Acta Cryst. (1991). C**47**, 993–995

Structure of Tetramethylammonium 7,8,9,10,11,12-Hexachloro-1,2,3,4,5,6-hexahydro-1-carba-*closo*-dodecaborate(1 −)

By T. Jelínek

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 *Řež u Prahy, Czechoslovakia*

and J. Fábry,* L. Hummel, K. Malý and V. Petříček

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 *Praha* 8, *Czechoslovakia*

(*Received* 12 *March* 1990; *accepted* 13 *August* 1990)

Abstract. $C_4H_{12}N^+.CH_6B_{11}Cl_6^-$, $M_r = 423{\cdot}97$, monoclinic, $P2_1/c$, $a = 11{\cdot}074\,(2)$, $b = 11{\cdot}538\,(2)$, $c = 15{\cdot}367\,(2)$ Å, $\beta = 90{\cdot}25\,(1)^\circ$, $V = 1963{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}45\,(1)$, $D_x = 1{\cdot}434$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$, $\mu = 0{\cdot}891$ mm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0{\cdot}049$, $wR = 0{\cdot}062$ for 3050 observed reflections. The positions of all H atoms were determined from difference Fourier maps. The mean values of chemically equivalent interatomic distances in the carborane cage are in good agreement with previous determinations of carboranes. The maxima in the Fourier maps which belonged to the methyl C atoms were elongated but not split, which may be an indication of either continuous disorder or intensive temperature movement. Some of the Cl···methyl distances are shorter (approximately 0·3 Å) than the sum of relevant van der Waals radii (3·8 Å), all other distances are longer.

Introduction. The aim of the present study was to determine the structure of $[N(CH_3)_4]^+.[CB_{11}H_6Cl_6]^-$.

Experimental. The preparation is described by Plešek, Jelínek, Drdákova, Heřmánek & Štíbr (1984), Plešek, Jelínek & Štíbr (1984) and Jelínek, Plešek, Heřmánek & Štíbr (1986). D_m was determined by flotation (*n*-hexane/dimethyl iodide). A colourless crystal of irregular shape (approximately 0·4 × 0·4 × 0·8 mm) was mounted on a four-circle Hilger & Watts diffractometer equipped with an Nb β filter.

Cell parameters were determined by least squares from 50 reflections ($3 < \theta < 14^\circ$). 50 reflections, not necessarily the same as in the previous procedure, were scanned to obtain profiles and widths of peaks at various angles and directions [method suggested by Clegg (1981)]. The widths of peaks evaluated by the method of Lehmann & Larsen (1974) were widened by adding 0·16° 2θ (Blessing, Coppens & Becker, 1974). $\omega/2\theta$ step-scan mode (one step = 0·08° 2θ), scan speed varied from 1 to 8° 2θ min^{-1}, the scan range was between 19 and 36 steps. *hkl* range $0 \le h \le 14$, $0 \le k \le 15$, $-20 \le l \le 20$. The learnt-profile method (Diamond, 1969; Clegg, 1981) was used for obtaining intensities and their e.s.d.'s.

Three standard reflections were measured after every 30 reflections and a small variation of their intensities (±5%) was observed. Linear correction for this variance and Lp corrections were applied. Absorption correction was neglected. The number of independent reflections was 4739, the number of observed reflections was 3050 [$I > 1{\cdot}96\sigma(I)$].

The analogous structure of $[N(CH_3)_4]^+.[CB_{11}H_6Br_6]^-$ (Fábry, Hummel, Malý, Petříček & Jelínek, 1984) yielded the approximate fractional coordinates of Cl atoms. The positions of other atoms were found in difference Fourier maps. Maxima from the methyl C atoms were elongated and maxima from the H atoms were smeared; the centroids of the latter were, however, in positions where methyl H atoms would be expected.

The structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = [\sigma^2(F_o) + (0{\cdot}03|F_o|)^2]$ where $\sigma(F_o)$ is derived from counting statistics. As the unconstrained refinement of methyl groups failed due to shifts of H atoms into an improbable configuration, a constrained refinement of methyl groups was applied. Each of the four methyl groups was replaced by a 'virtual' group with fixed tetrahedral geometry (C_{methyl}—H = 0·95 Å).

The constrained refinement of $[N(CH_3)_4]^+$ reduced the number of parameters refined for the methyl H atoms from 48 to 7: four angles of rotation about N—C_{methyl} axes (e.s.d. of each rotation angle about 3°) and three isotropic temperature factors for each H atom of the 'virtual' methyl group.

