$C_{16}H_{20}N_6O_4S$

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1-Diisopropylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane(12), (1), and 1,2-Bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane(12), (2), at 193 K

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Abstract

In the title compound (1), $C_9H_{27}B_{10}P$, the methyl and diisopropylphosphine groups are bonded to the C atoms of the 1,2-dicarbaborane cage. Bond lengths in (1) are P—C(cage) 1.876 (6) Å and C(cage)—C(cage) 1.731 (9) Å. In the 1,2-bis(diisopropylphosphine)-substituted carborane (2), $C_{14}H_{38}B_{10}P_2$, the P—C(cage) distances are 1.894 (3) and 1.891 (3) Å, and the C(cage)—C(cage) distance is 1.719 (3) Å. In both compounds, the P atoms are shifted from their expected positions towards the other cluster C atom resulting in low values of the P—C(cage)—C(cage) angles.

Comment

Computational studies on 1,2-dithioether-substituted 1,2-dicarba-*closo*-dodecaboranes, or *o*-carboranes, using semi-empirical quantum-mechanical calculations (CNDO, MNDO) suggest extremely long C—C distances. This implies that, to quantify HOMO–LUMO caps or other electronic properties, these otherwise useful calculations are not feasible unless the molecular parameters (distances and angles) are precisely known.

To overcome this difficulty we propose that the C—C distances in *o*-carborane derivatives can be empirically derived from:

$$d = d_o + \Sigma a_i + \Sigma S_i$$

where d is the C—C distance in the carborane derivative, d_o the C—C distance [1.634 (3) Å] in C-non-substituted *o*-carborane (Šubrtová, Línek & Hašek, 1980), a_i is the additive electronic contributions and S_i the additive steric contributions.

In order to ascertain the a_i and S_i values it is necessary to synthesize many carborane derivatives, incorporating various types of C substituents, and solve their crystal structures. For this purpose, we synthesized the title compounds (1) and (2). Unfortunately, we have not been able to obtain good crystals of (1) despite many attempts. Though the data quality of (1) is modest and the obtained bond parameters not as accurate as those of (2), the data it produces are significant both from a qualitative viewpoint and for use in semi-empirical methods. If the above equation is rewritten as

$$d = d_o + \Sigma(a_i + S_i)$$

the total contribution to the C—C bond distance of every radical can be estimated. Although the C—C distances in (1) and (2) are used with care, it appears that the —CH$_3$ contribution to the C—C distance is comparable to that of the P[CH(CH$_3$)$_2$]$_2$ group. This may suggest similar orbital contributions of both fragments to the cluster's cohesion, which could imply a simple σ-bond interaction. The reasonably good agreement between experimental and semi-empirically calculated results for phosphine-substituted *o*-carborane derivatives supports this hypothesis. To the contrary, large discrepancies have been found when S-substituted fragments are bonded to *o*-carborane. In that case other interactions besides the σ bonding may take place.

(1) (2)
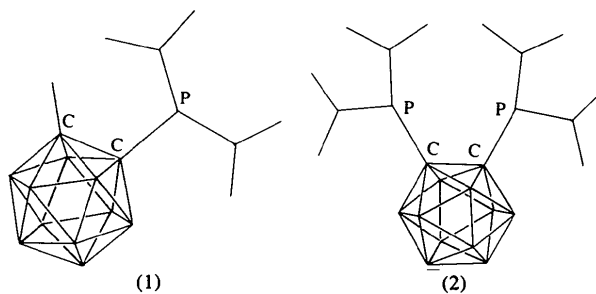
In (1) the P atom is bonded in a pyramidal arrangement to two C atoms of two isopropyl groups and to the C(1) atom of the carborane moiety. The P—C bond lengths are equal within experimental error. In 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane, (3) (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994), and 1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane, (4) (Kivekäs, Teixidor, Viñas & Nuñez, 1995), the P—C(cage) distances agree with that

