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The synthesis and molecular and crystal structures of 1-methyl-2-carboxy-1,2-dicarba-*closo*-dodecaborane(12), 1-phenyl-2-carboxy-1,2-dicarba-*closo*-dodecaborane(12) and 1-phenyl-2-benzoyl-1,2-dicarba-*closo*-dodecaborane(12)

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Abstract

The structures of 1-Me-2-COOH-1,2-*closo*-C₂B₁₀H₁₀ (1), 1-Ph-2-COOH-1,2-*closo*-C₂B₁₀H₁₀ (2) and 1-Ph-2-COPh-1,2-*closo*-C₂B₁₀H₁₀ (3) have been determined by X-ray crystallography. In 1 the orientation of the COOH group is defined by $\theta_{COOH} = 65.0(2)_{syn}^{\circ}$, and this group H-bonds to that in a second molecule via a centrosymmetric eight-membered ring, $R_2^2(8)$. DFT calculations on the parent species 1-COOH-1,2-*closo*-C₂B₁₀H₁₁ reveal that the structure with $\theta_{COOH} = 90_{syn}^{\circ}$ is preferred, with a barrier to COOH rotation of $\approx 17 \text{ kJ mol}^{-1}$. Similar calculations on 1 yield a lower rotational barrier, $\approx 7 \text{ kJ mol}^{-1}$, because internal H-bonding is now denied. In compound 2 the COOH group is twisted to lower θ values [5.0(3)° and 39.7(3)°] but both crystallographically independent molecules exist as dimers in the solid state by virtue of $R_2^2(8)$ rings. Compound 2 crystallises from wet solvent as a monohydrate, the structure of which reveals a non-planar centrosymmetric $R_4^4(12)$ ring and near-orthogonal Ph and COOH substituents [$\theta_{Ph} = 6.7(2)$ and $\theta_{COOH} = 78.0(2)_{syn}^{\circ}$]. In compound 3 molecular association by H-bonding is blocked, so 3 serves as a useful comparative structure for 2.

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1. Introduction

Over the last few years the field of crystal engineering, part of which involves the development of rational strategies for the design of new crystalline materials, has emerged as an area of significant research activity [1]. Although the use of heteroboranes in studies of crystal engineering has begun to be exploited only fairly recently [2] the potential is vast. Heteroboranes are generally chemically and thermally stable species, existing as polyhedra or fragments of polyhedra of differing size and shape, but having architectures that are wellunderstood [3]. Isomeric possibilities mean that C-substituted (hetero)carboranes have the potential to function as supramolecular building blocks with differing directionalities in two-dimensions, which can further be expanded into three-dimensions via additional B-atom substitution [4]. Moreover, heteroboranes are usually neutral or anionic, but can also be cationic [5], thus further extending their potential applications as building block units.

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There are currently two main strategies for crystal engineering, based on the use of either co-ordinate bonds or weaker intermolecular interactions. Within the latter area, H-bonding has attracted most interest due to its relative strength and directionality [6]. Carboxylic acid groups are frequently used in the field of crystal engineering because they are capable of forming various types of hydrogen bonds between themselves and/or with other species such as solvents [7]. Accordingly, we have begun a systematic study of the crystal structures of carboxylic acid carboranes, their derivatives, and related species, in order further to increase our understanding of the effect of the carboxy group on the cage and any other substituents. We have already described $1-COOH-1, 2-closo-C_2B_{10}H_{11}$ [2m] (a dimer), 1,2- $(COOH)_2$ -1,2-*closo*-C₂B₁₀H₁₀ · 1/2C₂H₅OH [2p] and $1-CH_2OMe-2-COOH-1, 2-closo-C_2B_{10}H_{10}$ [2q] (both tetramers). Herein we report the structures of the methyl derivatives 1-Me-2-COOH-1,2-closoand phenyl $C_2B_{10}H_{10}$ and 1-Ph-2-COOH-1,2-*closo*- $C_2B_{10}H_{10}$, as well as that of the related species 1-Ph-2-COPh-1,2-clo $so-C_2B_{10}H_{10}$. Although the compounds described in this paper do not themselves give rise to extended arrays via H-bonding they do afford us a greater understanding of substituent effects in carborane structures that will be important if carboranes are to be used for crystal engineering in the future.

