 441(3)	1 505(3)	6 366(6)	4·6(3)
B(2 <i>A</i>)	5 326(4)	900(4)	5 910(8)	5·7(5)
B(3 <i>A</i>)	5 075(4)	925(4)	7 235(7)	5·3(4)
B(4 <i>A</i>)	4 914(4)	1 476(4)	7 208(7)	5·6(4)
B(5 <i>A</i>)	5 016(4)	1 749(4)	5 911(8)	5·2(4)
B(6 <i>A</i>)	5 238(4)	1 380(4)	5 055(7)	4·4(4)
B(7 <i>A</i>)	4 638(4)	383(4)	6 352(7)	5·2(4)
B(8 <i>A</i>)	4 369(4)	729(4)	7 199(8)	6·0(4)
B(9 <i>A</i>)	4 298(4)	1 229(4)	6 340(8)	5·2(4)
B(10 <i>A</i>)	4 538(4)	1 153(5)	5 029(7)	6·1(5)
B(11 <i>A</i>)	4 747(4)	670(4)	5 010(7)	5·7(5)
B(12 <i>A</i>)	4 129(4)	539(4)	5 874(8)	6·2(4)
N(1 <i>A</i>)	6 020(3)	1 919(3)	6 674(5)	6·3(3)
C(2 <i>A</i>)	6 109(4)	2 253(4)	7 647(8)	8·0(5)
C(3 <i>A</i>)	6·396(3)	2 270(4)	5 693(9)	9·0(5)
N(2 <i>A</i>)	4 608(3)	782(3)	966(5)	5·8(4)
C(4 <i>A</i>)	4 614(6)	297(5)	460(10)	13·7(9)
C(5 <i>A</i>)	4 571(8)	1 186(6)	300(10)	17·0(10)
C(6 <i>A</i>)	5 027(8)	1 060(10)	1 790(20)	25·0(10)
C(7 <i>A</i>)	4 053(4)	611(5)	1 650(10)	15·2(8)
Molecule <i>B</i>				
C(1 <i>B</i>)	4 883(3)	2 770(3)	1 964(6)	4·6(3)
B(2 <i>B</i>)	4 208(3)	2 267(3)	2 423(7)	4·3(3)
B(3 <i>B</i>)	4 654(5)	2 756(4)	3 318(7)	6·1(5)
B(4 <i>B</i>)	5 049(4)	3 408(4)	2 587(8)	5·8(4)
B(5 <i>B</i>)	4 849(4)	3 256(4)	1 201(8)	5·9(4)
B(6 <i>B</i>)	4 321(4)	2 518(4)	1 129(7)	5·0(4)
B(7 <i>B</i>)	3 934(4)	2 592(4)	3 204(8)	5·8(4)
B(8 <i>B</i>)	4 484(5)	3 324(5)	3 335(9)	7·2(5)
B(9 <i>B</i>)	4 571(4)	3 621(4)	2 023(7)	4·9(4)
B(10 <i>B</i>)	4 130(4)	3 056(4)	1 097(7)	5·5(5)
B(11 <i>B</i>)	3 727(3)	2 433(4)	1 878(7)	4·7(4)
B(12 <i>B</i>)	3 897(4)	3 081(3)	2 454(8)	5·3(4)
N(1 <i>B</i>)	5 281(2)	2 583(3)	1 779(6)	5·9(3)
C(2 <i>B</i>)	5 636(4)	2 616(4)	2 629(9)	9·0(5)
C(3 <i>B</i>)	5 636(4)	2 829(4)	760(10)	9·8(5)
N(2 <i>B</i>)	4 128(2)	2 800(2)	7 367(4)	4·0(3)

TABLE I
(Continued)

