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Trends in *ortho*-carboranes $1-X-2-R-1, 2-C_2B_{10}H_{10}$ (R = Ph, Me) bearing an *exo*-CN-bonded substituent group (X = NO, N=NR' or NHR'')

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ABSTRACT

The preparation and crystal structures of four ortho-carboranyl-nitrogen compounds, $PhCb^{o}N=N(C_{6}H_{4}Me-4)$ (1), $PhCb^{o}NHNH(C_{6}H_{4}Me-4)$ (2), $MeCb^{o}NHNHPh$ (3) and $PhCb^{o}NHOH$ (4) $(Cb^{\circ} = 1,2-C_2B_{10}H_{10})$; nitrogen groups at cage carbon C1, Ph or Me at C2), the last as a 1,4-dioxane solvate, are reported. Comparisons of their structures with those of other ortho-carboranyl-nitrogen systems studied earlier reveal further correlations between their cage C-C and exo-C-N bond distances and bond orders. Substituent orientations and bond distances (cage C1-C2, exo-C1-N) in RCb^oNHR^{''} systems (R = Ph or Me at C2) are consistent with dative π -bonding from a nitrogen lone pair into the cage carbon p-AO otherwise responsible for cage C1–C2 σ bonding. Their C1–C2 bond distances are remarkably sensitive to the planar (sp^2) or pyramidal (sp^3) nature of the NHR'' group. The N=O and N=NR' residues in RCb^oX prefer to be orientated in plane with the cage C1-C2 in contrast to the RCb^oNHR'' systems. Correlations between their cage C-C and exo-C-N bond distances and the ¹¹B NMR chemical shifts of their antipodal boron atoms reflect the π -bonding characteristics of the nitrogen substituent.

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1. Introduction

The remarkable capacity of π -donor substituents, attached to carbon atoms of an ortho-carborane C₂B₁₀ cage, to influence cage C1–C2 bond lengths was first detected some two decades ago [1] with the structural characterisation of the proton sponge salt of the anion PhCb^oO⁻, (Cb^o = $1,2-C_2B_{10}H_{10}$; O⁻ at cage carbon C1, Ph at C2) followed by many related studies [2,3-7] on ortho-carboranes containing thiolato and phosphino groups. However, this area has only recently been documented systematically by experimental and computational studies on systems RCb^oX and XCb^oX in which X is a potential π -donor such as NH₂, OH, SH or anions derived therefrom by deprotonation [8,9]. Exo-C=X π -bonding in these systems between the cage carbon atom and substituent X involves a tangentially oriented p-AO on carbon that would otherwise be involved in cage bonding, and C1-C2 bond lengthening will occur if the *p*-AO used for *exo*-C=X π -bonding is the *p*-AO that in ortho-carborane itself is involved in C1–C2 σ -bonding (AO = atomic orbital; Fig. 1).

The extent to which the cage C1–C2 bond is affected by *exo* π bonding will therefore depend on the orientation of the substituent in the *exo*-CN systems explored here. Though many *ortho*-carborane derivatives with *exo*-C–N bonds are known, only three structural studies have been carried out elsewhere to our knowledge: the first was on a rhenium complex ⁱPrCb^oN₂Re(CO)₄ [10], which contains a 6-membered –Re–N=N–C–B–H– ring in which the metal atom is attached to one nitrogen atom and to a boron-attached hydrogen; the second was on a hydrazocarborane, HCb^oNRNHR (R = CO₂^tBu) [11], which contains an intramolecular cage C–H···O hydrogen bond [12]; and the third was on a zirconium complex, PhN₃Cb^oZrCp₂ [13], which contains a 3-membered ZrN₂ ring. All three systems thus contain intramolecular interactions that influence the orientation about nitrogen at C1 with respect to the cage C1–C2 bond.

In 2004, we reported the crystal structures of PhCb^oNH₂ and the adduct PhCb^oNH₂·OP(NMe₂)₃ which revealed six independent molecules with C1–C2 bond distances ranging between 1.74 and 1.85 Å [8]. We also reported improved syntheses of *ortho*-carborane nitroso derivatives RCb^oNO and dicarboranylamines (RCb^o)₂NH (R = Ph, Me) and discussed their structures, which in the case of the secondary amines (and amides [(RCb^o)₂N]⁻ derived therefrom) showed significant cage distortion (C1–C2 bond lengthening) attributable to *exo-C*=N π -bonding [14–16]. To supplement these studies, we have carried out a synthetic, spectroscopic, structural and computational investigation of the compounds

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Fig. 1. Orbitals involved in the *exo* π -bonding for RCb^oX where X is a π -donating group and R is not a donor group.

RCb^oX (R = Ph, Me; X = NNR', NHNHR', NHOH; R' = Ph or C₆H₄Me-4), and further spectroscopic and computational studies on systems with X = NH₂, NO, NHCb^oR and [NCb^oR]⁻, which have revealed hitherto unremarked characteristics and trends in *ortho*carborane systems RCb^oX containing *exo*-CN units, which we report here.