of (1), but the P—C(aryl) bonds are approximately 0.05 Å shorter than the P—C(cage) distances. In (1), the angles around C(1) vary considerably and indicate that the P atom is shifted away from its expected position and towards the C(2) and C(13) atoms, thus decreasing the P—C(1)—C(2) angle, and opening the P—C(1)—B(4) and P—C(1)—B(5) angles. On the other hand, the angles around C(2) vary only within about 3°. The P···C(13) distance is 3.277(7) Å, only about 0.25 Å shorter than the sum of the van der Waals radii (Bondi, 1964; Allinger, Hirsch, Miller, Tyminski & Van-Catledge, 1968). The P···C(13) distance, the angles around the cluster C atoms and the P—C(1)—C(2)—C(13) torsion angle indicate the absence of a significant repulsion between C(13) and P.
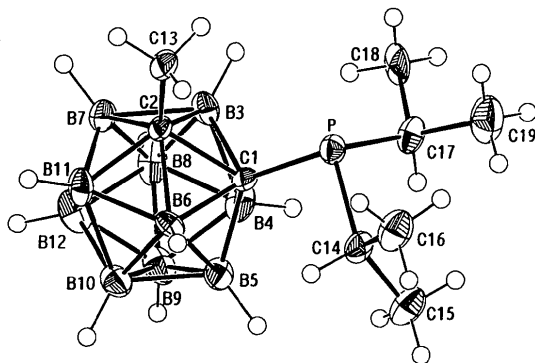

Fig. 1. View of the structure of (1) with displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Compound (2) has approximate C_2 symmetry and the twofold axis is located midway through the C(1)—C(2) and B(9)—B(12) bonds. The C(1)—C(2) distance does not deviate significantly from the corresponding distances in (1) and (3). Thus, owing to the inaccurate results of (1), we cannot obtain the possible minor difference in the C(1)—C(2) distance by changing the 2-methyl substituent of (1) to the diisopropylphosphine substituent of (2). However, the distances in these 1,2-substituted carboranes are significantly longer than in the 1-substituted compound (4) [1.666(9) Å], as expected. The P—C bond lengths in (2) show a similar trend to those observed in (3) and (4), with the P—C(cage) bond slightly longer than other P—C bonds. The C—C bond lengths in the diisopropyl groups are as expected, but the opening of the P(1)—C(16)—C(18) and P(2)—C(19)—C(20) angles is somewhat surprising. A similar opening has been observed for the P—C(14)—C(15) angle in (1).

The angles around the cluster C atoms in (2) show a trend similar to those around the diisopropylphosphine-substituted C(1) atom in (1): the angles vary considerably, the values for the P—C(cage)—C(cage) angles are low, while the P(1)—C(1)—B(4), P(1)—C(1)—B(5),

P(2)—C(2)—B(7) and P(2)—C(2)—B(11) angles are the most opened. The decrease of both P—C(cage)—C(cage) angles in (2) results in a short P(1)···P(2) distance of 3.193(1) Å, which is 0.51 Å shorter than the sum of the corresponding van der Waals radii (Bondi, 1964). However, the free-electron pairs of the P atoms are oriented away from each other. Moreover, the opening of the P(1)—C(1)—C(2)—P(2) torsion angle to 12.1(2)°, compared with the value of 0.5(8)° for the P—C(1)—C(2)—C(13) angle in (1), reduces the repulsion between the P atoms.
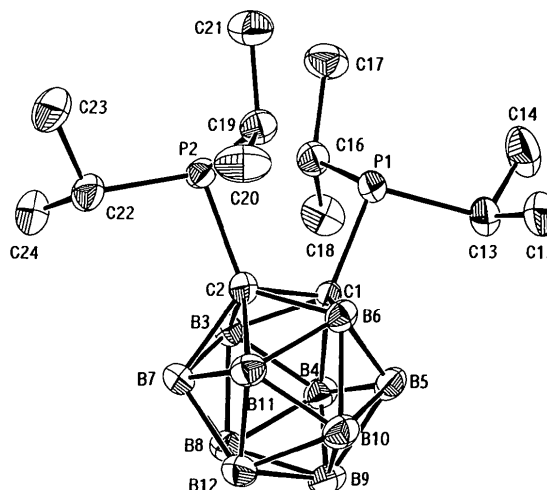

Fig. 2. View of the structure of (2) with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity.

The trend of decreasing P—C(cage)—C(cage) angles has also been found in (3) and (4). We proposed that the movement of the P atoms in the structures is probably due to the need to avoid repulsion between the organic substituents connected to the P atom and the carborane cage (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994). Taking into account the considerable repulsion between the cluster C-atom substituents, the observed configuration of (2) can be considered to balance the repulsion between the P atoms and between the bulky isopropyl groups and the carborane cage.

