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The Structure of Tetramethylammonium Undecahydro(triethylamine)-[I_{h-}(1551)-Δ^{20}-*closo*]dodecaborate(1−)*

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Abstract. $C_4H_{12}N^+.C_6H_{26}B_{12}N^-$, $M_r = 316.15$, monoclinic, $P2_1/c$, $a = 10.620$ (4), $b = 14.558$ (5), $c = 13.244$ (4) Å, $\beta = 90.40$ (3)°, $U = 2047.6$ Å^3, $Z = 4$ ion pairs, $D_x = 1.025$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71093$ Å, $\mu = 0.047$ mm^{-1}, $F(000) = 688$, $T = 295$ K, final $R = 0.0695$ for 965 observed reflections. $|NMe_4||Et_3NB_{12}H_{11}|$ forms as well separated ion pairs. In the anion the B_{12} fragment is not significantly distorted from an icosahedral geometry, and the B—N bond length, 1.632 (11) Å, compares favourably with that found in the previously studied potassium salt. The B_{12} framework is less distorted than that in the potassium salt.

Introduction. There has recently been some controversy concerning the relative importance of radial (cross-polyhedral) *versus* tangential B—B bonding in the series of *closo*-borane dianions $|B_nH_n|^{2-}$ (Fuller & Keppert, 1984; Housecroft & Wade, 1983). One potential method of quantifying the electron densities associated with these two kinds of interaction is through a series of deformation density studies.

In attempting to synthesize $|NMe_4|_2|B_{12}H_{12}|$ for this purpose we have serendipitously isolated a small amount of the compound $[NMe_4][Et_3NB_{12}H_{11}]$, characterized by the single-crystal X-ray diffraction study described herein. Shortly after completion of this work we became aware that the synthesis of $|NMe_4|-|Et_3NB_{12}H_{11}|$ had previously been reported, as had a crystallographic study of the potassium salt (Agafonov, Butman, Solntsev, Vinokurov, Zhukova & Kuznetsov, 1982).

* Nomenclature according to Casey, Evans & Powell (1983).

Experimental. To the solid product of an attempted synthesis of $|HNEt_3|_2[B_{12}H_{12}]$, prepared according to Miller & Muetterties (1967) but at somewhat reduced temperature (448 K), was added, dropwise, $0.2M$ NaOH with constant boiling. The resulting solution was cooled to room temperature, and an excess of aqueous $|NMe_4|Cl$ was added. On cooling to 276 K colourless crystals were deposited, which were collected, washed with cold water and recrystallized by slow evaporation of a solution in 2-methoxyethanol:water, 1:1. Clear colourless blocks, $0.03 \times 0.02 \times 0.02$ cm, mounted on a glass fibre; preliminary Weissenberg photography; CAD-4 diffractometer; lattice parameters from 25 centred reflections, $9 < \theta < 12°$; graphite-monochromated Mo $K\alpha$; for data collection $\theta_{max} = 20°$; $\omega-2\theta$ scan in 96 steps; ω-scan width $(0.8 + 0.35 \tan\theta)°$, rapid prescan, following which reflections with $I \geq 0.33\sigma(I)$ remeasured such that final net intensity had $I \geq 50\sigma(I)$, subject to a maximum measuring time of 100 s; no significant crystal movement or decay; 2039 data measured (h 0→10, k 0→14, l −12→12) over *ca* 53 h. X-ray exposure yielding 1902 unique data on merging ($R_{int} = 0.0361$); for structure solution and refinement 967 amplitudes used $|F \geq 2.0\sigma(F)|$; automatic direct methods (Sheldrick, 1984) and iterative refinement/ΔF syntheses (Sheldrick, 1976); full-matrix least squares (F); $w^{-1} = |\sigma^2(F) + 0.00268(F)^2|$; anisotropic thermal parameters for all non-H atoms; borane H atoms located from ΔF synthesis and positionally refined; methylene H atoms set in idealized positions, allowed to ride on respective C atoms; methyl functions treated as rigid groups allowed full rotation about C atom pivots, with chemical sense of resulting C—C—H angles checked; all