2. Experimental

2.1. Synthetic and spectroscopic studies

Experiments were performed under dry, oxygen-free N₂ using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Toluene, diethylether and $40-60^{\circ}$ petroleum ether were freshly distilled over Na. IR spectra were recorded as a CH₂Cl₂ solution or a KBr disk on a Perkin-Elmer Spectrum RX or 337 FTIR spectrophotometer. NMR spectra were recorded on a Varian Unity 300 or Bruker DPX 400 spectrometer as CDCl₃ solutions at ambient temperature, chemical shifts being recorded relative to SiMe₄ or CHCl₃ (¹H), $BF_3 \cdot OEt_2$ (¹¹B) and CDCl₃ (¹³C). Some ¹¹B NMR peak assignments were determined with the aid of ${}^{1}H{-}{{}^{11}B}$ (selective) spectra. ${}^{13}C$ NMR peak assignments corresponding to the aromatic carbons were determined with the benefit of ¹³C coupled spectra. Mass spectra were recorded on a VG Micromass 7070E instrument operating in the EI mode at 70 eV. Elemental analyses were determined by the departmental services at Heriot-Watt and Durham. The starting materials 1-Me-1,2-closo- $C_2B_{10}H_{11}$ [8] and 1-Ph-1,2-closo- $C_2B_{10}H_{11}$ [9] were prepared by literature methods or slight variants thereof. All other reagents were used as supplied.

2.1.1. Synthesis of 1-Me-2-COOH-1,2-closo- $C_2B_{10}H_{10}$ (1)

To a stirred solution of 1-Me-1,2-closo-C₂B₁₀H₁₁ (0.8 g, 5 mmol) in diethylether (25 ml) at 0 °C was added dropwise 1.1 equivalents of MeLi (as an ether solution). The solution was allowed to warm to room temperature, at which point gaseous CO₂ was bubbled through the solution for about 20-30 min. The milky solution thus formed was hydrolysed with 2 M HCl and transferred to a separating funnel. The ethereal layer plus ethereal washings of the aqueous layer were dried over MgSO₄ overnight. Removal of solvent afforded 1-Me-2-COOH-1,2-closo-C₂B₁₀H₁₀ (1) as an off-white microcrystalline solid. Yield: 0.69 g, 67%. Anal. Found: C, 23.7; H, 7.3. Calc. for $C_4H_{14}B_{10}O_2$: C, 23.8; H, 7.0%. IR $\nu(cm^{-1})$: 2630–2560 (s, BH), 1724 (s, CO). ¹H NMR, δ (ppm): 2.22 (s, CH₃). ¹¹B–{¹¹H} NMR, δ (ppm): 2.7 (1B), -2.4 (1B), -6.3 (8B).

2.1.2. Synthesis of 1-Ph-2-COOH-1,2-closo- $C_2B_{10}H_{10}$ (2)

Starting from 1-Ph-1,2-*closo*-C₂B₁₀H₁₁ (2.2 g, 10 mmol) in toluene (40 ml) and using one equivalent of nbutyllithium as deprotonating reagent, was similarly prepared 1-Ph-2-COOH-1,2-closo- $C_2B_{10}H_{10}$ (2) as a white solid, recrystallised from 40–60° petroleum ether. Yield: 1.48 g, 56%. Anal. Found: C, 40.6; H, 6.1; M_r (EI mass spectrum) 264 with typical carborane isotope pattern 258-268. Calc. for C₉H₁₆B₁₀O₂: C, 40.9; H, 6.1%; M_r 264. IR v(cm⁻¹): 3200–2800 (OH), 2651–2570 (s, BH), 1724 (s, CO). ¹H NMR, δ(ppm): 7.53 (d, 2H, *o*-C₆H₅), 7.36 (t, 1H, p-C₆H₅), 7.25 (t, 2H, m-C₆H₅), 3.05 (2H, B3,6H), 2.58 (1H, B9H), 2.49 (2H), 2.43 (3H, inc. B12H), 2.35 (2H). ¹¹B-{¹¹H} NMR, δ (ppm): -0.2 (1B, B9), -3.2 (1B, B12), -9.4 (4B), -10.3 (2B), -11.3 (2B, B3,6). ¹³C NMR, δ (ppm): 162.8 (CO), 130.7 (*i*, *o*-C₆H₅), 130.5 (p-C₆H₅), 128.6 (m-C₆H₅), 83.6 (C1), 75.3 (C2). Compound 2 can be recrystallised pure from dry $40-60^{\circ}$ petroleum ether, or recrystallised from wet solvents as the 1:1 water solvate, $2 \cdot H_2O$. Anal. Found: C, 38.3; H, 6.6; Calc. for $C_9H_{16}B_{10}O_2 \cdot H_2O$: C, 38.3; H 6.4%.