Experimental

Before use, 1-methyl-*o*-carborane and *o*-carborane (Dexsil Chemical Corporation) were sublimed under high vacuum. A 1.6 *M* solution of *n*-butyllithium in hexane from Fluka and chlorodiisopropylphosphine from Aldrich were used as purchased.

Compound (1) was synthesized as follows. To a three-necked round-bottom flask (250 ml) fitted with a dinitrogen inlet/outlet, containing deoxygenated dry ethyl ether (50 ml), 1-methyl-*o*-carborane (1.5 g, 9.4 mmol) was added. The mixture was cooled (ice–water) during the addition (10 min) of *n*-butyllithium (6 ml, 9.5 mmol). After stirring for 30 min at the ice–water temperature, the mixture was stirred

at room temperature for 30 min, and again cooled to 273 K before the addition of chlorodiisopropylphosphine (1.5 ml, 9.5 mmol) over 30 min.

The ice bath was removed, and the mixture was stirred for 4 d at room temperature, and under reflux for 30 min. Once cooled, the solution was concentrated under vacuum. Diethyl ether (15 ml) and water (20 ml) were added. Stirring was continued for 10 min before the two layers were separated. The diethyl ether extract was dried and evaporated under vacuum. Evaporation of the solvent yielded a white solid (1.7 g, 64%) which was recrystallized from diethyl ether/petroleum ether (1:1, v/v).

Analysis: calculated for $C_9H_{27}B_{10}P$, C 39.40, H 9.92%; found, C 39.66, H 9.89%. FTIR (KBr) ν (cm^{-1}): 2952, 2924, 2868 (C—H); 2614, 2579 (B—H). ^{1}H FTNMR (250 MHz, CDCl$_3$, 298 K, TMS) δ (p.p.m.): 1.27 (m, 12, CH$_3$), 2.09 (s, 3, CH$_3$), 2.20 (m, 2, CH). ^{11}B FTNMR (128 MHz, CDCl$_3$, 298 K, BF$_3$·Et$_2$O) δ (p.p.m.): −0.17 (d, $^1J_{B,H}$ = 148.6 Hz, 1B), −5.36 (d, $^1J_{B,H}$ = 152.0 Hz, 1B), −8.49 (d, $^1J_{B,H}$ = 131.6 Hz, 2B), −9.34 (d, $^1J_{B,H}$ = 165.1 Hz, 2B), −10.06 (d, $^1J_{H-H}$ = 127.7 Hz, 4B). ^{31}P FTNMR (161 MHz, CDCl$_3$, 298 K, H$_3$PO$_4$) δ (p.p.m.): 33.82 [s, P(^iPr)$_2$].

The procedure for (2) is as for (1) with the quantities: o-carborane 1.5 g, 10.4 mmol; n-butyllithium 13 ml, 20.8 mmol; chlorodiisopropylphosphine 3.31 ml, 41.6 mmol. After removal of the ice bath, the mixture was stirred for 16 h at room temperature and at reflux for 1 h. Once cooled, the mixture dried. Cold diethyl ether (15 ml) and water (30 ml) were added in this order. The organic layer was collected, dried with MgSO$_4$ and evaporated to dryness. The oily material obtained was dissolved in the minimum volume of diethyl ether. After 16 h at 263 K a crystalline solid was obtained (2.4 g, 61%). Suitable crystals for X-ray analysis were obtained from diethyl ether/petroleum ether (1:1, v/v).

Analysis: calculated for $C_{14}H_{38}B_{10}P_2$, C 44.66, H 10.17%; found C 44.79, H 10.33%. FTIR (KBr) ν (cm^{-1}): 3011, 2959, 2951, 2927, 2911, 2866, (C—H); 2660, 2613, 2602, 2577, 2567, 2557 (B—H). ^{1}H FTNMR (250 MHz, CDCl$_3$, 298 K, TMS) δ (p.p.m.): 2.35–2.30 (m, 2 –CH–), 1.42–1.30 (m, 12, –CH$_3$). ^{11}B FTNMR (128 MHz, CDCl$_3$, 298 K, BF$_3$, Et$_2$O) δ (p.p.m.): −0.02 (d, $^1J_{B,H}$ = 146 Hz, 2B), −7.04 (d, $^1J_{B,H}$ = 148 Hz, 2B), −9.91 (d, $^1J_{B,H}$ = 156 Hz, 6B). ^{31}P FTNMR (161 MHz, CDCl$_3$, 298 K, H$_3$PO$_4$) δ (p.p.m.): 32.79 [s, P(^iPr)$_2$].

