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Crystal engineering with heteroboranes. III. 2-Carboxy-1-methoxymethyl-1,2-dicarba-*closo*-dodecaborane(12)

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The title compound, 1-CH_2OCH_3-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ or $C_5H_{16}B_{10}O_3$, forms a discrete centrosymmetric tetramer, *via* hydrogen bonding, involving two inner and two outer carborane molecules. One conventional eight-membered hydrogen-bonded ring [graph set $R_2^2(8)$] is formed between two carboxylic acid groups of the inner carboranes. This interaction is then supplemented by an open finite hydrogen bond (graph set *D*) between the ether O atom of the inner carborane and the carboxylic acid H atom of the outer carborane.

Comment

Crystal engineering is a rapidly growing cross-disciplinary field that seeks to develop protocols for predicting and controlling the structures, and thus the functional properties, of solids. Heteroboranes have only relatively recently begun to be used for crystal engineering but have great potential (Centore *et al.*, 1994; Hosmane *et al.*, 1998; Macías *et al.*, 1999; Lee *et al.*, 2000; Hardie *et al.*, 2000; Hardie & Raston, 2000, 2001; Welch *et al.*, 2001; O'Dowd *et al.*, 2002). In order to explore crystal engineering with heteroboranes, we have begun a systematic study of the crystal and molecular structures of various carborane carboxylic acids. We have sucessfully determined and reported the structures of the monocarboxylic acids 1-COOH-1,2-*closo*-$C_2B_{10}H_{11}$ (Welch *et al.*, 2001), 1-Me-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ (Venkatasubramanian, Donohoe *et al.*, 2003) and 1-Ph-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ (Venkatasubramanian, Donohoe *et al.*, 2003), and the dicarboxylic acid 1,2-$(COOH)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Venkatasubramanian, Ellis *et al.*, 2003). All three monocarboxylic acids form discrete hydrogen-bonded dimers with or without solvent molecules, while the 1,2-di-

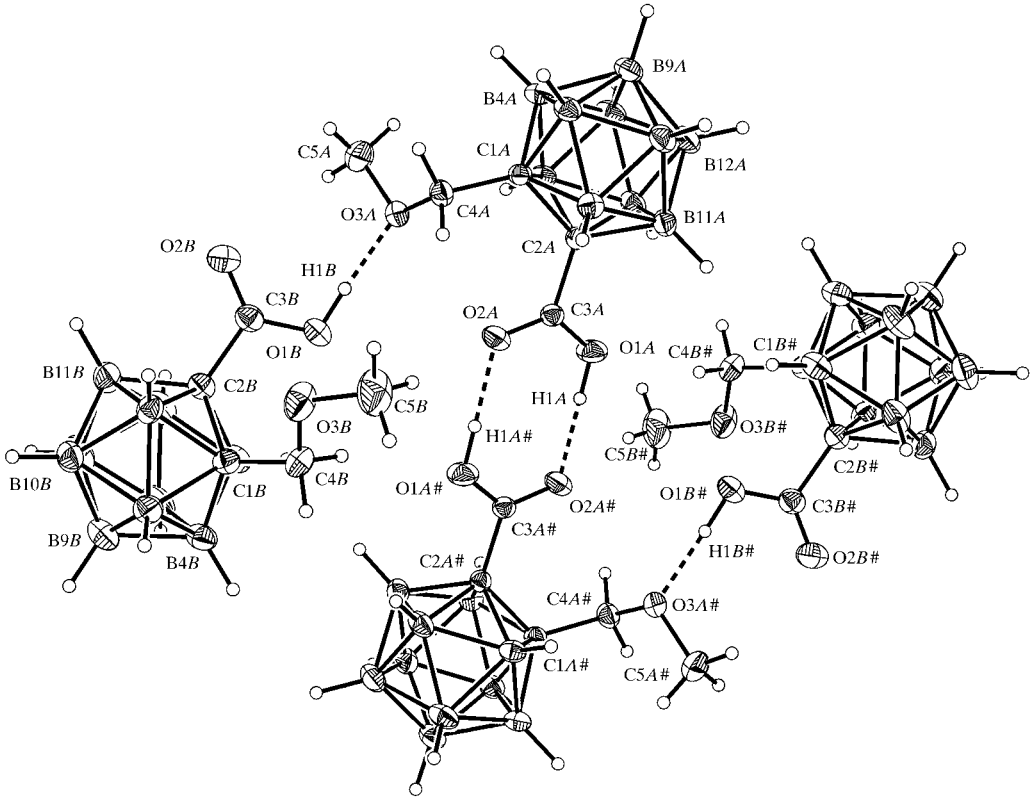

Figure 1
A perspective view of the tetramer of (I) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii. Hydrogen bonds are shown as dashed lines. Atoms marked with a hash (#) are at symmetry position $(-x, 1-y, -z)$.