Table 1. *Fractional coordinates of refined atoms with standard deviations*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$U_{eq}(\text{Å}^2)$
N(1)	0.7542 (6)	0.4135 (4)	0.1496 (5)	0.0459
C(11)	0.8688 (7)	0.3897 (5)	0.0908 (6)	0.0523
C(12)	0.6439 (7)	0.3615 (6)	0.1070 (8)	0.0710
C(13)	0.7290 (8)	0.5138 (5)	0.1430 (7)	0.0663
C(14)	0.7758 (8)	0.3870 (6)	0.2573 (6)	0.0659
N(2)	0.7255 (6)	0.6456 (4)	0.5476 (4)	0.0397
C(21)	0.5905 (8)	0.6685 (6)	0.5202 (7)	0.0617
C(22)	0.5177 (9)	0.7229 (6)	0.5992 (7)	0.0759
C(31)	0.7824 (8)	0.6085 (5)	0.4500 (6)	0.0538
C(32)	0.7816 (9)	0.6743 (7)	0.3600 (7)	0.0780
C(41)	0.7928 (8)	0.7332 (5)	0.5779 (6)	0.0548
C(42)	0.9350 (8)	0.7334 (7)	0.5682 (8)	0.0851
B(1)	0.7354 (8)	0.5666 (6)	0.6348 (7)	0.0374
B(2)	0.6013 (9)	0.5059 (6)	0.6781 (8)	0.0453
B(3)	0.6846 (8)	0.5815 (7)	0.7593 (7)	0.0427
B(4)	0.8459 (9)	0.5710 (7)	0.7343 (8)	0.0519
B(5)	0.8659 (9)	0.4905 (7)	0.6388 (8)	0.0498
B(6)	0.7129 (9)	0.4502 (6)	0.6019 (7)	0.0469
B(7)	0.6313 (9)	0.4754 (7)	0.8047 (8)	0.0466
B(8)	0.7819 (9)	0.5157 (6)	0.8395 (8)	0.0493
B(9)	0.8924 (8)	0.4588 (6)	0.7653 (8)	0.0478
B(10)	0.8121 (9)	0.3824 (6)	0.6832 (8)	0.0534
B(11)	0.6486 (10)	0.3952 (7)	0.7072 (8)	0.0537
B(12)	0.7587 (8)	0.3976 (7)	0.8085 (8)	0.0504
H(2B)	0.500 (5)	0.522 (4)	0.645 (4)	
H(3B)	0.649 (5)	0.648 (4)	0.785 (4)	
H(4B)	0.905 (5)	0.635 (4)	0.747 (4)	
H(5B)	0.933 (5)	0.497 (4)	0.584 (5)	
H(6B)	0.686 (5)	0.423 (4)	0.532 (5)	
H(7B)	0.567 (5)	0.470 (4)	0.868 (4)	
H(8B)	0.815 (5)	0.539 (4)	0.917 (4)	
H(9B)	0.998 (5)	0.442 (4)	0.792 (4)	
H(10B)	0.870 (5)	0.319 (4)	0.660 (4)	
H(11B)	0.584 (5)	0.338 (4)	0.710 (4)	
H(12B)	0.765 (5)	0.349 (4)	0.868 (4)	

C—H distances 1.08 Å; $U_H^* = 0.03828$ Å^2 (BH), 0.10191 Å^2 (NMe$_4$), 0.07802 Å^2 (CH$_2$CH$_3$) and 0.11726 Å^2 (CH$_2$CH$_3$); max. Δ/σ in final cycle 0.056; max. peak and min. trough in final ΔF synthesis 0.2131 and −0.2304 e Å^{-3}; goodness-of-fit parameter 0.985; neutral-atom scattering factors for C, N, B and H inlaid in *SHELX*76; computer programs: *SHELX*76 (Sheldrick, 1976), *SHELX*84 (Sheldrick, 1984), *CALC* (Gould & Taylor, 1983) and *ORTEP*II (Johnson, 1976).