Positions and anisotropic temperature factors were refined for all non-H atoms, positions and isotropic temperature factors for the carborane H atoms; a total of 239 parameters were refined.

---

* Author to whom correspondence should be addressed.

0108-2701/91/050993-03$03.00

Table 1. *Fractional atomic coordinates and B_{eq} values for non-*H *atoms* (*Hamilton*, 1959)

	x	*y*	*z*	B_{eq}(Å²)
C(1)	0·3025 (3)	0·7813 (3)	0·3226 (2)	3·89 (9)
B(2)	0·1618 (4)	0·8198 (4)	0·2890 (2)	3·53 (9)
B(3)	0·2936 (4)	0·8766 (4)	0·2383 (3)	3·80 (9)
B(4)	0·4081 (4)	0·7676 (4)	0·2430 (3)	4·0 (1)
B(5)	0·3471 (4)	0·6454 (4)	0·2966 (2)	3·81 (9)
B(6)	0·1952 (4)	0·6779 (3)	0·3251 (2)	3·53 (9)
B(7)	0·1116 (3)	0·6990 (3)	0·2279 (2)	2·91 (8)
B(8)	0·1733 (3)	0·8220 (3)	0·1746 (2)	2·92 (8)
B(9)	0·3257 (3)	0·7908 (3)	0·1461 (2)	3·22 (8)
B(10)	0·3589 (3)	0·6470 (3)	0·1819 (2)	3·27 (8)
B(11)	0·2273 (3)	0·5908 (3)	0·2333 (2)	2·99 (8)
B(12)	0·2131 (3)	0·6803 (3)	0·1388 (2)	2·75 (7)
Cl(7)	−0·04413 (7)	0·65999 (8)	0·21807 (6)	4·07 (2)
Cl(8)	0·08129 (7)	0·91467 (7)	0·10799 (6)	3·86 (2)
Cl(9)	0·39271 (8)	0·85137 (9)	0·05014 (6)	4·56 (2)
Cl(10)	0·45996 (8)	0·55319 (9)	0·12447 (7)	4·89 (3)
Cl(11)	0·19156 (9)	0·43990 (7)	0·22998 (5)	4·12 (2)
Cl(12)	0·16366 (8)	0·62331 (8)	0·03652 (5)	3·80 (2)
N	0·7595 (2)	0·7757 (2)	0·9822 (2)	3·43 (6)
C(2)	0·7541 (4)	0·8695 (5)	1·0480 (3)	6·0 (1)
C(3)	0·7111 (7)	0·6688 (5)	1·0175 (5)	9·4 (2)
C(4)	0·8856 (4)	0·7574 (5)	0·9548 (3)	6·1 (1)
C(5)	0·6877 (5)	0·8099 (6)	0·9058 (4)	8·4 (2)

Table 2. *Bond distances* (Å)

C(1)—B(2)	1.700 (5)	B(5)—B(6)	1·781 (6)
C(1)—B(3)	1·702 (5)	B(5)—B(10)	1·768 (5)
C(1)—B(4)	1·704 (5)	B(5)—B(11)	1·759 (5)
C(1)—B(5)	1·692 (6)	B(6)—B(7)	1·770 (5)
C(1)—B(6)	1·685 (5)	B(6)—B(11)	1·768 (5)
B(2)—B(3)	1·782 (6)	B(7)—B(8)	1·777 (5)
B(2)—B(6)	1·768 (6)	B(7)—B(11)	1·790 (5)
B(2)—B(7)	1·769 (5)	B(7)—B(12)	1·789 (5)
B(2)—B(8)	1·763 (5)	B(8)—B(9)	1·781 (5)
B(3)—B(4)	1·787 (6)	B(8)—B(12)	1·781 (5)
B(3)—B(8)	1·767 (5)	B(9)—B(10)	1·785 (6)
B(3)—B(9)	1·766 (5)	B(9)—B(12)	1·786 (5)
B(4)—B(5)	1·768 (6)	B(10)—B(11)	1·784 (5)
B(4)—B(9)	1·763 (5)	B(10)—B(12)	1·783 (5)
B(4)—B(10)	1·763 (6)	B(11)—B(12)	1·789 (5)
B(7)—Cl(7)	1·788 (4)	B(8)—Cl(8)	1·795 (4)
B(9)—Cl(9)	1·796 (4)	B(10)—Cl(10)	1·792 (4)
B(11)—Cl(11)	1·786 (4)	B(12)—Cl(12)	1·787 (3)
N—C(2)	1·482 (6)	N—C(4)	1·475 (5)
N—C(3)	1·451 (7)	N—C(5)	1·469 (6)

Table 3. *Average bond distances* (Å) *and standard deviations of chemically equivalent bonds in the carborane cage and of* B—Cl *bonds*

A representative of each type of bond is given.

