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

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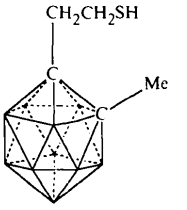
Abstract

In the title compound, $C_5H_{18}B_{10}S$, the mercaptoethyl and methyl groups are connected to the C atoms of the 1,2-dicarbaborane cage. The C_{cage}—C_{cage} distance is 1.670 (3) Å and the C—C_{cage}—C_{cage}—C torsion angle −1.2 (3)°.

Comment

In earlier papers, we have studied the elongation of the C1—C2 distance in 1,2-dicarba-*closo*-dodecaboranes and suggested an empirically derived equation to calculate this distance (Kivekäs *et al.*, 1994; Kivekäs, Sillanpää *et al.*, 1995). The C1—C2 bond length varies considerably, depending on the number of substituents and the atomic species connected to the cluster C atoms. Thus, values of 1.634 (3) and 1.57 (1)–1.61 (1) Å are reported for the 1,2-dihydrogen compounds 9,12-μ-[$(CH_3)_2CS_2$]-1,2-$C_2B_{10}H_{10}$ and CH_2(9-S-$C_2B_{10}H_{11}$)$_2$, respectively (Šubrtová *et al.*, 1980; Novák *et al.*, 1983). Much larger values of 1.816 (7), 1.826 (5) and 1.858 (5) Å are observed for compounds in which S atoms are connected to both the cluster C atoms (Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990). Generally, the contribution of C, Si and P to this lengthening is less than that of S and, moreover, it seems that aryl substituents have a greater tendency to elongate the bond than non-aryl substituents (Lewis & Welch, 1993). In order to study further the contribution of different types of C substituents on the lengthening of the C1—C2 bond, we have synthesized the title compound, (I), and determined its crystal structure.



(I)

In (I), the C14 atom is oriented away from C15, the S atom is *anti* in relation to the cluster C1 atom and, omitting H atoms, the molecule has a pseudo-mirror plane through atoms S, C1, C2, C13–C15, B9 and B12. The intramolecular C13···C15 distance of 3.106 (4) Å is only 0.2–0.3 Å shorter than the sum of the corresponding van der Waals radii (Allinger *et al.*, 1968; Bondi, 1964), indicating the absence of any noteworthy repulsion between C13 and C15. The C13—C1—C2—C15 torsion angle of −1.2 (3)° agrees well with the value of 0.5 (8)° in 1-P^{i}Pr$_2$-2-Me-1,2-$C_2B_{10}H_{10}$, but significantly higher values have been reported for compounds with bulky sustituents connected to both cluster C atoms: for instance, in 1,2-(P^{i}Pr$_2$)$_2$-1,2-$C_2B_{10}H_{10}$, the value is 12.1 (2)° (Kivekäs, Sillanpää *et al.*, 1995).

The C13—C1—*X* (*X* = B or C) angles vary from 116.7 (2) to 123.1 (2)°, and the C15—C2—*X* angles from 117.6 (2) to 120.8 (2)°. For compounds in which one or two bulky substituents such as P^{i}Pr$_2$ or PPh$_2$ are connected to cluster C atoms, variations of up to *ca* 21° on the corresponding angle values have been observed (Kivekäs, Sillanpää *et al.*, 1995; Kivekäs, Teixidor *et al.*, 1995; Sillanpää *et al.*, 1996; Teixidor *et al.*, 1997). This significant variation probably originates from the

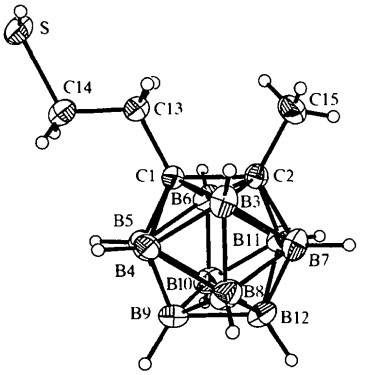


Fig. 1. View of the structure of (I), with displacement ellipsoids at the 30% probability level and H atoms shown as spheres of arbitrary radii.

repulsion between the carborane cage and the bulky substituents.