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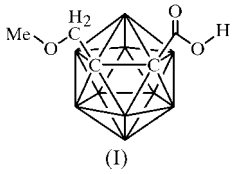
carboxylic acid forms tetramers incorporating an ethanol (solvent) molecule, the OH group of which is also involved in hydrogen bonding. 1,12-$(COOH)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ forms infinite hydrogen-bonded chains (Centore *et al.*, 1994). In this paper, we report the crystal and molecular structures of 1-CH_2OCH_3-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$, (I).



(I)

Compound (I) forms a centrosymmetric tetramer, with two crystallographically independent carborane molecules in the asymmetric fraction of the unit cell. The inner molecule (*A*) is bound to its inversion-related partner *via* a conventional double-hydrogen-bonded eight-membered ring involving the two carboxylic acid groups, denoted $R_2^2(8)$ in graph-set terminology (Etter, 1990; Etter *et al.*, 1990). The outer molecule (*B*) is linked to the inner molecule by a discrete hydrogen bond, graph set *D*, between its carboxy H atom and the ether O atom of molecule *A*. The dimensions within these two hydrogen bonds are similar to each other, and both hydrogen bonds are considered to be 'strong' (Desiraju & Steiner, 1999). The carboxyl C—O and C═O bonds in molecule *B* are clearly distinguished, at 1.320 (2) and 1.197 (2) Å, respectively, and are fully consistent with the results of previous studies (Leiserowitz, 1976). However, in molecule *A*, the distinction between C3*A*—O2*A* [1.250 (2) Å] and C3*A*—O1*A* [1.2601 (19) Å] is not so clear, possibly reflecting some degree of H-atom disorder in the eight-membered ring (see *Experimental*).

The conformation of the carboxy group, θ_{COOH} (the modulus of the average $C_{cage}—C_{cage}—C—O$ torsion angle; Venkatasubramanian, Donohoe *et al.*, 2003), in molecule *A* is 73.7 (2)°$_{syn}$, similar to that in 1-Me-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ [65.0 (2)°$_{syn}$; Venkatasubramanian, Donohoe *et al.*, 2003], whilst in molecule *B*, θ_{COOH} is 38.0 (2)°, close to the value in one of the crystallographically independent molecules of 1-Ph-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ [39.7 (3)°; Venkatasubramanian, Donohoe *et al.*, 2003]. At the same time, the conformation of the methoxymethyl substituent also differs between the two independent molecules of (I); in molecule *A*, the C1*A*—C4*A*—O3*A*—C5*A* torsion angle is −90.62 (18)°, whilst the corresponding angle in molecule *B* is −172.45 (17)°.

Within the carborane polyhedron, the C—C distances in both molecules *A* and *B* [1.669 (2) and 1.656 (2) Å, respectively] are longer than in the parent compounds, 1-CH_3OCH_2-1,2-*closo*-$C_2B_{10}H_{11}$ [1.636 (9) and 1.649 (8) Å; Shaw & Welch, 1992] and 1-COOH-1,2-*closo*-$C_2B_{10}H_{11}$ [1.631 (2) Å; Welch *et al.*, 2001], but fully comparable with that in 1-Me-2-COOH-1,2-*closo*-$C_2B_{10}H_{10}$ [1.6694 (17) Å; Venkatasubramanian, Donohoe *et al.*, 2003], reflecting the 1,2-disubstitution. The B—C and B—B distances span the ranges 1.703 (2)–1.744 (2) and 1.756 (2)–1.795 (3) Å, respectively.