Elemental analyses were performed using a Perkin-Elmer 240-B microanalyser. The ^{1}H NMR, ^{11}B NMR and ^{31}P NMR spectra were obtained with a Bruker AM 400WB or AC 250 instrument, and IR spectra of KBr pellets were recorded with a Nicolet 710-FT spectrophotometer.

Compound (1)

Crystal data

$C_9H_{27}B_{10}P$
M_r = 274.39
Orthorhombic
$Pbca$
a = 18.278 (12) Å
b = 13.866 (7) Å
c = 13.520 (5) Å
V = 3427 (3) Å^3
Z = 8
D_x = 1.064 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.0–15.9°
μ = 0.14 mm^{-1}
T = 193 K
Plate
0.35 × 0.30 × 0.15 mm
Colourless

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans
  T_{min} = 0.935, T_{max} = 1.000
4396 measured reflections
4396 independent reflections

1372 observed reflections
  [$F > 4\sigma(F)$]
θ_{max} = 27.5°
h = 0 → 23
k = 0 → 18
l = 0 → 17
3 standard reflections
  monitored every 150
  reflections
  intensity decay: 0.2%

Refinement

Refinement on F
R = 0.095
wR = 0.082
S = 1.442
1372 reflections
182 parameters
H-atom parameters not
  refined
w = $1/\sigma^2(F)$

$(\Delta/\sigma)_{max}$ = 0.046
$\Delta\rho_{max}$ = 0.5 e Å^{-3}
$\Delta\rho_{min}$ = −0.6 e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables*
  for X-ray Crystallography
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.8564 (1)	0.6286 (2)	0.3454 (1)	0.0243 (5)
C(1)	0.7789 (3)	0.6203 (5)	0.4360 (5)	0.020 (2)
C(2)	0.6935 (3)	0.6038 (5)	0.3834 (5)	0.020 (2)
B(3)	0.7343 (4)	0.5095 (7)	0.4439 (6)	0.026 (3)
B(4)	0.7796 (5)	0.5616 (8)	0.5480 (6)	0.034 (3)
B(5)	0.7680 (5)	0.6876 (7)	0.5395 (6)	0.027 (3)
B(6)	0.7150 (4)	0.7126 (6)	0.4321 (6)	0.023 (3)
B(7)	0.6398 (5)	0.5348 (7)	0.4572 (6)	0.034 (3)
B(8)	0.6934 (5)	0.5068 (8)	0.5633 (7)	0.034 (3)
B(9)	0.7127 (5)	0.6195 (8)	0.6207 (6)	0.038 (3)
B(10)	0.6738 (5)	0.7148 (7)	0.5495 (6)	0.031 (3)
B(11)	0.6281 (4)	0.6606 (7)	0.4487 (7)	0.031 (3)
B(12)	0.6272 (5)	0.6019 (7)	0.5651 (7)	0.037 (4)
C(13)	0.6873 (4)	0.5965 (6)	0.2721 (5)	0.033 (3)
C(14)	0.8932 (3)	0.7514 (6)	0.3758 (5)	0.028 (2)
C(15)	0.9472 (4)	0.7605 (6)	0.4609 (6)	0.042 (3)
C(16)	0.9239 (4)	0.7963 (6)	0.2814 (6)	0.042 (3)
C(17)	0.9287 (4)	0.5460 (6)	0.3930 (5)	0.031 (3)
C(18)	0.9070 (4)	0.4387 (6)	0.3899 (6)	0.041 (3)
C(19)	0.9955 (4)	0.5605 (6)	0.3258 (7)	0.053 (3)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

