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N-Butylpyridinium undecachloro-carbadodecaborate and comparison with similar compounds

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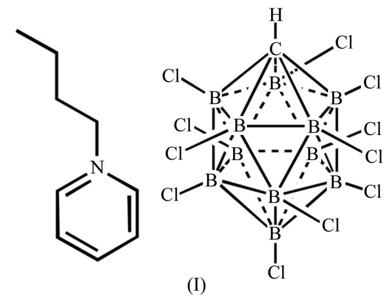
The title compound, $C_9H_{14}N^+\cdot CHB_{11}Cl_{11}^-$, was obtained in the course of our continuing studies of the low-melting salts of *closo*- and *nido*-carborane cage anions with alkylpyridinium and dialkylimidazolium cations. The title compound is the first example of a pyridinium salt of a perchlorinated carborane anion. The structure consists of one *N*-butylpyridinium cation counterbalanced by one perchlorinated carborane cage anion per asymmetric unit. By changing the counter-ion, different packings are observed, and to try to understand this the new structure is compared with five similar compounds.

Comment

In the last decade, the low-melting salts of the family of the title compound, *N*-butylpyridinium undecachlorocarbadodecaborate, (I), have been studied (Larsen *et al.*, 2000; Dymon *et al.*, 2008; Reed, 2010). Recently, the perchlorinated carborane species became available due to the work of Ozerov and co-workers (Gu *et al.*, 2010). Compound (I) is the first example of a pyridinium salt of a perchlorinated carborane anion. The general synthetic route to obtain such compounds involves metathesis of an alkylpyridinium halide with caesium carborane salts in dichloromethane, with concominent precipitation of the caesium halide by-product (for more details, see *Experimental*).

The structure of carborane (I) consists of one butylpyridinium cation counterbalanced by an undecachlorinated carborane cage anion per asymmetric unit (Fig. 1). Structural analysis of the cation shows no significant differences from a typical substituted pyridine. The larger displacement ellipsoid observed for atom C1 is due to thermal movement of this terminal C atom of the alkyl chain. Thermal motion of atom C1 makes the C1—C2 bond appear to be shorter than a typical C—C distance [C1—C2 = 1.408 (15) Å]. In the anion, all the B—B and B—Cl distances are ~1.8 Å and the different torsion angles (near 0°) are within the expected ranges for undecachlorocarbadodecaborate.



(I)

An intermolecular analysis shows that atom Cl8 in the undecachlorinated carborane interacts through a halogen–π interaction with the *N*-butylpyridinium cation [B8—Cl8→*Cg*1 = 3.768 (4) Å; *Cg*1 is the centroid of the pyridine ring] (halogen bonding is a highly directional interaction, more directional than hydrogen bonding and comparable in strength; Metrangolo *et al.*, 2008). It is important to point out that there is no evidence of strong π–π interactions between the *N*-butylpyridinium rings, so we can presume that the driving force for the crystal packing is related to the hydrogen-bond interaction H10···Cl2^{i} [2.94 (5) Å; symmetry code: (i) $-x + 1, -y + 1, -z + 1$] between undecachlorinated carboranes (see Fig. 2) (van den Berg & Seddon, 2003; Lu *et al.*, 2007). It is interesting to note the short Cl1···Cl1^{ii} distance of 3.410 (3) Å [symmetry code: (ii) $-x + 1, y, -z + \frac{1}{2}$], suggesting an interaction between these atoms, in addition to the short H···Cl cation–anion distances [minimum distance: H1*B*···Cl2^{iii} = 2.8838 (15) Å; symmetry code: (iii) $x, -y, z - \frac{1}{2}$].

A supramolecular analysis shows that the most relevant and strongest intermolecular interactions in this structure are

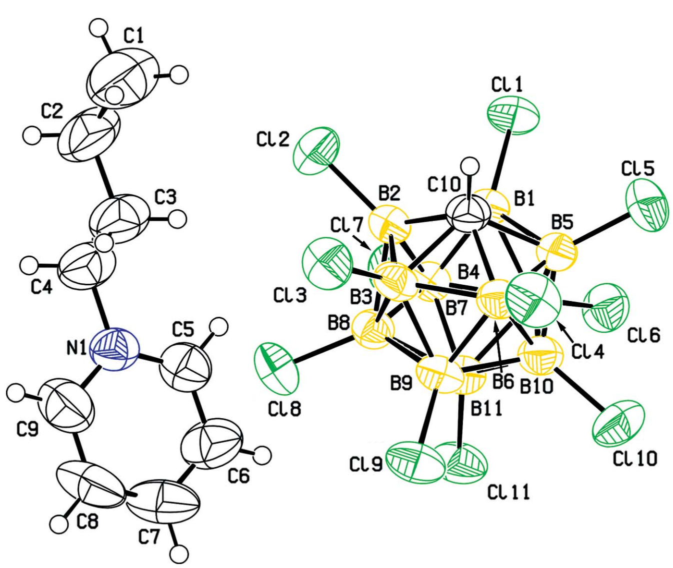


Figure 1
The molecular conformation and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