2.1.3. Synthesis of 1-Ph-2-COPh-1,2-closo- $C_2B_{10}H_{10}$ (3)

The compound 1-Ph-1,2-*closo*-C₂B₁₀H₁₁ (1.2 g, 5 mmol) in toluene (40 ml) was treated with *n*-butyllithium (2 ml of 2.5 M solution = 5 mmol). After heating to reflux for 30 min and cooling, PhCOCl (0.7 g, 5 mmol) was added. After further heating to reflux for 2 h, solvents were removed in vacuo and the residue dissolved in Et₂O and washed successively with NaHCO₃ (3 × 20 ml) and H₂O (4 × 30 ml). The ethereal layer was separated and dried over MgSO₄ overnight. Removal of solvent and recrystallisation from 40–60° petroleum ether afforded 1 Ph-2-COPh-1,2-*closo*-C₂B₁₀H₁₀ (3) as large white crystals. Yield: 1.00 g, 62%. *Anal.* Found: C, 55.6; H, 6.0; M_r (EI mass spectrum) 324, typical carborane isotope

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pattern 318–327. Calc. for $C_{15}H_{20}B_{10}O$: C, 55.5; H, 6.2%; M_r 324. IR $v(cm^{-1})$: 2621–2562 (s, BH), 1701 (s, CO). ¹H NMR, δ (ppm): 7.48 (d, 2H, o-C₆ H_5), 7.40 (t, 1H, p-C₆ H_5), 7.28–7.23 (m, 7H, C₆ H_5), 3.15 (2H, B3,6H), 2.55 (3H, inc. B9H), 2.39 (3H, inc. B12H), 2.33 (2H). ¹¹B– {¹¹H} NMR, δ (ppm): 0.2 (1B, B9), -3.0 (1B, B12), -9.3 (4B), -10.5 (4B, inc. B3,6). ¹³C NMR, δ (ppm): 185.5 (CO), 136.3 (*i*-COC₆H₅), 132.5 (*p*-COC₆H₅), 130.8 (*o*-C₆H₅), 130.6 (*i*, *p*-C₆H₅), 128.5 (*o*-COC₆H₅, *m*-C₆H₅), 127.9 (*m*-COC₆H₅), 85.0 (C1), 82.6 (C2).

2.2. Crystallographic studies

Single crystals of compounds 1, 2, $2 \cdot H_2O$ and 3 were grown from MeCN, dry 40-60° petroleum ether, CH₂Cl₂/40-60° petroleum ether, and hexane, respectively. Compounds 1 and 2 were studied at 160(2) K on a Bruker P4 diffractometer (Heriot-Watt University) with graphite-monochromated Mo Ka radiation $(\lambda = 0.71069 \text{ A})$ using ω scans. Compounds $2 \cdot H_2O$ and 3 were studied at 293(2) and 150(2) K, respectively, on a Rigaku AFC6S diffractometer (University of Durham) with graphite-monochromated Cu Ka radiation $(\lambda = 1.54178 \text{ Å})$ using ω scans. All structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares against F^2 , with nonhydrogen atoms assigned anisotropic displacement parameters [10]. For 1, all H atoms were refined positionally and thermally. For 2, only the hydroxy H atoms

Table 1	
Crystallographic	data

were allowed such refinement, all other H atoms being treated as riding. For $2 \cdot H_2O$ and 3 non-phenyl H atoms were refined independently and phenyl H atoms treated as riding. Table 1 lists details of unit cell data, intensity data collection and structure refinement.

2.3. Computational studies

DFT calculations on 1-COOH-1,2-*closo*-C₂B₁₀H₁₁ and 1-Me-2-COOH-1,2-*closo*-C₂B₁₀H₁₀ were performed using the ADF1999 programme [11] with the BP86 functional [12] and incorporating the quasi-relativistic corrections of Snijders and co-workers [13]. A double- ζ plus polarisation STO basis set was employed for all atoms and the frozen core approximation was applied (C, B: 1s). The C2–C1–C=O torsion angle, τ , was varied in nine steps of 22.5° from 0° to 180°, with full optimisation of the structure at every step. Within the COOH group the H–O–C=O torsion angle was originally set at 0° and did not deviate significantly from this during optimisation.