P—C(1)	1.876 (6)	C(1)—B(6)	1.73 (1)
P—C(14)	1.876 (8)	C(2)—C(13)	1.512 (9)
P—C(17)	1.863 (7)	C(14)—C(15)	1.52 (1)
C(1)—C(2)	1.731 (9)	C(14)—C(16)	1.53 (1)
C(1)—B(3)	1.74 (1)	C(17)—C(18)	1.54 (1)
C(1)—B(4)	1.72 (1)	C(17)—C(19)	1.53 (1)
C(1)—P—C(14)	100.6 (3)	B(6)—C(2)—C(13)	117.7 (6)
C(1)—P—C(17)	105.8 (3)	B(7)—C(2)—C(13)	120.3 (6)
C(14)—P—C(17)	103.2 (3)	B(11)—C(2)—C(13)	120.0 (6)
P—C(1)—C(2)	114.9 (4)	P—C(14)—C(15)	118.3 (6)
P—C(1)—B(3)	116.6 (5)	P—C(14)—C(16)	108.5 (5)
P—C(1)—B(4)	126.8 (5)	C(15)—C(14)—C(16)	111.1 (6)
P—C(1)—B(5)	126.5 (5)	P—C(17)—C(18)	113.8 (5)
P—C(1)—B(6)	116.4 (5)	P—C(17)—C(19)	106.3 (5)
C(1)—C(2)—C(13)	119.0 (5)	C(18)—C(17)—C(19)	108.3 (6)
B(3)—C(2)—C(13)	117.2 (6)		
C(14)—P—C(1)—C(2)			120.8 (5)
P—C(1)—C(2)—C(13)			0.5 (8)
C(17)—P—C(1)—C(2)			−132.1 (5)

Compound (2)

Crystal data

$C_{14}H_{38}B_{10}P_2$
$M_r = 376.50$
Monoclinic
$P2_1/c$
$a = 10.254\ (5)$ Å
$b = 17.128\ (6)$ Å
$c = 13.717\ (6)$ Å
$\beta = 104.39\ (4)°$
$V = 2334\ (2)$ Å^3
$Z = 4$
$D_x = 1.072$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 15.8–22.0°$
$\mu = 0.18$ mm^{-1}
$T = 193$ K
Plate
$0.44 \times 0.42 \times 0.24$ mm
Colourless

Data collection

Rigaku AFC-7S diffractom-
  eter
$\omega/2\theta$ scans
Absorption correction:
  ψ scans
  $T_{min} = 0.947$, $T_{max} = 1.000$
5555 measured reflections
5555 independent reflections

3897 observed reflections
  $[F > 4\sigma(F)]$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 17$
3 standard reflections
  monitored every 150
  reflections
  intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.053$
$wR = 0.050$
$S = 1.594$
3897 reflections
388 parameters
All H-atom parameters
  refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.114$
$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.3$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent
isotropic displacement parameters (Å^2) for (2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P(1)	1.06723 (6)	0.61769 (4)	0.28719 (5)	0.0242 (2)
P(2)	0.79661 (7)	0.52226 (4)	0.19710 (5)	0.0252 (2)
C(1)	0.9110 (2)	0.6811 (1)	0.2584 (2)	0.0227 (8)
C(2)	0.7688 (2)	0.6314 (1)	0.1964 (2)	0.0244 (8)
B(3)	0.7833 (3)	0.6656 (2)	0.3179 (2)	0.0253 (9)
B(4)	0.8672 (3)	0.7569 (2)	0.3266 (2)	0.028 (1)
B(5)	0.9063 (3)	0.7740 (2)	0.2101 (2)	0.028 (1)
B(6)	0.8467 (3)	0.6934 (2)	0.1292 (2)	0.0255 (9)
B(7)	0.6303 (3)	0.6737 (2)	0.2231 (2)	0.029 (1)
B(8)	0.6903 (3)	0.7534 (2)	0.3052 (2)	0.031 (1)
B(9)	0.7659 (3)	0.8206 (2)	0.2376 (2)	0.032 (1)
B(10)	0.7543 (3)	0.7815 (2)	0.1151 (2)	0.031 (1)
B(11)	0.6688 (3)	0.6909 (2)	0.1070 (2)	0.029 (1)
B(12)	0.6192 (3)	0.7693 (2)	0.1740 (3)	0.033 (1)
C(13)	1.2027 (3)	0.6929 (2)	0.2998 (2)	0.034 (1)
C(14)	1.3368 (3)	0.6643 (2)	0.3682 (3)	0.051 (1)
C(15)	1.2229 (3)	0.7090 (2)	0.1949 (2)	0.044 (1)
C(16)	1.0747 (3)	0.5776 (2)	0.4144 (2)	0.0303 (9)
C(17)	1.1743 (3)	0.5088 (2)	0.4333 (2)	0.043 (1)
C(18)	1.0948 (3)	0.6320 (2)	0.5046 (2)	0.040 (1)
C(19)	0.8446 (3)	0.5045 (2)	0.0769 (2)	0.0327 (9)
C(20)	0.7432 (4)	0.5188 (2)	-0.0230 (2)	0.052 (1)
C(21)	0.9089 (3)	0.4239 (2)	0.0810 (2)	0.044 (1)
C(22)	0.6224 (3)	0.4846 (2)	0.1823 (2)	0.036 (1)
C(23)	0.6128 (3)	0.4007 (2)	0.1408 (3)	0.054 (1)
C(24)	0.5886 (3)	0.4820 (2)	0.2847 (3)	0.048 (1)