The C1—C2 distance of 1.670 (3) Å in (I) agrees well with the above-mentioned observation that aryl substituents have a greater tendency to elongate the bond than non-aryl substituents (Lewis & Welch, 1993). Thus, in (I), the C1—C2 distance is significantly longer than that in the 1,2-dihydrogen compound 9,12-μ-[$(CH_3)_2CS_2$]-1,2-$C_2B_{10}H_{10}$ [1.634 (3) Å], but shorter than those in compounds with one or two aryl groups directly connected to the cluster C atoms, *viz.* 1-(PhC≡C)-2-Ph-1,2-$C_2B_{10}H_{10}$ [1.710 (2) Å] and 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ [1.733 (4) and 1.720 (4) Å] (Clegg *et al.*, 1993; Lewis & Welch, 1993). The C1—C2 distance in (I) also agrees well with the corresponding value of 1.684 (6) Å in 1,2-μ-($CH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2$)-1,2-$C_2B_{10}H_{10}$ (Hobrey *et al.*, 1993).

Experimental

Butyllithium (12.6 mmol; 1.3 *M* in *n*-hexane) was added to a solution of 1-Me-1,2-$C_2B_{10}H_{11}$ (12.6 mmol; 2.0 g) in dry diethyl ether (60 ml) at 273 K. The suspension was stirred at this temperature for 0.5 h, maintained at 298 K for the same period and cooled again to 273 K. Then ethylene sulfide (C_2H_4S; 12.6 mmol; 0.76 g) was added slowly over a period of 0.5 h. The ice bath was removed, the stirring continued for 4 h and water (30 ml) was added. The mixture was thoroughly shaken and the two layers were separated. The diethyl ether layer was washed twice with water (2 × 30 ml) and the aqueous layer with diethyl ether (30 ml). The combined organic solutions were dried over $MgSO_4$. The filtrate was evaporated to yield an oil (2.1 g, 77%) which was extracted with hot petroleum ether. Transparent crystals were obtained by slow evaporation of petroleum ether. Analysis calculated for $C_5H_{18}B_{10}S$: C 27.50, H 8.31, S 14.68%; found: C 28.27, H 8.17, S 14.14%; IR (KBr): ν (cm^{-1}) 2952, 2875 (C—H), 2587 (B—H), 1441 (C—H); ^{1}H NMR (250 MHz, $CDCl_3$, 298 K, TMS, p.p.m.): δ = 2.05 (*s*, 3H, –CH_3), 2.41–2.61 (*m*, 2H, –CH_2–), 2.71–2.88 (*m*, 2H, CH_2—S), 3.36 (*s*, 1H, SH); ^{11}B NMR (128 MHz, $CDCl_3$, 298 K, $BF_3.Et_2O$, p.p.m.): δ = −3.75 [*d*, ^1J(BH) = 153 Hz, 1B], −5.31 [*d*, ^1J(BH) = 151 Hz, 1B] −9.98 [*d*, ^1J(BH) =125 Hz, 8B]; ^{13}C NMR (62.5 MHz, $CDCl_3$, 298 K, TMS, p.p.m.): δ = 23.24 (–CH_3), 34.99 (–CH_2–), 36.34 (CH_2—S), 75.08 (B—C), 76.12 (B—C).

Crystal data

$C_5H_{18}B_{10}S$
M_r = 218.35
Monoclinic
$P2_1/c$
a = 13.637 (2) Å
b = 7.866 (2) Å
c = 12.844 (1) Å
β = 109.574 (8)°
V = 1298.1 (4) Å^3
Z = 4
D_x = 1.117 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 16.4–17.4°
μ = 0.205 mm^{-1}
T = 295 (2) K
Plate
0.38 × 0.32 × 0.23 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.93, T_{max} = 0.95
2402 measured reflections
2287 independent reflections
1561 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 25°
h = −16 → 15
k = −9 → 0
l = 0 → 15
3 standard reflections
every 150 reflections
intensity decay: 0.40%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.172
S = 1.055
2286 reflections
148 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0892P)^2 + 0.288P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.201 e Å^{-3}
$\Delta\rho_{min}$ = −0.194 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—C14	1.801 (3)	C1—C2	1.670 (3)
S—H1	1.11 (4)	C2—C15	1.517 (4)
C1—C13	1.530 (3)	C13—C14	1.478 (4)
C13—C1—C2	117.0 (2)	C15—C2—C1	119.2 (2)
C13—C1—B4	122.2 (2)	C15—C2—B11	120.1 (2)
C13—C1—B5	123.1 (2)	C15—C2—B7	120.8 (2)
C13—C1—B6	117.8 (2)	C15—C2—B3	118.3 (2)
C13—C1—B3	116.7 (2)	C15—C2—B6	117.6 (2)

H atoms were refined at their calculated positions, except that bonded to S.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1018). Services for accessing these data are described at the back of the journal.