3. Results and discussion

3.1. Syntheses and spectroscopy

The carboxycarboranes $1-Me-2-COOH-1,2-closo-C_2B_{10}H_{10}$ (1) and $1-Ph-2-COOH-1,2-closo-C_2B_{10}H_{10}$ (2)

	1	2	2·H ₂ O	3
Colour and habit	colourless plate	colourless block	colourless block	colourless block
Crystal size (mm)	0.14 imes 0.80 imes 0.98	0.20 imes 0.20 imes 0.33	0.24 imes 0.30 imes 0.54	0.15 imes 0.30 imes 0.30
Formula	$C_4H_{14}B_{10}O_2$	$C_9H_{16}B_{10}O_2$	$C_9H_{16}B_{10}O_2 \cdot H_2O$	$C_{15}H_{20}B_{10}O$
M	202.25	264.32	282.33	324.41
System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
T (K)	160(2)	293(2)	160(2)	150(2)
a (Å)	12.073(2)	12.3493(13)	10.330(2)	10.469(8)
b (Å)	7.0945(8)	13.2722(12)	22.151(4)	15.154(7)
c (Å)	13.4283(12)	18.4075(16)	7.0260(10)	11.945(8)
β(°)	102.235(12)	90.632(8)	106.240(10)	106.57(5)
$U(Å^3)$	1124.0(3)	3016.9(5)	1543.5(5)	1816(2)
Z	4	8	4	4
D_{calc} (Mg m ⁻³)	1.195	1.164	1.215	1.186
$\mu ({\rm mm}^{-1})$	0.066 (Mo Ka)	0.489 (Cu Ka)	0.072 (Mo Kα)	0.458 (Cu Ka)
F(000)	416	1088	584	672
$\theta_{\text{datacollection}}$ (°)	3.10-24.99	4.11-60.00	2.05-25.01	4.84-75.09
Data measured	2663	7262	5279	5320
Unique data, R _{int}	1970, 0.0336	3951, 0.0343	2726, 0.0499	3491, 0.0794
Data $I > 2\sigma(I)$	1775	2479	2000	2481
R, wR_2 , (all data)	0.0446, 0.1195	0.0923, 0.1390	0.0730, 0.1133	0.1068, 0.2462
S (all data)	1.058	1.021	1.015	0.880
a, b	0.0728, 0.2098	0.0770, 0.3147	0.0461, 0.4911	0.1860, 0
Variables	201	387	251	276
$ ho_{ m max}, ho_{ m min}~({ m e}{ m \AA}^{-3})$	0.2610, -0.278	0.160, -0.156	0.223, -0.207	0.300, -0.275

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, \quad wR_{2} = [\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum w(F_{o}^{2})^{2}]^{1/2}, \quad (where \ w^{-1} = [\sigma^{2}(F_{o})^{2} + (aP)^{2} + bP] \quad \text{and} \ P = [0.333(F_{o})^{2} + 0.667(F_{c})^{2}]), \\ S = [\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / (n - p)]^{1/2}, \quad (where \ n \text{ is the number of data and } p \text{ the number of parameters}).$

were prepared in good yields by the established [14,15] method of deprotonation of the corresponding 1-R-1,2closo-C₂B₁₀H₁₁ species with LiR', addition of CO₂, and protonation during aqueous work-up. Although 1 and 2 are known species [14,15], spectroscopic characterisation has not previously been reported.

Spectroscopically, both 1 and 2 are consistent with time-averaged C_s molecular symmetry (or, of course, simple coincidence), arising from C(O)OH/C(OH)O exchange and/or rotation of the COOH group about the C_{cage} -C bond. The ¹¹B-{¹H} NMR spectrum of 1 at 128 MHz is fairly uninformative, with only three resonances of relative integrals 1:1:8 (high frequency to low frequency), each appearing as doublets (${}^{1}J_{BH} \approx 140$ Hz) in the proton-coupled spectrum. In contrast, the ${}^{11}B-{}^{1}H$ spectrum of 2 is somewhat more informative. The presumed 2+2+2+2 low-frequency co-incidence of 1 (assuming time-averaged C_s symmetry) is partially resolved (appearing as a 4[2+2]:2:2 set of three peaks). Moreover, the highest and lowest frequency resonances have been assigned. Given that we assign the highest-frequency BH resonance in the ¹H spectrum (3.05 ppm) of 2 to B3,6Hon the basis of several precedents [16], then by ${}^{1}H - {}^{11}B$ (selective) spectroscopy the lowest-frequency ¹¹B resonance (-11.3 ppm) is due to B3,6. It is well established that B atoms antipodal to C in closo carboranes occur at high frequency [17], and therefore the two resonances at -0.2 and -3.2 ppm are due to B9 and B12. Of these we assign the resonance at -0.2 ppm to B9 and that at -3.2 ppm to B12 by analogy with the B9,12 chemical shifts in the disubstituted analogues 1,2-(COOH)₂-1,2-*closo*-C₂B₁₀H₁₀ (0.3 ppm) [2p] and 1,2- $Ph_2-1,2-closo-C_2B_{10}H_{10}$ (-2.7 ppm), ¹ respectively. In the ¹H NMR spectra of **1** and **2** the OH peak shift varies with concentration and the presence of water. The ¹³C NMR spectrum of 2 is fully assigned, albeit with overlapping resonances at 130.7 ppm.