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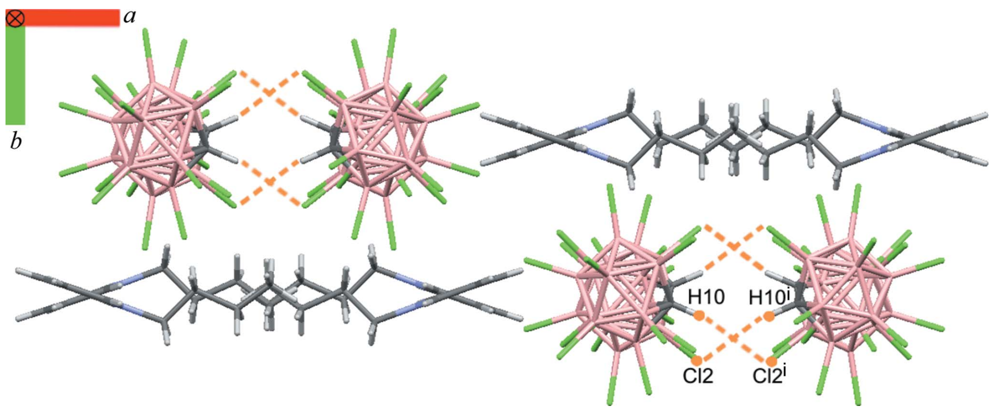

Figure 2
The H···Cl interactions (dotted lines) in the crystal packing of (I). [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