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(*S*)-*N*-Triphenylmethylpyroglutamyl Fluoride†

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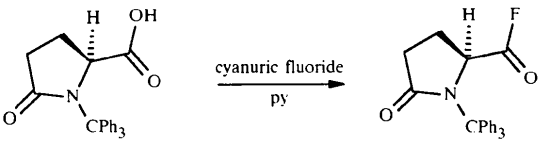
Abstract

The title compound, $C_{24}H_{20}FNO_2$, is the product of the reaction of (*S*)-*N*-triphenylmethylpyroglutamic acid with cyanuric fluoride in the presence of pyridine. The crystal structure determination shows the presence of two crystallographically independent molecules, with the two pyrrolidinyl rings adopting slightly different conformations.

† Alternative name: (*S*)-5-fluoroformyl-1-triphenylmethylpyrrolidin-2-one.

Comment

Treatment of N^{α}-triphenylmethylamino acids with cyanuric fluoride in the presence of pyridine provides access to the corresponding fluorides, which are powerful acylating agents suitable for use in peptide synthesis (Karigiannis *et al.*, 1998). These agents react much faster with amino components than the corresponding benzotriazolyl 'active' esters (Barlos *et al.*, 1984), and thus we decided to determine the structure of the title compound, (II), prepared from the readily available (*S*)-*N*-triphenylmethylpyroglutamic acid, (I) (Papaioannou *et al.*, 1995), using X-ray analysis. Fluoride (II) was the only one of the recently prepared N^{α}-triphenylmethylamino acid fluorides (Karigiannis *et al.*, 1998) which could be obtained in a suitable crystalline form for crystallographic analysis. In addition, in the 200 MHz ^{1}H NMR spectrum of (II), the H5 proton appears at 4.353 p.p.m. as a doublet, with J = 9.21 Hz, although it would be expected to couple with the two vicinal protons at C4 and the F atom.



(I) (II)

The crystal structure determination of (II) shows the presence of two independent molecules in the asymmetric unit, *A* and *B*, with the two pyrrolidinyl rings adopting slightly different conformations. Thus, in molecules *A* and *B*, the C4 atom deviates from the plane defined by the amide function by 0.467 (7) and 0.296 (6) Å, respectively. Furthermore, one of the faces of the fluoroformyl group appears to be screened by one of the phenyl groups of the triphenylmethyl (trityl) function, leaving the other face susceptible to nucleophilic attack. This, at least in part, together with the strong electron-withdrawing character of the F atom and its much smaller size compared to the benzotriazolyloxy group of the corresponding 'active' esters of N^{α}-tritylamino acids, should account for the higher reactivity of the N^{α}-tritylamino acid fluorides towards nucleophiles. On the other hand, the crystal structure of (II) shows that in both independent pyrrolidinyl rings, the conformation about the C4—C5 bond tends to be eclipsed, with a staggering angle of about 20° [C3—C4—C5—N1 = 22.2 (4) and 19.2 (3)° for *A* and *B*, respectively]. Consequently, the torsion angles H4*A*1—C4*A*—C5*A*—H5*A* and H4*B*1—C4*B*—C5*B*—H5*B*, and H4*A*2—C4*A*—C5*A*—H5*A* and H4*B*2—C4*B*—C5*B*—H5*B*, are about −100 and 20°, respectively. Moreover, the orientation of the fluoroformyl substituent can be defined by the C4—C5—C6—F1 torsion angle, whose value is −87.2 (4) and −80.8 (4)° in *A* and *B*, respectively. Thus, the relative orientation of H5 with respect to F1, *i.e.* given