We have also prepared 1-Ph-2-COPh-1,2-closo-C₂B₁₀H₁₀ (**3**), a further known compound [18,19] not previously characterised spectroscopically. Both the ¹H and ¹¹B spectra are only partially assigned, but reveal clear evidence for time-averaged C_s molecular symmetry (which must involve rotation of the COPh group about the C_{cage}-C bond that is rapid on the NMR timescale at 293 K). Thus H3 and H6 are equivalent (3.15 ppm) and the ¹¹B spectrum appears as a 1:1:2+2:2+2 pattern (high to low frequency). Again the two highest-frequency ¹¹B resonances are due to the B atoms antipodal to C [17], with that at higher frequency (δ 0.2, B9) opposite the carboxy substituent. The ¹³C NMR spectrum of **3** is fully assigned, albeit with overlapping resonances at 130.6 and 128.5 ppm.

3.2. Structural and computational studies

We performed crystallographic analyses of compounds 1 and 2 to investigate the influence (if any) of adjacent Me and Ph substituents on the ability of the COOH group to participate in intermolecular H-bonding. A structural study of 3 was undertaken for comparison with that of 2, since in 3 H-bonding is blocked by the OH unit of 2 having been replaced by Ph.

In broad terms, compound **1** forms a double Hbonded dimer in the solid state (Fig. 1) via the mutual association of two carboxylic acid groups in an eightmembered ring about a crystallographic inversion centre, denoted $R_2^2(8)$ in graph-set terminology [20]. Essentially the same situation is seen in both crystallographically independent molecules of **2**, Fig. 2 showing the dimer of molecule **A**. In the water solvate $2 \cdot H_2O$ two molecules of H_2O are incorporated into the Hbonded ring to give a 12-membered ring, $R_4^4(12)$, shown in Fig. 3.

3.2.1. Intramolecular parameters in 1 and 2

Since we have previously reported crystallographic studies of 1-COOH-1,2-*closo*-C₂B₁₀H₁₁ (I) [2m] and 1,2-(COOH)₂-1,2-*closo*-C₂B₁₀H₁₀ · 1/2C₂H₅OH (II) [2p] it is instructive, on more detailed analysis, to consider first the influence of the Me and Ph groups of 1 and 2 on intramolecular parameters involving the COOH group. Table 2 summarises C1–C2, C–COOH, and θ_{COOH} (the modulus of the average C_{cage}–C₋O torsion angle) for 1, 2 (two independent molecules) and 2 · H₂O, as well as for the mono- and dicarboxycarboranes referred to above. For completeness, θ_{Ph} [21] (the modulus of the average C_{cage}–C_{cage}–C_{Ph}–C_{Ph} torsion angle) is also given for 2 and 2 · H₂O. Our definition of θ_{COOH} here [2p,2q]



Fig. 1. Perspective view of the H-bonded dimer of compound 1. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms.

¹ 128.38 MHz, CDCl₃, δ relative to neat BF₃ · OEt₂ at 0 ppm: -2.6 (2B, B9,12), -9.3 (4B, B4,5,7,11), -10.6 (2B, B8,10), -11.6 (2B, B3,6).



Fig. 2. Perspective view of the H-bonded dimer of compound **2** (molecule A only). Thermal ellipsoids are drawn at the 30% probability level, except for H atoms.



Fig. 3. Perspective view of the H-bonded dimeric unit of compound $2 \cdot H_2 O$. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms.

differs from that originally used [2m] for 1-COOH-1,2closo-C₂B₁₀H₁₁ and 1,2-(COOH)₂-1,2-closo-C₂B₁₀H₁₀ but is preferred as it is now calculated in an analogous way to θ_{Ph} . Complete listings of derived molecular parameters for 1, 2 and 2 · H₂O have been deposited as supplementary material.