Atoms	x/a	y/b	z/c	B_{eq}
C(4B)	3 587(4)	2 412(5)	7 928(9)	11·5(6)
C(5B)	4 181(6)	3 386(5)	7·639(8)	11·1(9)
C(6B)	4 641(4)	2 818(5)	7·835(8)	9·8(7)
C(7B)	4 120(5)	2 743(4)	6 147(8)	8·8(6)
Molecule C				
C(1C)	1 220(3)	1 796(3)	5 414(6)	4·7(3)
B(2C)	1 697(4)	1 617(4)	6 004(8)	4·9(4)
B(3C)	1 794(4)	1 889(4)	4 633(7)	5·1(4)
B(4C)	1 538(3)	2 376(4)	4 614(7)	4·7(4)
B(5C)	1 357(4)	2 465(3)	5 943(7)	4·1(3)
B(6C)	1 417(4)	1 978(4)	6 800(8)	6·1(4)
B(7C)	2 356(4)	2 122(4)	5 520(8)	5·7(4)
B(8C)	2 273(4)	2 591(4)	4 645(7)	5·2(4)
B(9C)	2 037(4)	2 974(4)	5 447(9)	6·2(4)
B(10C)	1 954(4)	2 707(4)	6·772(8)	5·5(4)
B(11C)	2 162(4)	2 155(4)	6 833(7)	4·6(4)
B(12C)	2 509(4)	2 763(4)	6 058(7)	5·0(4)
N(1C)	625(2)	1 397(2)	5 169(6)	6·0(3)
C(28)	314(4)	1 054(4)	6 004(9)	10·0(5)
C(3C)	562(4)	1 063(4)	4 180(10)	10·5(5)
N(2C)	2 062(2)	2 571(2)	772(4)	3·5(3)
C(4C)	1 534(5)	2 060(4)	1 293(9)	12·0(6)
C(5C)	2 525(7)	2 498(8)	1 110(10)	21·0(20)
C(6C)	2 193(5)	3 088(4)	1 415(9)	10·8(7)
C(7C)	1 919(7)	2 537(7)	9 668(8)	15·0(10)
Molecule D				
C(1D)	1 776(4)	5 029(4)	3 090(8)	4·9(4)
B(2D)	2 219(6)	4 791(5)	2 590(10)	6·8(6)
B(3D)	1 977(4)	4 629(5)	4 004(9)	5·1(4)
B(4D)	1 272(6)	4 533(6)	3 990(10)	6·5(6)
B(5D)	1 084(4)	4 639(5)	2 675(9)	4·9(5)
B(6D)	1 649(4)	4 766(4)	1 782(9)	4·4(4)
B(7D)	1 908(6)	4 067(5)	3 090(10)	6·4(6)
B(8D)	1 339(5)	3 927(5)	4 002(8)	4·8(5)
B(9D)	808(4)	3 955(4)	3 239(8)	4·9(4)
B(10D)	1 080(5)	4 119(5)	1 770(9)	5·4(5)
B(11D)	1 708(5)	4 162(5)	1 808(8)	5·4(5)
B(12D)	1 206(5)	3 651(5)	2 663(9)	4·9(5)

TABLE I
 (Continued)

Atoms	x/a	y/b	z/c	B_{eq}
N(1D)	1 999(3)	5 620(3)	3 365(8)	6·3(4)
C(2D)	2 354(5)	5 839(5)	4 360(10)	9·0(6)
C(3D)	2 235(5)	6 006(4)	2 390(10)	7·8(5)
N(2D)	1 292(3)	4 089(3)	7 693(6)	5·0(3)
C(4D)	1 244(7)	4 156(9)	8 862(9)	18·0(10)
C(5D)	722(5)	3 849(6)	7 150(10)	10·5(7)
C(6D)	1 682(6)	4 653(8)	7 210(10)	18·4(9)
C(7D)	1 623(6)	3 828(8)	7 370(10)	15·0(10)
Molecule E				
C(1E)	1 807(3)	576(3)	9 799(6)	4·9(3)
B(2E)	1 590(4)	− 101(4)	9 335(8)	5·2(4)
B(3E)	1 987(4)	506(4)	8 503(7)	5·3(4)
B(4E)	2 456(4)	1 126(4)	9 430(7)	5·9(4)
B(5E)	2 350(4)	796(4)	778(7)	4·7(4)
B(6E)	1 845(4)	70(4)	674(6)	4·7(4)
B(7E)	2 200(4)	26(3)	8 522(6)	4·4(4)
B(8E)	2 676(5)	737(4)	8 529(8)	6·3(5)
B(9E)	2 932(4)	920(4)	9 966(9)	6·6(4)
B(10E)	2 560(4)	287(4)	729(8)	5·7(4)
B(11E)	2 093(4)	− 251(3)	9 845(8)	5·3(4)
B(12E)	2 789(4)	236(4)	9 421(8)	5·7(4)
N(1E)	1 392(3)	767(3)	42(6)	6·6(3)
C(2E)	1 060(4)	533(4)	997(8)	8·2(5)
C(3E)	1 062(4)	753(4)	9 042(9)	8·8(5)
N(2E)	2 530(2)	519(2)	4 371(5)	5·0(3)
C(4E)	2 560(5)	623(6)	5 600(7)	14·0(10)
C(5E)	3 040(4)	1 016(5)	3 862(8)	9·9(6)
C(6E)	2 400(8)	9 972(4)	4 110(10)	18·0(10)
C(7E)	2 058(5)	611(7)	4 020(10)	14·0(10)
Molecule F				
C(1F)	3 430(3)	5 118(3)	8 678(8)	4·1(3)
B(2F)	3 378(4)	4 602(4)	7 826(7)	3·4(4)
B(3F)	3 997(4)	5 255(4)	7 929(7)	4·6(4)
B(4F)	4 099(4)	5 524(4)	9 234(8)	4·0(4)
B(5F)	3 539(5)	5 025(5)	41(9)	5·7(5)
B(6F)	3 110(4)	4 432(5)	9 184(9)	4·5(4)
B(7F)	4 059(5)	4 676(5)	7 863(9)	5·3(5)
B(8F)	4 508(4)	5 263(4)	8 715(8)	3·8(4)