Table 4. *Selected geometric parameters (Å, °) for (2)*

P(1)—C(1)	1.894 (3)	C(2)—B(6)	1.726 (4)
P(1)—C(13)	1.870 (3)	C(2)—B(7)	1.713 (4)
P(1)—C(16)	1.859 (3)	C(2)—B(11)	1.723 (4)
P(2)—C(2)	1.891 (3)	C(13)—C(14)	1.540 (4)
P(2)—C(19)	1.860 (3)	C(13)—C(15)	1.529 (5)
P(2)—C(22)	1.862 (3)	C(16)—C(17)	1.539 (4)
C(1)—C(2)	1.719 (3)	C(16)—C(18)	1.521 (4)
C(1)—B(3)	1.728 (4)	C(19)—C(20)	1.520 (4)
C(1)—B(4)	1.724 (4)	C(19)—C(21)	1.526 (4)
C(1)—B(5)	1.719 (4)	C(22)—C(23)	1.540 (4)
C(1)—B(6)	1.743 (4)	C(22)—C(24)	1.529 (5)
C(2)—B(3)	1.738 (4)		
C(1)—P(1)—C(13)	101.2 (1)	P(2)—C(2)—B(7)	123.2 (2)
C(1)—P(1)—C(16)	104.1 (1)	P(2)—C(2)—B(11)	130.6 (2)
C(13)—P(1)—C(16)	108.1 (1)	P(1)—C(13)—C(14)	111.6 (2)
C(2)—P(2)—C(19)	103.3 (1)	P(1)—C(13)—C(15)	108.0 (2)
C(2)—P(2)—C(22)	101.7 (1)	C(14)—C(13)—C(15)	108.8 (3)
C(19)—P(2)—C(22)	107.7 (1)	P(1)—C(16)—C(17)	108.2 (2)
P(1)—C(1)—C(2)	112.9 (2)	P(1)—C(16)—C(18)	120.2 (2)
P(1)—C(1)—B(3)	121.0 (2)	C(17)—C(16)—C(18)	112.4 (2)
P(1)—C(1)—B(4)	129.8 (2)	P(2)—C(19)—C(20)	120.0 (2)
P(1)—C(1)—B(5)	123.5 (2)	P(2)—C(19)—C(21)	108.8 (2)
P(1)—C(1)—B(6)	111.6 (2)	C(20)—C(19)—C(21)	111.9 (2)
P(2)—C(2)—C(1)	112.3 (1)	P(2)—C(22)—C(23)	109.6 (2)
P(2)—C(2)—B(3)	110.6 (2)	P(2)—C(22)—C(24)	109.9 (2)
P(2)—C(2)—B(6)	121.5 (2)	C(23)—C(22)—C(24)	107.7 (3)
C(13)—P(1)—C(1)—C(2)		156.7 (2)	
C(16)—P(1)—C(1)—C(2)		-91.2 (2)	
C(19)—P(2)—C(2)—C(1)		-93.4 (2)	
C(22)—P(2)—C(2)—C(1)		155.0 (2)	
P(1)—C(1)—C(2)—P(2)		12.1 (2)	

In (1), non-H atoms were refined with anisotropic displacement parameters and H atoms were placed at calculated positions (C—H = 0.95 Å, B—H = 1.10 Å, U_H equal to U_{eq} of carrying atom) and not refined. The high R and wR values are consequences of the mosaic of the crystal. In (2), non-H atoms were refined with anisotropic and H atoms with isotropic displacement parameters.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1993b); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *Xtal*3.2 (Hall, Flack & Stewart, 1992); molecular graphics: *ORTEP*II (Johnson, 1976) in *Xtal*3.2.