In compound 1 the orientation of the COOH group with respect to C1 is specified by $\theta_{\text{COOH}} = 65.0(2)_{\text{syn}}^{\circ}$, the subscript [necessary for large θ_{COOH} ($\geq 45^{\circ}$) values] identifying that the C=O moiety is roughly syn to C1. The C1–C2 distance, 1.6694(17) Å and C2–C21 distance, 1.5172(16) Å, are 0.04 and 0.01 Å longer, and the C1–C2–C21 angle, 118.75(10)°, is 4° wider, than the corresponding parameters in **I**, collectively suggesting a degree of intramolecular steric crowding between the Me and COOH substituents in 1. ² Since such crowding could have been relieved by re-orientation of the COOH group, we were prompted to investigate the preferred orientation of the carboxy group in carboxycarboranes I and 1 by DFT calculations. Fig. 4 shows (upper plot) the energy of I as a function of fixed C_{cage}-C_{cage}-C=O torsion angle, τ , varied in 22.5° steps from 0° to 180°, with full structural optimisation at each stage; $\tau = 0°$ corresponds to $\theta_{\text{COOH}} = 90_{\text{syn}}^\circ$, $\tau = 90°$ corresponds to $\theta_{\text{COOH}} = 0°$, and $\tau = 180°$ corresponds to $\theta_{\text{COOH}} = 90_{\text{anti}}^\circ$. The orientation $\theta_{\text{COOH}} = 90_{\text{syn}}^\circ$ is preferred to $\theta_{\text{COOH}} = 90_{\text{anti}}^\circ$ by $\approx 6 \text{ kJ mol}^{-1}$, and the barrier to rotation is $\approx 17 \text{ kJ mol}^{-1}$. In I the observed [2m] orientation, $87.5(2)_{\text{syn}}^\circ$, is close to the optimal one predicted.

The lower plot in Fig. 4 shows the result of a similar DFT calculation on 1 drawn on the same scale as the upper plot. This time the energy profile is flatter (barrier to rotation $\approx 7 \text{ kJ mol}^{-1}$) which we ascribe to the $\theta_{\rm COOH} = 90_{\rm anti}^{\circ}$ and (particularly) the $\theta_{\rm COOH} = 90_{\rm syn}^{\circ}$ orientations no longer being stabilised by intramolecular H-bonding, as was the case with I. Such intramolecular H-bonding, involving the relatively acidic proton on C2, has recently been noted [22] in 1-(C₅H₄N-2')-1,2-closo- $C_2B_{10}H_{11}$ and its 4'-Br analogue, both of which have a C_{cage}-C_{cage}-C-N torsion angle close to 0°. In 1 the observed 25° twist about the C-COOH bond $[\theta_{\text{COOH}} = 65.0(2)_{\text{syn}}^{\circ}]$, presumably due to the steric influence of the adjacent Me group, is accurately reproduced in the calculations, which show a minimum energy when τ is $\approx 30^{\circ}$.

The 1,2-dicarboxycarborane crystallises as the $\cdot 1/2C_2H_5OH$ solvate, II [2p]. In II there are four crystallographically independent carborane molecules arranged in two centrosymmetric tetrameric units held together by H-bonding that incorporates the solvate. Every carborane has one COOH in a low and one COOH in a high θ orientation (half the high θ orientations are syn, half are anti). The experimental data in Table 2 reveal a definite pattern – high θ (whether syn or anti) is associated with a C–COOH bond length of ≈ 1.51 Å and low θ is associated with a measurably longer C–COOH bond, $\approx 1.52-1.53$ Å. This pattern is reproduced in the DFT calculations on I, which give C–COOH 1.515 ($\theta = 90_{syn}^{\circ}$), 1.514 ($\theta = 90_{anti}^{\circ}$) and 1.525 Å ($\theta = 0^{\circ}$).

Compound 2 crystallised from dry solvent has two crystallographically independent molecules (A and B) per asymmetric unit. In both A and B the orientations of Ph and COOH substituents are characterised by low θ

² Further evidence for intramolecular crowding in **1** is demonstrated from fully optimised MP2/6-31G* geometries of 1-Me-1,2-*closo*-1,2- $C_2B_{10}H_{11}$ and **1** where the C–C–C(Me) angle widens from 118.4° to 120.6°, respectively. The crystallographic structure of the carborane 1-Me-1,2-*closo*-1,2- $C_2B_{10}H_{11}$ remains unreported (search of the Cambridge Crystallographic Database, version 5.24, July 2003).