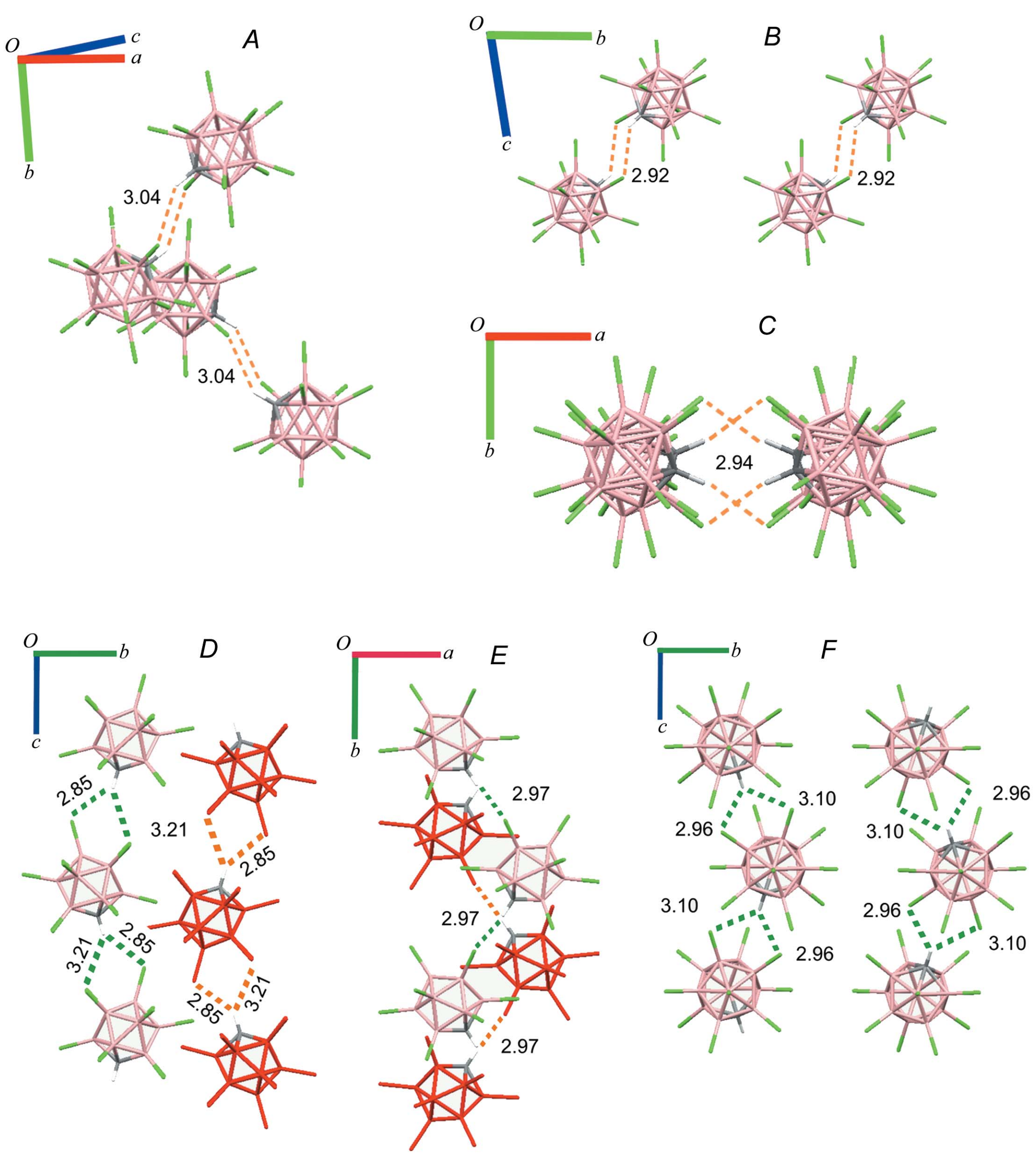

Figure 3
The packing arrangements for undecachlorocarbadodecaborate with different counter-ions. *A*, *B* and *C* are larger counter-ions, and *D*, *E* and *F* are smaller counter-ions, where *A* is Me_3–Si–H–Si–Me_3 (Hoffmann *et al.*, 2006), *B* is *N*-butylpyridinium (this work), *C* is $(C_3H_7)_3$–Si–(ODCB) (ODCB is *o*-dichlorobenzene; Hoffmann *et al.*, 2006), *D* is Me–Cl–Me (Stoyanov *et al.*, 2010), *E* is Et–Cl–Et (Stoyanov *et al.*, 2010) and *F* is $[H(MeOH)_3]^+$ (Stoyanov *et al.*, 2008). Distances are given in Å.

clearly the already-mentioned hydrogen bonds. A dimer-like anionic substructure can be described as a result of the above-mentioned contacts (Fig. 2). An adequate expansion allows the visualization of the infinite columnar arrangement built by these dimeric units, where the alternating positions of the carborane are evidenced by the torsion angle between subsequent units [C10$\cdots$*Ce*$\cdots$$Ce^{iv}$$\cdots$$C10^{iv}$ = 32.91°; *Ce* is the centroid of the undecachlorocarbadodecaborate cage; symmetry code: (iv) $x, -y + 1, z + \frac{1}{2}$; see Table 1 for more details].

A similar columnar arrangement is formed by the counter-ions. The alkyl chains are located tail-to-tail in *x*, but shifted by around 4 Å [C1$\cdots$$C1^{v}$ = 4.09 (2) Å; symmetry code: (v) $-x + 1, y, -z + \frac{1}{2}$]. The aromatic rings of contiguous *N*-butylpyridinium cations in the column are alternating, with an angle of ~38° between pyridine rings [C7—N1—$N1^{iv}$—$C7^{iv}$ = 38.2 (3)°; see Fig. 2].

The different packing arrangements of the undecachlorocarbadodecaborate were studied by the analysis of a set of five similar compounds (Fig. 3 and Table 1). One major difference observed in the crystal packing (Fig. 3) is related to the intermolecular C—H$\cdots$Cl interactions between pairs of undecachlorocarbadodecaborate units. It was found that where the counter-ion is large, the carboranes associate in pairs to form column of dimers [Fig. 3; structures *A*, *B* (present structure) and *C*], but there is a variation in the torsion angle defined by the two C$\cdots$*Ce* vectors in the dimers, and also in that relating the centroids of the undecachlorocarbadodecaborate into the double chain; the torsion angle changes as a result of the approach between dimers (shortest distance H$\cdots$Cl). In the case of structure *C*, the first of these angles has increased to 76° which leads to the separations between chains being controlled by the H$\cdots$Cl distance (being shorter and equal). In contrast, for the smaller cations (Fig. 3; structures *D*, *E* and *F*), single strands are formed, where there is a bifurcated interaction of the H atom with two Cl atoms of the adjacent undecachlorocarbadodecaborate unit. Adjacent channels can be coplanar or displaced. The overall packing is therefore seen to be a balance between the various interactions available along with the relative sizes and shapes of the components.

Experimental

The title compound was obtained by a metathesis reaction between caesium undecachlorocarbadodecaborate and *N*-butylpyridinium chloride in a dichloromethane–acetone mixture under aerobic conditions. *N*-Butylpyridinium chloride (100 mg) was dissolved in dichloromethane (20 ml). An equimolar quantity of caesium undecachlorocarbadodecaborate was dissolved in a dichloromethane–acetone mixture (1:1 *v*/*v*, 10 ml) and the resulting solution was added to the *N*-butylpyridinium chloride solution. The formation of a white precipitate was evident almost immediately. The reaction mixture was stirred at room temperature for 30 min. Subsequently, the solution was filtered through a Celite plug to remove the CsCl precipitate. The mother liquor was pumped off to dryness, the oily residue was redissolved in a small amount of dry dichloromethane and colourless scale-like crystals of (I) were grown by slow vapour diffusion of hexane into a dichloromethane solution at 243 K.