Bond	Average bond distance
C(1)—B(2)	1·697 (8)
B(2)—B(3)	1·777 (9)
B(2)—B(8)	1·765 (4)
B(7)—B(8)	1·783 (5)
B(7)—B(12)	1·786 (4)
B(7)—Cl(7)	1·791 (4)

Table 4. *Shortest intermolecular distances* (Å) *between methyl groups and carborane ligands*

Cl···Cl	Cl(7)···Cl(11^{i})	3·707 (1)
Cl···$H_{carborane}$	H(2)*···Cl(12^{ii})	3·27 (3)
$H_{carborane}$···C_{methyl}	H(4)†···C(5^{iii})	3·30 (3)
Cl···C_{methyl}	Cl(10)···C(3^{iv})	3·502 (7)
	Cl(11)···C(2^{v})	3·556 (5)
	Cl(12)···C(4^{vi})	3·663 (4)
	Cl(8)···C(4^{vi})	3·671 (5)
	Cl(11)···C(4^{viii})	3·736 (5)
	Cl(12)···C(3^{vii})	3·739 (6)
	Cl(8)···C(2^{vi})	3·771 (5)

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, (-y+\frac{1}{2})+1, z+\frac{1}{2}$; (iii) $x, (-y+\frac{1}{2})+1, (z+\frac{1}{2})-1$; (iv) $x, y, z-1$; (v) $-x+1, (y+\frac{1}{2})-1, (-z+\frac{1}{2})+1$; (vi) $x-1, y, z-1$; (vii) $-x+1, -y+1, -z+2$; (viii) $-x+1, -y+1, -z+1$.

* B(2)—H(2) = 1·08 (4) Å.

† B(4)—H(4) = 1·26 (3) Å.

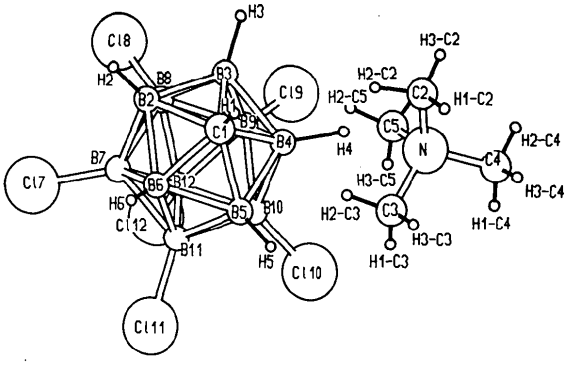

Fig. 1. View of the structural motif of $[N(CH_3)_4]^+.[CB_{11}H_6Cl_6]^-$.

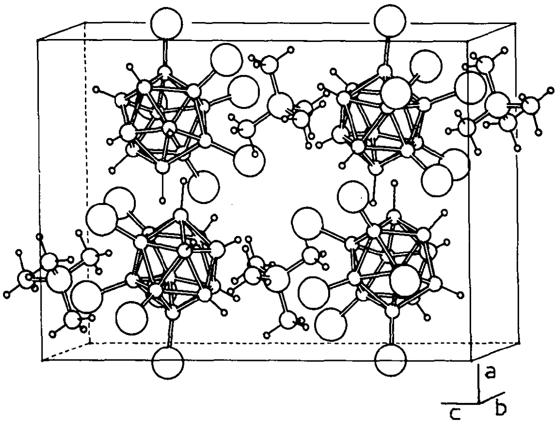

Fig. 2. View of the unit cell of $[N(CH_3)_4]^+.[CB_{11}H_6Cl_6]^-$.

The extinction correction was insignificant. Scattering factors (including anomalous dispersion) were taken from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1974, Vol. IV).

The final $R = 0{\cdot}081$ and $wR = 0{\cdot}076$ for all reflections, and $R = 0{\cdot}062$ and $wR = 0{\cdot}049$ for observed reflections only. $S = 1{\cdot}267$, $U_{0\cdot01} = (1{\cdot}233,\ 1{\cdot}302)$ (Abrahams, 1969), $(\Delta/\sigma)_{max} < 0{\cdot}03$, $(\Delta/\sigma)_{average} < 0{\cdot}01$. Residual electron densities are $\Delta\rho_{max} = 0{\cdot}42$, $\Delta\rho_{min} = -0{\cdot}41$ e Å^{-3}. All calculations were performed using the *SDS* system of programs (Petříček & Malý, 1988).

