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Crystal engineering with heteroboranes. I. 1-Carboxy-1,2-dicarba-*closo*-dodecaborane(11)

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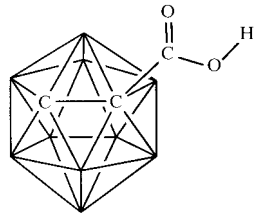
The title compound, $C_3H_{12}B_{10}O_2$ or 1-COOH-1,2-*closo*-$C_2B_{10}H_{11}$, forms centrosymmetric dimers through intermolecular hydrogen bonding between the carboxylic acid groups, resulting in the formation of an eight-membered ring [$R_2^2(8)$]. The C═O bond of the carboxylic acid group almost eclipses the unsubstituted cage C atom, with a C—C—C—O torsion angle of 2.6 (2)°.

Comment

The usefulness of heteroboranes in studies of crystal engineering has only recently begun to be exploited (Centore *et al.*, 1994; Davidson *et al.*, 1996; Hosmane *et al.*, 1998; Lee *et al.*, 2000), yet such compounds have a number of potential advantages in this respect. Heteroboranes are generally thermally and chemically stable compounds. They exist as polyhedra or fragments of polyhedra of differing size and shape, but have architectures that are well understood (Wade, 1976). Isomeric possibilities mean that C-substituted heterocarboranes have the potential to function as supramolecular building blocks with differing directionalities. Significant variation is also possible in the number and nature of the substituents that can be attached to the B atoms of heteroboranes, affording these species the potential to act as supramolecular building blocks in three dimensions. Finally, heteroboranes are usually neutral or anionic, but can also be cationic (see, for example, Douek & Welch, 1993).

Within the field of crystal engineering, the carboxylic acid group is frequently used to afford supramolecular assemblies through intermolecular H···O bonding (Leiserowitz, 1976). Accordingly, we have begun a systematic study of the crystal chemistry of carboxylic acid carboranes and their derivatives. Herein, we describe the structure of the simplest carboxylic acid carborane, namely 1-carboxy-1,2-dicarba-*closo*-dodecaborane(11), (I).

Compound (I) crystallizes as a dimer, linked by two O—H···O hydrogen bonds about a centre of inversion (Fig. 1), typical of the packing of carboxylic acid units (Leiserowitz, 1976). In graph-set terminology (Etter, 1990; Etter & MacDonald, 1990), this motif is denoted $R_2^2(8)$. The only other carboxylic acid carborane to be structurally characterized so far is 1,12-$(COOH)_2$-1,12-*closo*-$C_2B_{10}H_{10}$, (II) (Centore *et al.*, 1994). In (II), the molecules pack as linear hydrogen-bonded chains. The dimensions of the hydrogen bond in (I) (Table 2) identify it as 'strong' (Desiraju & Steiner, 1999) and bear good comparison with the corresponding O···O distance in (II) (2.639 Å).



(I)

In carboxylic acid derivatives of 1,2-dicarbaborane, we may define the orientation of the carboxylic acid group by θ, the C2—C1—C3—O2 torsion angle. In compound (I), $\theta = 2.6\ (2)^\circ$. This is complemented by a C1—C2 bond of 1.632 (2) Å, in excellent agreement with that in the parent compound 1,2-*closo*-$C_2B_{10}H_{12}$ [1.630 (6) Å; Davidson *et al.*, 1996], and by a C1—C3 bond of 1.507 (2) Å.

The C—B distances span the range 1.690 (2)–1.729 (2) Å and the B—B distances span the range 1.759 (2)–1.795 (3) Å.