TABLE I
(Continued)

Atoms	x/a	y/d	z/c	B_{eq}
B(9F)	4 234(4)	5 112(4)	92(7)	3·7(4)
B(10F)	3 604(4)	4 384(4)	9 966(8)	4·7(4)
B(11F)	3 522(4)	4 164(4)	8 742(9)	4·9(4)
B(12F)	4 205(5)	4 547(5)	9 230(10)	5·6(5)
N(1F)	3 039(3)	5 323(3)	8 476(7)	6·0(4)
C(2F)	2 896(6)	5 562(7)	9 340(10)	10·6(8)
C(3F)	3 201(5)	5 695(5)	7 540(10)	8·9(6)
N(2F)	3 854(3)	4 629(3)	4 103(5)	4·2(3)
C(4F)	4 464(6)	4 813(6)	4 210(20)	16·8(9)
C(5F)	3 596(7)	4 070(5)	4 661(9)	12·2(8)
C(6F)	3 636(7)	4 978(7)	4 560(10)	13·0(10)
C(7F)	3 765(5)	4 608(6)	2 883(9)	10·1(7)

C(1) from the plane of its neighbours is less by more than 11 pm — it is 83·35 pm. The distance of B(12) from the plane of its neighbours is only slightly shorter than in the $B_{12}H_{12}$ framework — it is 93·63 pm.

The arrangement of the molecules exhibits still other interesting geometric features. Both of the building units (ions) of the compound may be represented by circumscribed spheres (when disregarding the dimethylamino group attached to the carbaborane cage). Choosing the centroid of the cage as the representative point of the anion and the central nitrogen atom of the tetramethylammonium as the representative point of the cation it is possible to describe the crystal structure in a simple way:

(i) Around each of the 3-fold axes there is a “wreath” of six formula units, which simulates a non-spacegroup (i.e. local) point symmetry $\bar{3}$. The pseudo-centers of inversion on the 3-fold axes $(2/3, 1/3, 8)$ and $(1/3, 2/3, 8)$ are shifted by very nearly $-c/3$ and $+c/3$ in the “z” direction with respect to the pseudo-center on the axis $0, 0, z$. Thus, the crystal structure simulates the $R\bar{3}$ space group.

(ii) Inspecting separately the six centroids arranged around one of the axes, e.g. the $0, 0, z$ axis, it may be seen that the two planes perpendicular to c defined by them are shifted by almost exactly $c/6$ with respect to their pseudo-center of inversion. There are not six, but only three (slightly corrugated) planes of cages perpendicular to c in the unit cell. The same holds for the cations, which are shifted by nearly $c/2$ in the “z” direction with respect to the cages.

