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7,8-Bis(pyridinium-2-ylthio)-7,8-dicarba-*nido*-undecaborate Trifluoromethanesulfonate

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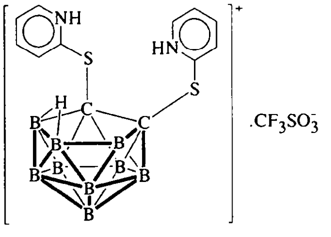
Abstract

In the title compound, $C_{12}H_{20}B_9N_2S_2^+.CF_3SO_3^-$, the open B_3C_2 face of the carborane contains three terminal H atoms and one bridging B—H—B unit, with B—H distances of 1.12 (3) and 1.39 (3) Å. The S—C—C/N angles to the pyridinium groups differ appreciably, possibly because of H···H steric interactions between pyridinium and carborane. Hydrogen bonds of the form N—H···O link two anions and two cations over an inversion centre.

Comment

We are interested in ligands based on the partially degraded 1,2-dicarba-*closo*-dodecaborane derivatives, the 7,8-dicarba-*nido*-undecaborates, *e.g.* the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate anion $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and its transition metal complexes (Jones, Villacampa, Crespo, Gimeno & Laguna, 1997; Crespo, Gimeno, Jones & Laguna, 1996, and references therein). We have also begun to study related sulfur-containing ligands and present here the structure of the zwitterionic salt 7,8-bis(pyridinium-2-ylthio)-7,8-dicarba-*nido*-undecaborate trifluoromethanesulfonate, (I).



(I)

As can be seen in Fig. 1, atoms C7, C8, S1 and S2 are approximately coplanar (mean deviation 0.06 Å), but the pyridinium groups point to opposite sides of this plane, with C21—S2···S1—C11 130.7 (1)°. The C—S bond lengths of 1.778 and 1.782 (2) Å to the carborane and of 1.749 and 1.765 (2) Å to the pyridinium groups may be regarded as normal. The C—S—C angles differ appreciably [102.3 (1) at S1 and 107.5 (1)° at S2] for no obvious reason; the major differences in the S—C—N/C angles [S1—C11—N16 114.8 and S2—C21—N26 116.2 (2)° *cf.* S1—C11—C12 127.3 and S2—C21—C22 125.5 (2)°] may be attributed to unfavourable steric interactions between the H11 or H22 atoms and the carborane unit [H12···H10*B* 2.22 and H22···H2 2.54 Å].

We have determined the structures of seven heavy-atom derivatives of the above-mentioned diphosphine (references above and unpublished work). The light-atom (B/C) positions were necessarily imprecise and the carborane H-atom positions extremely imprecise. How-

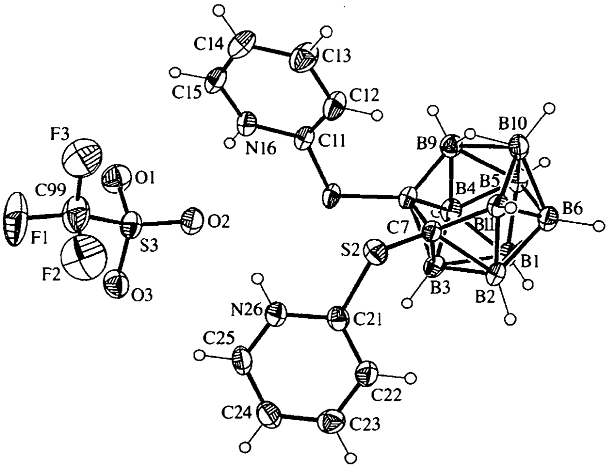


Fig. 1. The ionic title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

ever, in all cases but one, the four open-face H atoms were tentatively established as three terminal (B—H) and one (semi-) bridging (H—B—H). A previous light-atom structure, the tetramethylammonium salt of the diphosphine anion (Teixidor *et al.*, 1995) was not precise enough to provide further information. We wished to obtain a more reliable determination and this is provided by the current structure with freely refined H atoms; the B9—B10 bond is asymmetrically bridged, with B10—H10*B* 1.12 (3), B9—H10*B* 1.39 (3) Å and B10—H10*B*—B9 95 (2)°.

The carborane bond lengths involving carbon are C7—C8 1.595 (3), open face C—B 1.622 and 1.628 (4), and interior C—B 1.710–1.731 (4) Å. The bridged B—B bond (B10—B9) is, at 1.864 (4) Å, at least 0.04 Å longer than all other B—B bonds.

The ionic packing involves dimeric units linked by hydrogen bonds over an inversion centre. Associated dimensions are N26···O2 2.725 (3), H26···O2 1.89 Å and N26—H26···O2 158.0°, and N16···O3^{i} 2.792 (3), H16···O3^{i} 1.93 Å and N16—H16···O3^{i} 164.7° [symmetry code: (i) $-x$, $-y$, $1-z$]. (Because these H atoms were idealized, e.s.d.'s are not quoted.) The S—O bond not involved in hydrogen bonding is shorter than the other two; S3—O1 1.429 (2), S3—O3 1.445 (2) and S3—O2 1.448 (2) Å.

Experimental

Crystals of the title compound were obtained as a by-product from the reaction of the *closo*-derivative $C_2B_{10}H_{10}$-(2-$SC_5H_4N)_2$ with silver trifluoromethanesulfonate in dichloromethane.

Crystal data

$C_{12}H_{20}B_9N_2S_2^+.CF_3SO_3^-$
$M_r = 502.78$
Monoclinic
$P2_1/n$
$a = 11.4438\,(12)$ Å
$b = 9.5077\,(10)$ Å
$c = 21.497\,(3)$ Å
$\beta = 98.245\,(10)°$
$V = 2314.8\,(5)$ Å^3
$Z = 4$
$D_x = 1.443$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 66 reflections
$\theta = 4.7$–$12.5°$
$\mu = 0.364$ mm^{-1}
$T = 173\,(2)$ K
Tablet
0.60 × 0.60 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{min} = 0.826$, $T_{max} = 0.930$
4219 measured reflections
4069 independent reflections
2682 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0203$
$\theta_{max} = 25°$
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 1$
$l = -25 \rightarrow 0$
3 standard reflections every 247 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0349$
$wR(F^2) = 0.0807$
$S = 0.872$
4069 reflections
314 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.233$ e Å^{-3}
$\Delta\rho_{min} = -0.279$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C11	1.749 (2)	C8—C7	1.595 (3)
S1—C8	1.778 (2)	C8—B9	1.628 (4)
S2—C21	1.765 (3)	C7—B11	1.622 (4)
S2—C7	1.782 (2)	B9—B10	1.864 (4)
B2—C7	1.728 (3)	S3—O1	1.429 (2)
B3—C8	1.725 (4)	S3—O3	1.445 (2)
B3—C7	1.731 (4)	S3—O2	1.448 (2)
B4—C8	1.710 (4)		
C11—S1—C8	102.31 (12)	C12—C11—S1	127.3 (2)
C21—S2—C7	107.46 (11)	N26—C21—S2	116.2 (2)
N16—C11—S1	114.8 (2)	C22—C21—S2	125.5 (2)

B atoms were refined anisotropically but with 33 similarity restraints to *U* components of neighbouring atoms. Most H atoms were refined using a riding model; the B—H atoms of the carborane open face were located in difference syntheses and refined freely.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1234). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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