Crystal data

$C_9H_{14}N^+\cdot CHB_{11}Cl_{11}^-$
M_r = 657.22
Monoclinic, $C2/c$
a = 32.929 (3) Å
b = 10.2492 (6) Å
c = 17.6340 (19) Å
β = 111.100 (12)°
V = 5552.4 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.11 mm^{-1}
T = 298 K
0.1 × 0.1 × 0.05 mm

Data collection

Oxford Gemini E CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.203, T_{max} = 1.000
14744 measured reflections
5577 independent reflections
3411 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.233
S = 1.05
5577 reflections
302 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Methyl and methylene H atoms were idealized at C—H = 0.96 and 0.97 Å, respectively, and allowed to ride. Aromatic ring H atoms were idealized at C—H = 0.93 Å. H-atom displacement parameters were taken as $U_{iso}(H) = 1.5U_{iso}(C)$ for methyl groups or $1.2U_{iso}(C)$ otherwise. Atom H10 of the undecachlorocarbadodecaborate anion was located in a difference Fourier map and refined freely.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3157). Services for accessing these data are described at the back of the journal.

References

Berg, J. A. van den & Seddon, K. R. (2003). *Cryst. Growth Des.* **3**, 643–661.
Dymon, J., Wibby, R., Kleingardner, J., Tanski, J. M., Guzei, I. A., Holbrey, J. D. & Larsen, A. S. (2008). *Dalton Trans.* pp. 2999–3006.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gu, W., McCulloch, B. J., Reibenspies, J. H. & Ozerov, O. V. (2010). *Chem. Commun.* pp. 2820–2822.

Table 1
Structural comparison of different undecachlorocarbadodecaborate salt compounds.

Superscripts i, ii, iii, iv and v refer to different symmetry operations according to each structure, *x* refers to the corresponding C number and *Ce* denotes the centroid of the undecachlorocarbadodecaborate anion; ODCB is *o*-dichlorobenzene.

Counter-ion	$C_x\cdots Ce\cdots Ce^{v}\cdots C_x^{v}$ (°)	$Ce^{i}\cdots Ce^{ii}\cdots Ce^{iii}\cdots Ce^{iv}$ (°)	Cl···H (Å)†	Distance between chains (Å)‡	Distance between chains (Å)§
A $Me_3Si–H–SiMe_3$	0	180	3.04	3.73	3.79, 3.83
B $C_4H_9–C_5H_5N$	33	176	2.94	3.56, 4.43	3.76, 3.94
C $(C_3H_7)_3–Si–(ODCB)$	76	167	2.92	2.92	3.78, 4.08
D Me–Cl–Me	0	116	2.97	3.52, 4.06	3.45
E Et–Cl–Et	89	152	2.85, 3.21	3.58, 3.67	3.58, 3.67
F $[H(MeOH)_3]^+$	107	147	2.96, 3.10	3.36	3.46, 3.58

† The closest H···Cl distance forming dimers or not, depending on the compound. ‡ The minimum Cl···Cl distance between undecachlorocarbadodecaborate anions along the chain. § The minimum Cl···Cl distance between undecachlorocarbadodecaborate anions of different chains. References: entries *A* and *C*: Hoffmann *et al.* (2006); *B*: this work; *D* and *E*: Stoyanov *et al.* (2010); *F*: Stoyanov *et al.* (2008).

Hoffmann, S. P., Kato, T., Tham, F. S. & Reed, C. A. (2006). *Chem. Commun.* pp. 767–769.

Larsen, A. S., Holbrey, J. D., Tham, F. S. & Reed, C. A. (2000). *J. Am. Chem. Soc.* **122**, 7264–7272.

Lu, Y.-X., Zou, J.-W., Wang, Y.-H. & Yu, Q.-S. (2007). *Int. J. Quantum Chem.* **107**, 1479–1486.

Metrangolo, P., Meyer, F., Pilati, T., Resnati, G. & Terraneo, G. (2008). *Angew. Chem. Int. Ed.* **47**, 6114–6127.

Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Reed, C. A. (2010). *Acc. Chem. Res.* **43**, 121–128.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stoyanov, E. S., Stoyanova, I. V., Tham, F. S. & Reed, C. A. (2008). *J. Am. Chem. Soc.* **130**, 12128–12138.

Stoyanov, E. S. Stoyanova, I. V., Tham, F. S. & Reed, C. A. (2010). *J. Am. Chem. Soc.* **132**, 4062–4063.