Experimental

Compound (I) was prepared according to the procedure of Heying *et al.* (1963) for other monosubstituted carborane carboxylic acids. MeLi was added dropwise as an ether solution to a stirred solution of 1-CH_2OCH_3-1,2-*closo*-$C_2B_{10}H_{11}$ in ether at 273 K, in a ratio of 1:1. Gaseous CO_2 was passed through the solution at room temperature for 20 min. The solution was then hydrolysed with 2 *M* HCl. On removal of the solvent from the ether solution, an off-white crystalline solid remained. Diffraction quality crystals of (I) were grown from a mixture of dichloromethane and 40–60 petroleum ether (1:5) by solvent diffusion. Analysis calculated for $C_5H_{16}B_{10}O_3$: C 25.84, H 6.94%; found: C 25.44, H 7.13%. Spectroscopic analysis, IR (ν, cm^{-1}): 2589 (B—H), 1760, 1728 (C═O); ^{11}B-{^1H} FT–NMR (128.4 MHz, p.p.m.): 2.12 (1B), −0.69 (1B), −7.51 (8B). The carboxylic acid H atoms were not observed in the ^1H NMR spectrum, due to fast intermolecular exchange. Signals due to the CH_2 (4.05 p.p.m.) and CH_3 (3.25 p.p.m.) H atoms were observed. NMR spectra were recorded from a $CDCl_3$ solution at 293 K on a Bruker DPX400 spectrometer. The IR spectrum was recorded using a Perkin–Elmer Spectrum RX FT–IR system spectrophotometer and a KBr pellet.

Crystal data

$C_5H_{16}B_{10}O_3$
M_r = 232.28
Monoclinic, $C2/c$
a = 22.746 (2) Å
b = 9.6990 (10) Å
c = 23.439 (3) Å
β = 102.296 (10)°
V = 5052.1 (10) Å^3
Z = 16
D_x = 1.222 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 41 reflections
θ = 3.6–16.7°
μ = 0.07 mm^{-1}
T = 160 (2) K
Block, colourless
0.24 × 0.20 × 0.18 mm

Table 1
Selected geometric parameters (Å, °).

C1*A*—C4*A*	1.535 (2)	C1*B*—C4*B*	1.517 (2)
C2*A*—C3*A*	1.516 (2)	C2*B*—C3*B*	1.526 (2)
C4*A*—O3*A*	1.411 (2)	C4*B*—O3*B*	1.404 (2)
O3*A*—C5*A*	1.443 (2)	O3*B*—C5*B*	1.428 (2)
C1*A*—C2*A*—C3*A*	120.98 (12)	C1*B*—C2*B*—C3*B*	119.73 (14)
C2*A*—C1*A*—C4*A*	121.82 (12)	C2*B*—C1*B*—C4*B*	119.28 (14)
C1*A*—C4*A*—O3*A*	113.90 (13)	C1*B*—C4*B*—O3*B*	109.44 (14)
C2*A*—C3*A*—O1*A*	114.77 (14)	C2*B*—C3*B*—O1*B*	112.29 (14)
C2*A*—C3*A*—O2*A*	119.79 (14)	C2*B*—C3*B*—O2*B*	121.40 (16)
O1*A*—C3*A*—O2*A*	125.42 (15)	O1*B*—C3*B*—O2*B*	126.26 (16)
C4*A*—O3*A*—C5*A*	115.22 (13)	C4*B*—O3*B*—C5*B*	111.58 (15)
C4*A*—C1*A*—C2*A*—C3*A*	3.9 (2)	C4*B*—C1*B*—C2*B*—C3*B*	−1.1 (2)
C1*A*—C2*A*—C3*A*—O1*A*	164.45 (13)	C1*B*—C2*B*—C3*B*—O1*B*	53.25 (19)
C1*A*—C2*A*—C3*A*—O2*A*	−17.1 (2)	C1*B*—C2*B*—C3*B*—O2*B*	−129.22 (18)
C2*A*—C1*A*—C4*A*—O3*A*	−69.56 (18)	C2*B*—C1*B*—C4*B*—O3*B*	55.16 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O3*A*	0.95 (3)	1.70 (3)	2.6473 (17)	174 (2)
O1*A*—H1*A*···O2*A*^{i}	0.96 (2)	1.71 (2)	2.6707 (17)	175 (2)

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

Data collection

Siemens *P*4 diffractometer
ω scans
5399 measured reflections
4418 independent reflections
3670 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 25^\circ$
$h = -1 \rightarrow 26$
$k = -1 \rightarrow 11$
$l = -27 \rightarrow 27$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.129$
$S = 1.03$
4418 reflections
334 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 3.9862P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

The carboxylic acid H atoms were located from a difference Fourier map. The position and U_{iso} value of atom H1*B* were allowed to refine freely in subsequent refinement cycles. The O1*A*—H1*A* distance was restrained to 0.96 (2) Å and U_{iso}(H1*A*) was set to $1.5U_{eq}$(O1*A*). The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with U_{iso}(H) = $1.5U_{eq}$(C), but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.99 Å and B—H = 1.12 Å) and constrained to ride on their parent atoms, with U_{iso}(H) = $1.2U_{eq}$(parent atom).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; 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: LN1176). Services for accessing these data are described at the back of the journal.

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