TABLE II

Review of interatomic distances (pm) of the non-hydrogen atoms of the $CB_{11}H_{11}$ framework and of the $N(CH_3)_4^+$ cations in the molecules $A-F$ and overall with e.s.d.'s in parentheses. The e.s.d.'s of the minimal and maximal values are as given by the LS program, the e.s.d.'s of the mean values are calculated from the deviations of the single values with respect to the number of bonds of the same type; the number of bonds per molecule is given in parentheses

Statistical parameter	Molecule							Overall mean, minimum, maximum
	A	B	C	D	E	F		
	C(1)—B bond (5)							
Mean	169.0(6)	171.4(5)	174.5(6)	174.7(7)	173.3(5)	171.0(6)	(30 bonds)	
Minimum	161.2(14)	165.7(15)	168.1(11)	171.0(13)	169.7(12)	166.6(14)	172.3(2)	
Maximum	174.2(11)	176.2(12)	178.5(12)	182.3(18)	178.5(14)	173.3(15)	161.2(14)	
	B—B bond (25)							
Mean	176.6(3)	175.5(3)	176.0(3)	177.4(3)	176.7(3)	175.2(3)	(150 bonds)	
Minimum	167.1(20)	165.8(15)	168.2(16)	165.3(21)	165.1(17)	158.5(15)	176.2(1)	
Maximum	186.1(15)	182.0(17)	185.0(18)	190.8(15)	189.7(12)	186.6(11)	158.5(15)	
	N(2)—C(i) bond (4) $i = 4, 5, 6, 7$							
Mean	146.8(9)	150.7(6)	146.6(7)	147.3(9)	147.4(7)	148.1(9)	(24 bonds)	
Minimum	141.0(20)	148.1(10)	139.5(12)	145.1(25)	138.2(14)	145.7(24)	147.8(3)	
Maximum	157.8(14)	156.1(16)	154.9(10)	150.2(14)	152.3(11)	150.7(13)	138.2(14)	
							157.8(14)	

TABLE III

Positional parameters with their estimated standard deviations ($\cdot 10^4$) of the centroids of the carborane icosahedra

Molecule	<i>x</i>	<i>y</i>	<i>z</i>
<i>A</i>	4 811(1)	1 053(1)	6 124(2)
<i>B</i>	4 392(1)	2 924(1)	2 218(2)
<i>C</i>	1 860(1)	2 286(1)	5 724(2)
<i>D</i>	1 502(2)	4 356(2)	2 892(3)
<i>E</i>	2 274(1)	411(1)	9 627(2)
<i>F</i>	3 807(1)	4 842(1)	8 958(2)

TABLE IV

Review of distances (pm) with e.s.d.'s in parentheses between ions. The anions are represented by the centroid of the carborane icosahedron, the cations by the central nitrogen atom

Ion	Nearest neighbours	Minimal distance	Maximal distance
Anion Cation			
<i>A</i>	<i>A, A, B, B, D, E, F</i>	595·6(7)	637·6(12)
<i>B</i>	<i>A, A, B, B, C, E, F</i>	596·3(6)	649·3(5)
<i>C</i>	<i>B, C, C, D, E, E, F</i>	594·6(6)	634·4(7)
<i>D</i>	<i>A, C, D, D, E, F, F</i>	590·6(8)	639·0(8)
<i>E</i>	<i>A, B, C, C, D, E, E</i>	583·1(7)	651·5(5)
<i>F</i>	<i>A, B, C, D, D, F, F</i>	597·1(7)	633·8(7)
Overall anion-cation		583·1(7)	651·5(5)
Anion Anion			
<i>A</i>	<i>B, B, D, E, F</i>	710·1(5)	754·2(4)
<i>B</i>	<i>A, A, C, E, F</i>	710·5(3)	753·5(4)
<i>C</i>	<i>B, D, E, E, F</i>	707·4(7)	753·5(4)
<i>D</i>	<i>A, C, E, F, F</i>	707·4(7)	748·2(6)
<i>E</i>	<i>A, B, C, C, D</i>	710·5(3)	754·2(4)
<i>F</i>	<i>A, B, C, D, D</i>	710·1(5)	748·2(6)
Overall anion-anion		707·4(7)	754·2(4)
Cation Cation			
<i>A</i>	<i>B, B, D, E, F</i>	665·2(9)	779·2(9)
<i>B</i>	<i>A, A, C, E, F</i>	661·6(7)	779·2(9)
<i>C</i>	<i>B, D, E, E, F</i>	664·7(11)	777·5(8)
<i>D</i>	<i>A, C, E, F, F</i>	664·7(11)	776·7(13)
<i>E</i>	<i>A, B, C, C, D</i>	661·6(7)	775·8(8)
<i>F</i>	<i>A, B, C, D, D</i>	665·8(7)	776·7(13)
Overall cation-cation		661·6(7)	779·2(9)

