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Methyltriphenylphosphonium 2-methyl-1-sulfido-1,2-dicarba-*closo*-dodecaborane(12)

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Abstract

In the title compound, $CH_3(C_6H_5)_3P^+ \cdot C_3H_{13}B_{10}S^-$, the negative charge of the sulfido group connected to the carborane cage is balanced by the phosphonium cation. In the cation, one of the three phenyl groups is disordered, exhibiting two orientations. In the anion, the C_{cage}—C_{cage} distance is 1.792 (5) Å.

Comment

In 1,2-dicarba-*closo*-dodecaboranes, the C_{cage}—C_{cage} or C1—C2 bond length varies considerably, depending on the number of substituents and atom species connected to the cluster C atoms. Thus, values of 1.57 (1)–1.634 (3) Å are reported for the 1,2-H_2 compounds (Šubrtová *et al.*, 1980; Novák *et al.*, 1983), and much larger values of 1.816 (6)–1.858 (5) Å are observed for compounds in which S atoms are connected to both cluster C atoms (Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990). In recent papers, we have studied the elongation of the C1—C2 distance and suggested an empirically derived equation to calculate this distance (Kivekäs *et al.*, 1994, 1995). In order to synthesize new ligands for complexation and to study further the contribution of different types of C_{cage} substituents on the lengthening of the C1—C2 bond, we have now synthesized the title compound, (I), and determined its crystal structure.

(I)
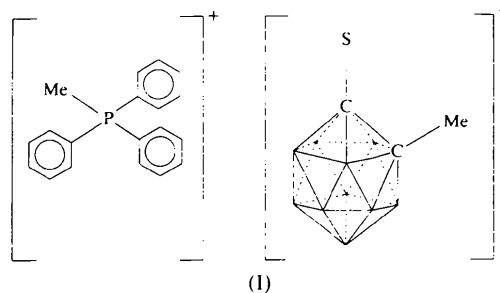
The structure of (I) consists of discrete $CH_3(C_6H_5)_3P^+$ and $C_3H_{13}B_{10}S^-$ ions without any close contact between them. In the $CH_3(C_6H_5)_3P^+$ cation, one of the phenyl groups is disordered, exhibiting two orientations, with a dihedral angle between these two phenyl orientations of 33.0 (12)°. The bond parameters of the cation are as expected.

In the $C_3H_{13}B_{10}S^-$ anion, the sulfido and methyl groups are connected to the cluster C atoms of
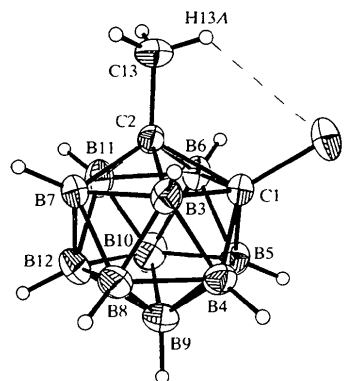

Fig. 1. A simplified view of the anion of (I) with displacement ellipsoids at the 20% probability level and H atoms shown as spheres of an arbitrary radius.

the 1,2-dicarba-*closo*-dodecaborane moiety. The C13—C2—C1—S torsion angle is $-0.3(5)°$; the S—C1—X [118.0(3)–124.2(3)°] and C13—C2—X angles [116.3(3)–122.9(4)°] ($X = C_{cage}$ or B) do not show much variation. One of the methyl H atoms is oriented toward the S atom and the H13A4$\cdots$S distance of 2.68 Å indicates a hydrogen bond between the methyl group and the S atom (Taylor & Kennard, 1982).

The C1—C2 distance [1.792(5) Å] in (I) is significantly shorter than the equivalent bond [1.816(6)–1.858(5) Å] in 1,2-S_2-substituted *closo* compounds (Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990). This is in line with the observation (Kivekäs *et al.*, 1994) that the contribution of the carbon substituent to the lengthening of C1—C2 bond is smaller than that of the sulfur.