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Compound	x	<u>C1-C2</u>	<u>С-СООН</u>	An ^a	Accoub	Reference
-		01 02	0.00011	OPh	OCOOH	
1	Н	1.631(2)	1.507(2)	_	87.5(2) _{syn}	[2m]
II (A) ^c	COOH	1.660(2)	1.527(3)	_	5.3(2)	[2p]
			1.515(3)		74.5(2) _{anti}	
II (B)	COOH	1.651(2)	1.523(3)	_	0.6(2)	[2p]
			1.510(3)		87.9(2) _{syn}	
II (C)	COOH	1.652(2)	1.525(2)	_	4.9(2)	[2p]
			1.510(3)		89.2(2) _{syn}	
II (D)	COOH	1.653(2)	1.522(3)	_	14.1(2)	[2p]
			1.514(3)		60.2(2) _{anti}	
1	Me	1.6694(17)	1.5172(16)	_	65.0(2) _{syn}	this work
2(A) ^d	Ph	1.678(3)	1.509(4)	26.6(3)	5.0(3)	this work
2(B)	Ph	1.691(3)	1.504(4)	16.2(3)	39.7(3)	this work
$2\cdot\mathbf{H}_{2}\mathbf{O}$	Ph	1.705(2)	1.517(2)	6.7(2)	78.0(2) _{syn}	this work

Table 2 Summary of C1–C2 and C–COOH distances (Å) and Ph and COOH orientations (°) for carboxycarboranes

 $^{a}\theta_{Ph}$ defined [21] as the modulus of the average C_{cage} - C_{cage} - C_{Ph} - C_{Ph} torsion angle.

^b θ_{COOH} defined as the modulus of the average C_{cage} - C_{cage} - C_{cage} - C_{cage} - C_{cage} atom to which COOH is *not* bound as either syn or anti. These terms correspond to τ values of 0° and 180° respectively (Fig. 4).

^cFour crystallographically independent molecules.

^d Two crystallographically independent molecules.





 $C_{cage}\mathchar`-C=O$ torsion angle, $\tau\,(^o)$

Fig. 4. Plot of relative energy of 1-COOH-1,2-*closo*-C₂B₁₀H₁₁ (I) and 1-Me-2-COOH-1,2-*closo*-C₂B₁₀H₁₀ (I) as a function of the C_{cage}-C_{cage}-C=O torsion angle, τ , by DFT calculation.

values (broadly similar to the situation observed in 1,2diaryl-1,2-*closo*-C₂B₁₀ species [23]), but in **2**(**A**) the Ph group is the more twisted $[\theta_{Ph} = 26.6(3)^\circ, \theta_{COOH} =$ $5.0(3)^\circ]$ whilst in **2**(**B**) θ_{COOH} is the greater $[\theta_{Ph} =$ $16.2(3)^\circ, \theta_{COOH} = 39.7(3)^\circ]$. In **2** C1–C2 distances are marginally larger, and C–COOH distances marginally shorter, than those in **1**. When crystallised from wet solvent, 1-Ph-2-COOH-1,2-*closo*-C₂B₁₀H₁₀ crystallises as the monohydrate $2 \cdot H_2O$ and incorporates two molecules of H₂O in an extended (12-membered) H-bonded ring system. In $2 \cdot H_2O$ the COOH group stands effectively perpendicular to the Ph ring, $\theta_{COOH} = 78.0(2)_{syn}^{\circ}$, reminiscent of its relative orientation in 1. The C-COOH distance in $2 \cdot H_2O$ is identical to that in 1, but C1-C2 is the longest of all the structures described herein.

3.2.2. Intermolecular parameters in 1 and 2

As previously noted, both 1 and 2 form centrosymmetric eight-membered H-bonded rings in the solid state $[R_2^2(8)]$ whilst $2 \cdot H_2 O$ forms a centrosymmetric 12-membered ring that incorporates water $[R_4^4(12)]$. Parameters involved in these H-bonding rings are summarised in Table 3.

According to current conventions [24], all the Hbonds observed in this study are classified as "strong", with H···O distances (d) < 2 Å and O–H··· O angles (δ) close to 180°. The planar eight-membered cyclic Hbonded homodimer of two COOH groups observed in **1** and **2** is ubiquitous [7] for this well-known supramolecular synthon [1] and dimensions within it are quite standard. The 12-membered H-bonded ring of **2**·H₂**O** is of approximate chair conformation. Within it, H3A···O2[#], d = 1.87(4) Å, appears somewhat weaker than H1···O3, d = 1.65(3) Å, and the former is accompanied by an angle ϕ at the COOH acceptor that is close to 180° (c.f. ϕ in **1** and **2** near 120°). A search of the Cambridge Crystallographic Database (version 5.24,

Table 3 Hydrogen bonding distances (Å) and angles (°) in the carboxycarborane compounds 1 and 2