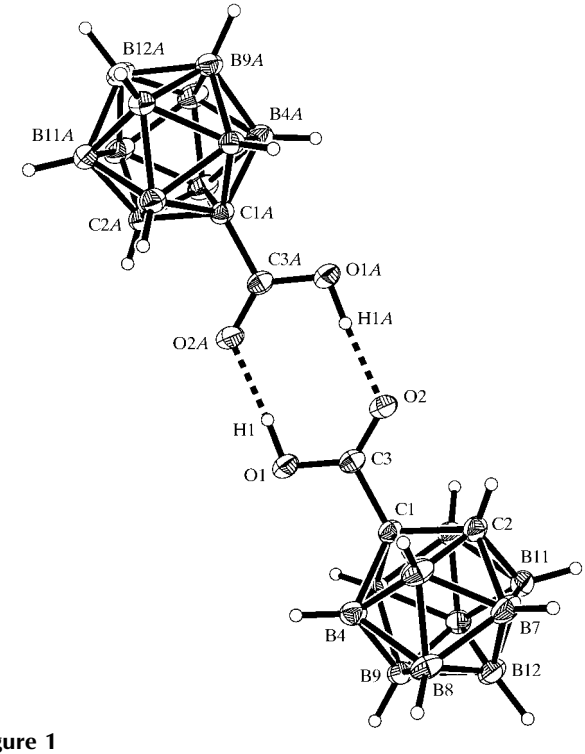


Figure 1
A perspective view of the dimer of (I) with displacement ellipsoids shown at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are shown as dotted lines. The suffix *A* denotes the molecule at $1 - x, -y, -z$.

There is no evidence for disorder of the C2 vertex, identified on the twin bases of refined (as B) isotropic displacement parameters and intra-cage distances.

Experimental

Compound (I) was prepared according to the literature method of Zakharkin & Grebennikov (1967), in 73% yield, and crystals were grown by evaporation of an acetonitrile solution. Analysis, calculated for $C_3H_{12}B_{10}O_2$: C 19.1, H 6.4%; found: C 18.3, H 6.90%; ^{1}H FT–NMR (400.1 MHz, TMS, δ, p.p.m.): 4.00 (1H, *s*, C—H); ^{11}B{^{1}H} FT–NMR (128.4 MHz, $BF_3{\cdot}OEt_2$, δ, p.p.m.): 0.77 (2B), −5.97 (2B), −8.79 (2B), −10.52 (2B), −11.65 (2B). NMR spectra were recorded from a solution in $CDCl_3$ at 293 K on a Bruker DPX400 spectrometer.

Crystal data

$C_3H_{12}B_{10}O_2$
M_r = 188.23
Monoclinic, $P2_1/c$
a = 6.988 (2) Å
b = 12.031 (3) Å
c = 12.869 (4) Å
β = 103.33 (2)°
V = 1052.8 (5) Å^3
Z = 4
D_x = 1.188 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 46 reflections
θ = 3.2–12.5°
μ = 0.07 mm^{-1}
T = 160 (2) K
Needle, colourless
0.82 × 0.24 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
ω scans
2577 measured reflections
1849 independent reflections
1557 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25°
$h = -1 \rightarrow 8$
$k = -14 \rightarrow 1$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

C1—C3	1.507 (2)	B5—B9	1.780 (2)
C1—C2	1.631 (2)	B5—B6	1.791 (2)
C1—B5	1.709 (2)	B6—B10	1.759 (2)
C1—B4	1.710 (2)	B6—B11	1.781 (3)
C1—B6	1.728 (2)	B7—B12	1.776 (3)
C1—B3	1.729 (2)	B7—B11	1.777 (3)
C2—B11	1.690 (2)	B7—B8	1.782 (3)
C2—B7	1.694 (2)	B8—B9	1.788 (3)
C2—B6	1.723 (2)	B8—B12	1.790 (3)
C2—B3	1.724 (3)	B9—B12	1.774 (3)
B3—B8	1.766 (3)	B9—B10	1.789 (3)
B3—B7	1.780 (3)	B10—B11	1.779 (3)
B3—B4	1.795 (3)	B10—B12	1.794 (3)
B4—B9	1.780 (3)	B11—B12	1.778 (3)
B4—B8	1.782 (2)	O1—C3	1.3050 (19)
B4—B5	1.786 (3)	O2—C3	1.2170 (19)
B5—B10	1.779 (3)		
C3—C1—C2	114.30 (12)	C3—C1—B3	115.72 (12)
C3—C1—B5	122.84 (12)	O2—C3—O1	126.16 (14)
C2—C1—B4	111.44 (12)	O2—C3—C1	121.19 (14)
C3—C1—B6	113.67 (12)	O1—C3—C1	112.65 (13)
C2—C1—C3—O2	2.6 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.95 (3)	1.72 (3)	2.6655 (16)	177 (2)

Symmetry code: (i) $1-x, -y, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.119
S = 1.02
1849 reflections
184 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.3182P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

All H atoms (both cage and COOH) were located from a difference Fourier map and refined [B—H = 1.08 (2)–1.11 (2) Å], but boron-bound H atoms were restrained with B—H = 1.10 (2) Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1160). Services for accessing these data are described at the back of the journal.

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