Experimental

Commercial 1-methyl-*o*-carborane was sublimed under high vacuum at 0.01 mm Hg (1 mm Hg = 133.322 Pa) prior to use. 1-Methyl-2-thiol-*o*-carborane was synthesized according to the literature procedure of Teixidor, Rius *et al.* (1990). The solvent was placed under vacuum to eliminate dissolved oxygen. All organic and inorganic salts were analytical reagent grade and were used as received. The reaction was carried out under an N_2 atmosphere employing Schlenk techniques. The IR spectrum was obtained using KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H NMR (300.0 MHz), $^{13}C\{^1H\}$ NMR (75.4 MHz), $^{31}P\{^1H\}$ NMR (121.5 MHz) and $^{11}B\{^1H\}$ NMR (96.3 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shift values for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to an internal standard of SiMe$_4$ in deuterated solvents. Chemical shift values for ^{11}B NMR spectra were referenced relative to external BF$_3$·OEt$_2$. The chemical shift value for the $^{31}P\{^1H\}$ NMR spectrum was referenced relative to external 85% H_3PO_4. To a three-necked round-bottomed flask (15 ml) containing deoxygenated methanol (10 ml) were added sodium metal (24.2 mg, 1.05 mmol) and 1-methyl-2-thiol-*o*-carborane (200 mg, 1.05 mmol). The mixture was stirred at room temperature for 1 h. After removal of the solvent *in vacuo*, the residue was dissolved in water (5 ml) and an excess of methyltriphenylphosphonium bromide in water (10 ml) was added to afford a white solid, (I) (yield 430.8 mg; 88%). Spectroscopic data: FTIR (KBr), ν (cm^{-1}): (B—H) 2565, 2530; ^1H NMR (CD$_3$CN), δ (p.p.m.): 2.11 (*s*, 3H, C$_c$—CH$_3$), 3.24 [*d*, ^1J(H,P) = 15 Hz, 3H, $C_{19}H_{18}P^+$], 7.84–7.94 (*m*, 15H, $C_{19}H_{18}P^+$); ^{11}B NMR (CD$_3$CN), δ (p.p.m.): -5.25 (2B), -6.72 [*d*, ^1J(B,H) = 146.3 Hz, 3B], -10.30 [*d*, ^1J(B,H) = 171.4 Hz, 2B], -12.21 (3B); $^{31}P\{^1H\}$ NMR (CD$_3$CN), δ (p.p.m.): 23.1 (*s*, $C_{19}H_{18}P^+$); $^{13}C\{^1H\}$ NMR (CD$_3$CN), δ (p.p.m.): 8.0 [*d*, ^2J(C,P) = 57.9 Hz, $C_{19}H_{18}P^+$], 23.0 (C$_c$—CH$_3$), 120.34 (*s*, $C_{19}H_{18}P^+$), 130.3 [*d*, J(C,P) = 12.1 Hz, $C_{19}H_{18}P^+$], 133.4 [*d*, J(C,P) = 11.3 Hz, $C_{19}H_{18}P^+$], 135.1 [*d*, J(C,P) = 3.0 Hz, $C_{19}H_{18}P^+$].

Crystal data

$C_{19}H_{18}P^+ \cdot C_3H_{13}B_{10}S^-$
$M_r = 466.60$
Monoclinic
$P2_1/c$
$a = 12.386(3)$ Å
$b = 15.837(2)$ Å
$c = 14.515(3)$ Å
$\beta = 105.00(2)°$
$V = 2750.2(9)$ Å^3
$Z = 4$
$D_x = 1.127$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 5.86–8.13°$
$\mu = 0.186$ mm^{-1}
$T = 294(2)$ K
Cube
$0.32 \times 0.22 \times 0.16$ mm
Colourless

Data collection

Rigaku AFC-5S diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5056 measured reflections
4819 independent reflections
2323 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25.16°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 18$
$l = -17 \rightarrow 16$
3 standard reflections every 150 reflections intensity decay: <0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.161$
$S = 0.997$
4819 reflections
340 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.205$ e Å^{-3}
$\Delta\rho_{min} = -0.228$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