$O_1 - \underbrace{\frac{r}{U_1}H_2}_{\delta} - \underbrace{\frac{r}{U_2}O_2}_{\phi} Y$								
Compound	O_1	Н	O_2	Y	r	d	δ	ϕ
1	01	H1	O2 ^a	C21 ^a	0.90(2)	1.75(2)	175(2)	122(2)
2(A)	OIA	HOA	O2A ^a	C19A ^a	1.11(6)	1.55(6)	171(4)	128(4)
2(B)	O1B	HOB	O2B ^a	C19B ^a	1.02(5)	1.61(5)	176(4)	124(4)
$2 \cdot H_2O$	01	H1	O3	H3A	0.90(3)	1.65(3)	173(3)	120(3)
	01	H1	O3	H3B			~ /	120(3)
$2\cdot H_2O$	O3	H3A	O2 ^a	C21 ^a	0.85(4)	1.87(4)	172(3)	174(3)

^a Atom generated by inversion in centre of H-bonding ring.

July 2003) reveals 57 similar 12-membered rings involving two COOH groups and two H₂O molecules in the current literature, of which 42 do not involve charged species. In only 15 cases are all four H...O distances <2 Å, with the shortest distances [H_{COOH}... O_{H2O} 1.43; $H_{H2O} \cdots O_{COOH}$ 1.61 Å] recorded for 1,3,5cyclohexanetricarboxylic acid monohydrate [25]. The H-bonded distances observed in $2 \cdot H_2 O$ are most clearly mirrored in 2,3-dihydroxysuccinic acid monohydrate [26] $[H_{COOH} \cdots O_{H2O} \ 1.64; H_{H2O} \cdots O_{COOH} \ 1.90 \ A].$

3.2.3. The structure of 3

As a complement to the crystallographic study of 2 we have also determined the structure of the phenylbenzoylcarborane 3. Fig. 5 shows a perspective view of a single molecule and Table 4 hosts selected intramolecular parameters.

Compound 3 crystallises as discrete molecules with no significant intermolecular contacts - replacing the carboxy group of 2 with the benzoyl group prevents association via H-bonding. As far as we are aware this structural study is the first reported of a simple carborane ketone, i.e. carborane-C(O)-R. The C1-C2 distance, 1.695(3) A, identical to that in related acetato compound $[\{1-Ph-2-COO(Sn^{n}Bu_{2})-1,2-closo-C_{2}B_{10}H_{10}\}_{2}O]_{2}$ [27]

Fig. 5. Perspective view of compound 3. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms.

Table 4				
Selected interatomic distant	nces (Å) and	interbond	angles (°)	for 3

Bond distances C(1)–C(2) C(1)–C(13) C(2)–C(19)	1.695(3) 1.507(3) 1.547(3)	C(19)–O C(19)–C(20)	1.210(3) 1.485(3)
<i>Bond angles</i> C(2)–C(19)–C(20) C(2)–C(19)–O	124.2(9) 117.2(9)	O-C(19)-C(20)	93.48(9)

and similar to those in 2, is shorter than that in 1,2-Ph₂- $1,2-closo-C_2B_{10}H_{10}$ [23a] [1.727(6) A, averaged over the two crystallographically independent molecules]. The cage-bound Ph group is oriented with $\theta_{\rm Ph} = 6.9(2)^{\circ}$. The primary benzoyl orientation θ_{benz} (the modulus of the average C1-C2-C19-O and C1-C2-C19-C20 torsion angles) is $12.3(2)^{\circ}$, and there is a twist of $48.8(2)^{\circ}$ about the C19-C20 bond, as is clearly evident from Fig. 5.

4. Conclusions

In the solid state the substituted carboxy carboranes 1-R-2-COOH-1,2-closo-C2B10H10 give rise to homodimers with eight-membered H-bonded rings (R = Me, 1; $\mathbf{R} = \mathbf{Ph}, \mathbf{2}$). The monohydrate $\mathbf{2} \cdot \mathbf{H}_2 \mathbf{O}$ crystallises with a 12-membered H-bonded ring incorporating two carboxylic acid groups and one water molecule. In 1 the orientation of the COOH group is close to that shown computationally to be preferred and a similar orientation persists in $2 \cdot H_2 O$, whilst in 2 it is twisted to a much lower θ_{COOH} value. In the context of the relative orientations of cage substituents, 2 is similar to 1-Ph-2-COPh-1,2-closo- $C_2B_{10}H_{10}$ (3), which crystallises as discrete monomers.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 214908 (1), 214909 (2), 214910 (2·H₂O) and 214911 (3). Copies of this infor-



mation may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http//www.ccdc.cam.ac.uk).

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