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1-Diphenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) at 153 K

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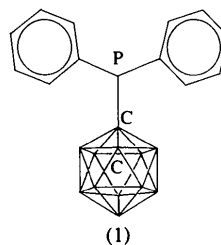
(*Received 25 November 1994; accepted 21 February 1995*)

Abstract

The title molecule, C$_{14}$H$_{21}$B$_{10}$P, assumes *m* symmetry, with the P atom, the two cluster C atoms and the two B atoms forming the mirror plane. Bond lengths are P—C(cage) 1.871 (6), P—C(aryl) 1.828 (4) and C(cage)—C(cage) 1.666 (9) Å.

Comment

Considerable variation in the C1—C2 bond length has been observed for 1,2-*RR'*-1,2-dicarba-*closo*-dodecaborane derivatives, depending on substituents *R* and *R'*. A C1—C2 distance of 1.634 (3) Å is reported for 9,12-μ-[(CH$_3$)$_2$CS$_2$]-1,2-C$_2$B$_{10}$H$_{10}$, in which H atoms are attached to both cluster C atoms (Šubrtová, Línek & Hasek, 1980), and much longer distances of 1.858 (5) and 1.826 (5) Å are reported for 1,2-μ-S(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$)S-C$_2$B$_{10}$H$_{10}$, in which S atoms are bonded to both cluster C atoms (Teixidor, Viñas, Rius, Miravitlles & Casabó, 1990). Recently, we suggested an explanation for the lengthening of the C1—C2 bond (Kivekäs, Sillanpää, Teixidor, Viñas

& Nuñez, 1994) and proposed empirically derived equations for calculating the C1—C2 distances in *o*-carborane derivatives (Kivekäs, Sillanpää, Teixidor, Viñas, Nuñez & Abad, 1995). Computational studies of dithioether *o*-carborane compounds using semi-empirical quantum-mechanical calculations (CNDO and MNDO) suggest extremely long and unrealistic C1—C2 distances. To obtain more realistic C1—C2 distances in *o*-carborane derivatives using CNDO and MNDO methods, crystal structure analyses of numerous compounds incorporating various types of C substituents are required. To this end, we have synthesized the title compound, (1), and determined its crystal structure at 153 K.

(1)

In (1), the P atom is bonded in a pyramidal arrangement to a C atom of each of the phenyl groups, and C1 of the carborane moiety. The molecule assumes *m* symmetry, with the P atom, the two cluster C atoms and two B atoms (B7 and B8) occupying the mirror plane. The P—C(cage) bond is longer than the P—C(aryl) bonds and the bond lengths do not deviate significantly from those reported for 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane, (2) (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994). However, there are slight differences in the C—P—C angles between the two compounds.

The most notable difference between (1) and the 2-methyl substituted derivative (2) is in the molecular symmetry. Compound (2) assumes C_1 symmetry and the orientation of the phenyl groups with respect to the carborane cage is significantly different from that in (1), where the symmetry is *m*. In (2), the C(aryl)—P—C1—C2 torsion angles are 95.8 (3) and −154.9 (3)°, while in (1) the angle is 124.6 (1)°. This difference may be attributed to packing effects.

Although the orientations of the phenyl groups differ in the two compounds, the bond angles of the diphenyl-phosphine groups and those around C1 show similar trends. The P—C(aryl)—C(aryl) angles are significantly different and opening of the P—C9—C14 angle in (1) can also be assumed to result from the mutual repulsion between the two phenyl rings. In the borane polyhedron, the C1—B bond lengths are equal but the angles around C1 vary from 108.5 (4) to 129.7 (3)°. The considerable opening of the P—C1—B3 angle is probably due to the need to avoid repulsion between the phenyl groups and the carborane polyhedron.