2. Results and discussion

In this section, we outline the synthetic procedures used to prepare the new compounds, and describe their structures. We then explore the structural, bonding and spectroscopic characteristics of *ortho*-carboranyl-nitrogen systems RCb^oN=O, RCb^oN=NR' and RCb^oNHR'' in general, including both the new systems and those previously characterised [8,14]. We also compare the structural and bonding relationships of these 3D pseudoaromatic cages with 2D aromatic ring analogues.

2.1. Synthetic aspects

Scheme 1 summarises the experimental procedures used for the syntheses of the carboranes investigated in this definitive study. Synthetic methods that have not been reported in our earlier papers [8,14] are described in detail in Section 4. The azocarboranes were synthesised using a reported literature procedure [17]. The reductions of the nitroso-carboranes RCb^oNO with hydrogen using a palladium/carbon catalyst gave the known [18,19] hydroxylamines RCb^oNHOH in high yields. High-yield reductions of the azocarboranes RCb^oNHNHAr were carried out here using the reducing agents LiAlH₄ and Zn/HCl.

2.2. Structural aspects: new experimentally determined structures

2.2.1. The azo-carborane PhCb^oN₂(C_6H_4 Me-4) (**1**) and hydrazocarboranes PhCb^oNHNH(C_6H_4 Me-4) (**2**) and MeCb^oNHNHPh (**3**)

The crystal structures of these three compounds were determined by X-ray diffraction (for details, see Section 4). Their molecular structures are illustrated in Figs. 2 and 3.

The structures of the azo-carborane (1) and its hydrazo analogue (2) (Fig. 2) are similar, differing significantly, and as expected, only in the bond lengths and angles in the region of their -N=N- and -N(H)N(H)- units. Their NN links, at 1.250(2) in (1) and 1.409(2) Å in (2), are of normal length for double and single bonds, respectively, between nitrogen atoms. The CNN bond angles, at both ends of the N(1)–N(2) links, appear not to differ between the two ends (implying that the link to the carboranyl residue resembles that to the aryl group in both 1 and 2) nor between 1 and 2, suggesting both 1 and 2 contain sp^2 -hybridised



Scheme 1. Routes to carboranyl-nitrogen derivatives.



Fig. 2. Molecular structures of PhCb^oN₂C₆H₄Me (1) and PhCb^oNHNHC₆H₄Me (2). Selected bond distances (Å) and angles (°) for (1): N(1)–N(2) 1.250(2); N(2)–C(9) 1.428(3); C(2)–C(3) 1.509(3); N(1)–N(2)–C(9) 112.88(15); N(1)–N(2)–C(9)–C(14) 15.3(3). For (2): N(1)–N(2) 1.409(2); N(2)–C(9) 1.421(3); C(2)–C(3) 1.497(3); N(1)–N(2)–C(9) 115.73(16); N(1)–N(2)–C(9)–C(14) –25.7(3).

nitrogen atoms. In both **1** and **2**, the phenyl substituent on C(2) lies in a plane roughly perpendicular to the N(1)–C(1)–C(2) plane, as would be expected not only on steric grounds (to keep it away from the substituent on C(1)), but also as this is the orientation that optimises π -donation from ring to cage and causes *ca*. 0.03 Å C1–C2 bond lengthening [20–23].

The orientations of the azo and hydrazo substituents on C(1), however, differ significantly. In **1**, the azo N(1)–N(2)–C(9) unit lies in the N(1)–C(1)–C(2) plane, as in the nitroso carborane PhCb^oNO studied previously [14]. In **2**, the hydrazo N(1)–N(2)–C(9) unit is twisted out of the C(1)–C(2)–C(3) plane, clearly not on steric grounds, but to an extent that significantly ensures that the lone pair on N(1) lies in that plane. The view of **2** in Fig. 2 shows the *ortho* hydrogen atom on C(14) lying over, and attracted to, the π -cloud of the phenyl group on C(2), with an H…centroid distance of 2.65 Å, and this attraction is likely to be responsible for the orientation of the tolyl group.

The molecular structure of compound **3**, MeCb^oNHNHPh, shown in Fig. 3, differs from that of **2** in the orientation of the aryl-hydrazo group, away from the methyl substituent on C(2). However, the local geometry about N(1) resembles that in **2** in ensuring that the lone pair on N(1) lies in the N(1)–C(1)–C(2) plane.