Discussion. Table 1 lists fractional coordinates of refined atoms, and Fig. 1 illustrates a perspective view of the zwitterionic anion [Et$_3$NB$_{12}$H$_{11}$]$^-$. In Table 2 are contained interatomic distances.†

The crystallographic analysis reveals the species to be the salt [NMe$_4$][Et$_3$NB$_{12}$H$_{11}$]. It is probable that the |Et$_3$NB$_{12}$H$_{11}$]$^-$ ion is formed (as its [HNEt$_3$]$^+$ salt) as a minor impurity in the preparation of [HNEt$_3$]$_2$[B$_{12}$H$_{12}$]

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* The isotropic temperature factor defined as exp $\{-8\pi^2 U(\sin^2\theta/\lambda^2\}$.

† Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates, interbond angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42536 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from B$_{10}$H$_{14}$ and Et$_3$NBH$_3$, since a temperature of only 448 K was used and it has been suggested (Agafonov *et al.*, 1982) that the predissociation of Et$_3$NBH$_3$ is incomplete below 463 K.

Distances and angles within the [Et$_3$NB$_{12}$H$_{11}$]$^-$ anion studied herein are in broad agreement with those reported for the potassium salt. Thus, there is no systematic variation in B—B lengths involving the boron atom, B(1), that carries the NEt$_3$ substituent compared with those that do not. The B—N bond lengths in the K$^+$ and [NMe$_4$]$^+$ salts are identical, 1.646 (13) and 1.635 (12) Å (two independent ion pairs in the asymmetric unit) *versus* 1.632 (11) Å respectively. All these distances are marginally longer than that, 1.600 (4) Å, in *arachno*-9-Et$_3$N-6-SB$_9$H$_{11}$ (Hilty & Rudolph, 1979), probably a consequence of the greater coordination number of B in the icosahedron. Moreover, the
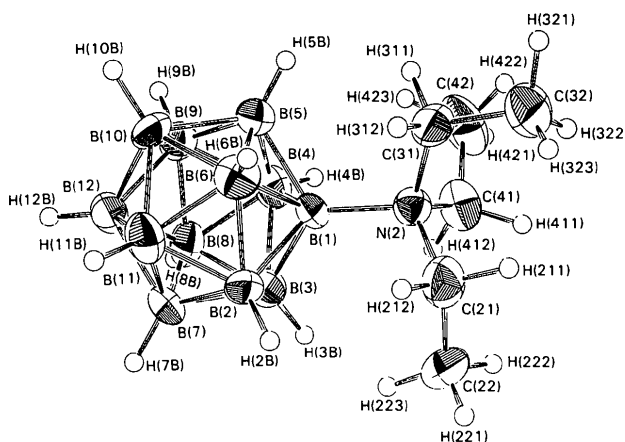

Fig. 1. View of the [Et$_3$NB$_{12}$H$_{11}$]$^-$ anion as its NMe$_4^+$ salt. Thermal ellipsoids are drawn at the 50% level, except for H atoms (radius 0.1 Å).

Table 2. *Interatomic distances* (Å)

N(1)—C(11)	1.490 (10)	B(4)—B(8)	1.751 (14)
N(1)—C(12)	1.502 (11)	B(4)—B(9)	1.754 (14)
N(1)—C(13)	1.488 (11)	B(4)—H(4B)	1.13 (6)
N(1)—C(14)	1.494 (11)	B(5)—B(6)	1.793 (14)
N(2)—C(21)	1.515 (10)	B(5)—B(9)	1.759 (14)
N(2)—C(31)	1.529 (10)	B(5)—B(10)	1.776 (14)
N(2)—C(41)	1.515 (10)	B(5)—H(5B)	1.03 (6)
N(2)—B(1)	1.632 (11)	B(6)—B(10)	1.796 (14)
C(21)—C(22)	1.527 (12)	B(6)—B(11)	1.750 (14)
C(31)—C(32)	1.530 (12)	B(6)—H(6B)	1.04 (6)
C(41)—C(42)	1.516 (12)	B(7)—B(8)	1.762 (14)
B(1)—B(2)	1.775 (13)	B(7)—B(11)	1.750 (14)
B(1)—B(3)	1.752 (13)	B(7)—B(12)	1.765 (14)
B(1)—B(4)	1.759 (13)	B(7)—H(7B)	1.09 (6)
B(1)—B(5)	1.774 (13)	B(8)—B(9)	1.745 (14)
B(1)—B(6)	1.766 (13)	B(8)—B(12)	1.784 (14)
B(2)—B(3)	1.771 (13)	B(8)—H(8B)	1.13 (6)
B(2)—B(6)	1.760 (14)	B(9)—B(10)	1.771 (14)
B(2)—B(7)	1.760 (13)	B(9)—B(12)	1.774 (14)
B(2)—B(11)	1.730 (14)	B(9)—H(9B)	1.20 (6)
B(2)—H(2B)	1.18 (6)	B(10)—B(11)	1.777 (14)
B(3)—B(4)	1.754 (14)	B(10)—B(12)	1.772 (14)
B(3)—B(7)	1.753 (13)	B(10)—H(10B)	1.15 (6)
B(3)—B(8)	1.760 (14)	B(11)—B(12)	1.774 (14)
B(3)—H(3H)	1.10 (6)	B(12)—H(12B)	1.05 (6)
B(4)—B(5)	1.738 (14)		