P—C15A	1.807(4)	P—C15B	1.785(6)
P—C21	1.780(4)	S—C1	1.735(4)
P—C14	1.795(3)	C1—C2	1.792(5)
P—C27	1.811(4)	C2—C13	1.510(5)
C15A—P—C21	112.9(3)	B4—C1—S	124.2(3)
C15A—P—C14	106.8(3)	B6—C1—S	118.0(3)
C15A—P—C27	108.2(3)	B3—C1—S	118.8(3)
C15B—P—C21	104.8(5)	S—C1—C2	118.9(3)
C15B—P—C14	111.4(5)	C13—C2—B11	122.9(4)
C15B—P—C27	111.4(5)	C13—C2—B7	122.1(4)
C21—P—C14	108.87(17)	C13—C2—B6	116.8(4)
C21—P—C27	108.83(16)	C13—C2—B3	117.0(4)
C14—P—C27	111.28(17)	C13—C2—C1	116.3(3)
B5—C1—S	123.9(3)		

One of the phenyl groups of the methyl triphenylphosphonium cation (C15–C20) is disordered, assuming two orientations with site occupancies of 0.619(19) for C15A–C20A and 0.381(19) for C15B–C20B. The disordered group was refined as a rigid group.

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N,N'-Diphenylbenzamidinium nitrate

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Abstract

The title compound, $C_{19}H_{17}N_2^+ \cdot NO_3^-$, consists of a diphenylbenzamidinium cation $[Ph(H)NC(Ph)N(H)Ph]^+$ hydrogen-bonded to a planar nitrate anion through an $N—H \cdots O$ interaction; both ions lie on a twofold axis. The hydrogen-bonded $N \cdots O$ distance is short at 2.7767 (19) Å, and placing the N—H protons in calculated positions gives an $N—H \cdots O$ angle of 173°. There are no other significant intermolecular interactions between the ions.

Comment

Following our earlier work on gallium complexes involving amidine ligands (Barker *et al.*, 1996), we are now investigating the properties of solutions containing amidines in the presence of gallium and nitrate ions in view of the pharmaceutical effects provided by the synergism of the species within such mixtures (Fimiani *et al.*, 1990; Bradley *et al.*, 1992). In the course of this work, crystals of the title compound, (I), were isolated from solutions containing gallium nitrate and the amidinium anion. The crystal structure of this material has been determined since it affords an opportunity to study the structural features of an N,N'-disubstituted amidinium cationic system for which only limited data have been published previously (Krechl *et al.*, 1989; Caron & Donohue, 1969). The structural details of these systems are also relevant to the emerging field of imprintable polymers (Wulff *et al.*, 1997; Wulff & Schonfeld, 1998).

(I)
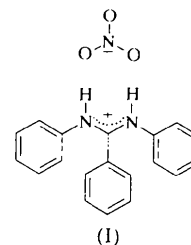
The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The illustrated structural unit has a twofold rotational axis through atoms O2, N1, C5, C4 and C1, which implies that the nitrate anion is accurately planar. The overall configuration of the amidinium cation resembles that of the $[PhNC(Ph)NPh]^-$ anion coordinated to a $GaMe_2$ fragment (Barker *et al.*, 1996). Thus, the phenyl ring on the central C atom is in a *cis* (Z) orientation with respect to the rings on the amine N atoms, and the two C—N bond lengths of the N—C—N amidine skeleton are now identical at 1.3266 (18) Å, rather than different [1.351 (7) and 1.295 (6) Å] as observed in the free ligand N,N'-diphenylbenzamidine (Alcock *et al.*, 1988). There is a slight twist in the C6—N2—C5—C4 fragment, with a torsion angle of 10.1 (2)°; furthermore, the plane of the central phenyl ring is aligned at 65.8 (1)° with respect to the plane of the terminal phenyl rings.

A notable feature of the structure is the significant hydrogen bonding between the N—H protons of the cation and the nitrate O atoms, which is consistent with both the broad N—H absorption at $3290\,cm^{-1}$ in the