(iii) Each anion has 7 nearest neighbouring cations in the range of distances (centroid to central nitrogen atom) from 661.6(7) to 779.2(9) pm and 5 nearest neighbouring anions in the range of distances from 707.4(6) to 754.2(4) and vice versa (see Table IV). The centroids are arranged in a quasi-cubic primitive point lattice with an average lattice parameter $a_{\text{cub}} = 737$ pm and an average interaxial angle $\alpha_{\text{cub}} = 87.68^\circ$. The mutual distance of the ions is in good agreement with their van der Waals radii, as derived from published data³⁵ as well as with the

TABLE V

Review of interatomic distances (pm) and angles ($^\circ$) in the dimethylamino groups *A–F* and overall with e.s.d.'s in parentheses. The e.s.d.'s of the minimal and maximal values are as given by the LS program, the e.s.d.'s of the mean values are calculated from the deviations of the single values with respect to the number of bonds (angles) of the same type

Type of bonds and angles	Molecule						Overall mean, minimum, maximum
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	
N(1)—C(1) (cage)	145.3(9)	142.4(13)	145.8(8)	144.4(13)	148.8(14)	144.6(14)	(6 bonds) 145.2(5) 142.4(13) 148.8(14)
N(1)—C(2) (Me)	144.1(12)	139.0(13)	135.5(12)	148.0(15)	141.7(12)	139.3(20)	(6 bonds) 141.3(6) 135.5(13) 148.0(15)
N(1)—C(3) (Me)	155.5(11)	151.3(13)	147.0(14)	150.3(14)	150.5(14)	144.2(15)	(6 bonds) 149.8(6) 144.2(15) 155.5(11)
C(1)—N(1)—C(2) (cage) (Me)	118.5(7)	119.0(8)	115.8(7)	117.7(10)	115.6(8)	118.7(10)	(6 angles) 117.6(3) 115.6(8) 119.0(8)
C(1)—N(1)—C(3) (cage) (Me)	113.6(6)	113.8(8)	111.8(6)	112.8(9)	112.0(8)	112.3(9)	(6 angles) 112.7(3) 111.8(6) 113.8(8)
C(2)—N(1)—C(3) (Me) (Me)	113.5(6)	108.6(7)	110.8(7)	114.0(7)	114.9(8)	109.5(11)	(6 angles) 111.9(3) 108.6(7) 114.9(8)

distances found in other boranes/borates^{26,28}. The crystal structure simulates a primitive cubic lattice realized by spheres of two magnitudes. One of the body diagonals of each cube is identical with one of the 3-fold axes of the trigonal system and its length is equal to the parameter c of the unit cell. Two vertices of each cube are placed on the 3-fold axes and are not occupied. The arrangement as a whole resembles the structure type $B2$ with one exception: two of the vertices of each cube

TABLE VI

Cartesian coordinates and bond lengths (pm) of the averaged framework $CB_{11}H_{11}$. The framework has a five-fold symmetry axis $0, 0, z$ and five mirror planes, the equation of one of them is $y = 0$ (the plane of atoms C(1), B(5), B(7) and B(12))

Atoms	Coordinates		
	x	y	z
C(1)	0·0	0·0	158·261
B(2)	121·775	-88·475	74·415
B(3)	121·775	88·475	74·415
B(4)	-46·514	143·156	74·415
B(5)	-150·523	0·0	74·415
B(6)	-46·514	-143·156	74·415
B(7)	150·080	0·0	-74·415
B(8)	46·377	142·735	-74·415
B(9)	-121·418	88·215	-74·415
B(10)	-121·418	-88·215	-74·415
B(11)	46·377	-142·735	-74·415
B(12)	0·0	0·0	-168·041

Bond lengths	Distance
C(1)—B(2), C(1)—B(3), C(1)—B(4), C(1)—B(5), C(1)—B(6)	172·30
B(2)—B(3), B(3)—B(4), B(4)—B(5), B(5)—B(6), B(6)—B(2)	176·95
B(2)—B(7), B(7)—B(3), B(3)—B(8), B(8)—B(4), B(4)—B(9), B(9)—B(5), B(5)—B(10), B(10)—B(6), B(6)—B(11), B(11)—B(2)	175·44
B(7)—B(8), B(8)—B(9), B(9)—B(10), B(10)—B(11), B(11)—B(7)	176·43
B(7)—B(12), B(8)—B(12), B(9)—B(12), B(10)—B(12), B(11)—B(12)	176·89

are vacant and consequently, the coordination of the ions is not $6 + 8 = 14$, but only $5 + 7 = 12$ (see Table IV).

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