conformation of the pendant NEt_3 function in the $|NMe_4|^+$ salt, defined by the three B(1)—N(2)—C(i1)—C(i2) torsion angles, 73·4 (9), 176·2 (9) and 81·9 (10)° (i = 1–3), closely corresponds to one of the two distinct conformations observed in the K^+ salt.

There is, however, slight indication that the icosahedral B_{12} framework of the $|NMe_4|^+$ salt is somewhat less distorted. Thus, the range of B—B connectivity lengths determined herein is 1·738 (14)–1·796 (14) Å, c.f. 1·74–1·83 Å for the K^+ salt. This may be a consequence of the weaker polarizing power of the quarternary ammonium cation *versus* the group I*A* cation, and is consistent with less observed distortion in $|HNEt_3|_2|B_{12}H_{12}|$ (Shoham, Schomburg & Lipscomb, 1980) than in $Ca|B_{12}H_{12}|$ (Solntsev, Kuznetsov & Ponomarev, 1976).

The $|NMe_4|^+$ cation has effective T_d point symmetry, and the conformation about each N—C bond is close to staggered. There are no serious contacts within or between ions, and a crystal packing diagram, as seen along the a axis, has been deposited.

We thank the SERC for support.

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Structure of (+)-5,6,7,8-Tetradehydro-3-methoxy-17-methylmorphinan-4-ol Hemihydrate, a Potential Morphinadien for Diels–Alder Reactions

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Abstract. $C_{18}H_{21}NO_2.\frac{1}{2}H_2O$, $M_r = 292\cdot4$, orthorhombic, $P2_12_12_1$, $a = 10\cdot480$ (4), $b = 14\cdot336$ (3), $c = 21\cdot274$ (3) Å, $V = 3196\cdot2$ Å^3, $Z = 8$, $D_x = 1\cdot22$ Mg m^{-3}, $\lambda(Mo\,K) = 0\cdot71069$ Å, $\mu = 0\cdot087$ mm^{-1}, $F(000) = 1256$, $T = 293$ K, $R = 0\cdot057$ for 3827 reflections. The H atom at C(14) is in the β position, which means that the B/C ring moiety of the title compound is *cis* fused and contains two double bonds in conjugation. The two independent molecules are linked together by one water molecule *via* hydrogen bonds of 2·769 (8) $|N(1)\cdots O(W)|$ and 2·651 (9) Å $|O(2)\cdots O(W)|$.

Introduction. The Diels–Alder reaction of opium alkaloid (−)-thebaine has been investigated with many dienophiles (Bentley, 1971). Several reaction products possess, after further modification, enhanced analgesic activity. Practically all these compounds have the $6\alpha,14\alpha$-ethenoisomorphinan skeleton with the lipophilic substituent at position 7α. Only recently did it become clear that isomeric ethenomorphinans are accessible starting from modified thebaine compounds (Crabbendam, Lie, Linders & Maat, 1984; van Koningsveld, Lie & Maat, 1984*b*). These findings raised our interest in other conjugated morphinans. Codeine (1) is first mesylated with mesyl chloride (methanesulfonyl chloride) and then converted into bromocodide (2) upon treatment with lithium bromide.

When bromocodide (2) is treated with zinc in ethanol, it loses the bromine atom and the $4,5\alpha$-epoxy bridge is opened affording the 5,7-morphinadien (3),