Discussion. Fractional coordinates and B_{eq} values are given in Table 1,* the intramolecular distances in Table 2. Those of the carborane cage are in very good agreement with previously determined structures (Císařová, 1985). It is worth emphasizing the regularity of the carborane cage (see also Table 3). The motif as well as packing of molecules in the unit cell are depicted in Figs. 1 and 2, respectively. van der Waals radii for relevant atoms or the methyl group are: H = 1·2, methyl = 2·0, Cl = 1·8 Å (*Handbook of Chemistry and Physics*, 1979). In Table 4 the shortest intermolecular distances between carborane ligands and methyl groups are listed. Although these distances where H atoms are involved are the least reliable, this overview illustrates that distances for all these pairs except Cl···methyl are somewhat longer than the sum of van der Waals radii. This may be qualitatively explained by the attraction of negative Cl atoms to the positive tetramethylammonium group.

---

* Lists of structure factors, anisotropic thermal parameters, bond angles, H-atom coordinates and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53482 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abrahams, S. C. (1969). *Acta Cryst.* **A25**, 165–173.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Císařová, I. (1985). PhD Thesis, Faculty of Science, Charles Univ., Prague, Czechoslovakia. (In Czech.)

Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Diamond, R. (1969). *Acta Cryst.* **A25**, 43–55.

Fábry, J., Hummel, L., Malý, K., Petříček, V. & Jelínek, T. (1984). Unpublished work.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Handbook of Chemistry and Physics (1979). Edited by R. C. Weast. Boca Raton, Florida: CRC Press.

Jelínek, T., Plešek, J., Heřmánek, S. & Štíbr, B. (1986). *Collect. Czech. Chem. Commun.* **51**, 819–929.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

Petříček, V. & Malý, K. (1988). *The SDS System.* A program package for X-ray structure determination. Institute of Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

Plešek, J., Jelínek, T., Drdáková, E., Heřmánek, S. & Štíbr, B. (1984). *Collect. Czech. Chem. Commun.* **49**, 1559–1562.

Plešek, J., Jelínek, T. & Štíbr, B. (1984). *Polyhedron*, **3**, 1351–1355.

Acta Cryst. (1991). C47, 995–998

Structure of Ethyl 5-Chloro-1-cyanomethyl-3-phenylindole-2-carboxylate

By T. N. Chandrakantha and Puttaraja

Department of Physics, Bangalore University, Jnana Bharathi Campus, Bangalore-560 056, India

and Vasantha Pattabhi

Department of Crystallography and Biophysics, Madras University, Guindy Campus, Madras-600 025, India

(*Received* 24 *May* 1990; *accepted* 21 *August* 1990)

Abstract. $C_{19}H_{15}ClN_2O_2$, M_r = 338·80, triclinic, $P\bar{1}$, a = 13·984 (2), b = 10·069 (2), c = 13·248 (1) Å, α = 72·61 (1), β = 82·60 (1), γ = 69·27 (2)°, V = 1668·9 (2) Å^3, Z = 4, D_m = 1·34 (5), D_x = 1·36 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 2·03 mm^{-1}, $F(000)$ = 704, T = 300 K, final R = 0·066 for 3915 observed reflections [$I \geq 3\sigma(I)$]. There are two independent molecules per asymmetric unit. The indole nucleus is slightly bent along the C(8)—C(9) bond. The phenyl ring connected to the indole rings is rotated about the C(3)—C(10) bond by 52·6 (5)° in molecule *A* and 49·9 (5)° in molecule *B*. The carboxyl group makes a dihedral angle of 25·3 (5)° with the mean plane of the indole rings in *A* and 14·7 (3)° in *B*. The C—C≡N chain is linear and is inclined at an angle of 86·1 (4)° to the mean plane of the indole rings in *A* and 83·3 (4)° in *B*.

Introduction. Indole and its derivatives possess various important pharmacological properties like central nervous system depressant, muscle relaxant and anti-allergic properties (Harris & Uhle, 1960; Wei & Stanley, 1970; Houlihah, 1973; White & Black, 1976; Ho, Haegman & Perisco, 1986). The title compound is an important precursor to a physiologically active tetrahydropyrazinoindole (Reynolds & Carson, 1970). It can be readily converted to 8-chloro-10-phenyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole in a single step by reductive cyclization using lithium aluminium hydride.

0108-2701/91/050995-04$03.00