2.2.2. The hydroxylamino-carborane PhCb^oNHOH (4)

The molecular structure of this compound (Fig. 4) was determined by single-crystal studies on a dioxane hemisolvate of composition PhCb^oNHOH·0.5dioxane. The orientations of both substituents on the carborane cage were found to resemble those already discussed for compounds **2** and **3**, and are in line with those found previously for PhCb^oNH₂ [8]. The phenyl group in **4** lies roughly perpendicular to the N(1)–C(1)–C(2) plane, and the HNOH



Fig. 3. Molecular structure of MeCb^oNHNHPh (**3**). Selected bond distances (Å) and angles (°): N(1)-N(2) 1.395(2), N(2)-C(9) 1.405(2), C(2)-C(3) 1.511(2), N(1)-N(2)-C(9) 119.17(13), N(1)-N(2)-C(9)-C(14) -19.0(2).



Fig. 4. Molecular structure of PhCb^oNHOH (**4**). The dioxane molecule in the crystal structure is not shown. Selected bond distances (Å): N(1)-O(1) 1.435(2); C(2)-C(3) 1.506(3).



Fig. 5. Supramolecular structure of PhCb^oNHOH·0.5dioxane. Selected intermolecular distances (Å) and angles (°): $O(1) \cdots O(2)$ 2.752(2), $N(1) \cdots O(1A)$ 3.209(2), $O(1) - H(2) \cdots O(2)$ 177(3), $N(1) - H(1) \cdots O(1A)$ 167(2). [O(1A) is generated from O(1) by screw-axis symmetry].

unit is oriented away from the phenyl group, like the HNNHR unit in **2**, implying that the lone pair on the nitrogen lies in the N(1)– C(1)–C(2) plane. In the crystal structure, intermolecular N–H···O hydrogen-bonding interactions between the hydroxylamino units link the molecules into (PhCb^oNHOH)_n chains, which in turn are interlinked by N–OH···O hydrogen bonds to both oxygen atoms of the dioxane molecules (Fig. 5).

2.3. Structural aspects: general characteristics of RCb^oN systems

The structures of the four compounds **1–4** described above, together with the four in our previous paper [14] [PhCb^oNO, (PhCb^o)₂NH, (MeCb^o)₂NH and the anion (PhCb^o)₂N⁻] and the amine PhCb^oNH₂ characterised earlier [8], provide a useful data bank from which to deduce some common characteristics of *ortho*-carboranyl-nitrogen systems. These include preferred orientations of the *exo*-nitrogen substituent with respect to the carborane cage, and systematic complementary trends in their *exo*-C(1)–N(1) and cage C(1)–C(2) bond distances; as the former shorten, the latter lengthen.

The compounds we have studied are of two formula types, RCb^oNHR'' and RCb^oN=Z. Their structures are shown in Figs. 6 and 7. The nitroso- and azo-carboranes PhCb^oN=O and PhCb^oN=N(C₆H₄Me-4) are of the latter type [14]. All of the other compounds are of the former type, including the anion (PhCb^o)₂N⁻ in which the lone pair left on deprotonation of the parent amine can be regarded as occupying the site vacated by proton.

Figs. 6 and 7 show the NHR" and N=Z units in their preferred orientations about the exo-C(1)–N(1) bond with respect to the carborane cage, with the substituents R" or Z leaning away from the

substituent R (Ph or Me) on the other cage carbon atom C(2). This orientation not only minimises steric non-bonding repulsive interactions between the groups on C(1) and C(2), but aligns the lone pair of electrons on the *exo*-nitrogen atom on C(1) in the C(2)–C(1)–N(1) plane for RCb^oNHR", the alignment best suited for dative π -bonding from the nitrogen lone pair into the *p*-AO on C(1) responsible for cage C(1)–C(2) σ -bonding, as shown in Fig. 6.

The extent to which *exo*-dative C=N π -bonding donation from the NHR" group occurs (and whether it does so at the expense of cage C(1)-C(2) σ -bonding) can be inferred from the experimental C(1)-C(2) and C(1)-N(1) distances in Table 1, in which compounds are listed in the order of their increasing cage C(1)-C(2) distances, which matches the sequence of decreasing C(1)-N(1) distances. Table 1 includes also torsion angles C(2)-C(1)-N(1)-Z/R'', which reveal that these compounds show some departures from the preferred orientations shown in Figs. 6 and 7; bond angles C(2)-C(1)-N(1), which show expected deviations from a normal angle of 121.7° for an exo-bond on a regular icosahedron; and the C(1)-N(1)-Z/R" bond angles at nitrogen, which for species RCb^oNHR" would be 120° for an ideal trigonal planar coordination at nitrogen (sp²) and 109° for pyramidal nitrogen (sp³). The data in Table 1 include the four distinct molecules of PhCb^oNH₂ in the asymmetric unit of the crystal structure and for the two distinct molecules of this same species in its hydrogen-bonded adduct with hexamethvlphosphoramide, PhCb^oNH₂·HMPA [8].

The range over which cage C(1)-C(2) bond distances vary in Table 1 (1.677(2)–1.995(3) Å, i.e. 0.32 Å) is more than twice the range over which *exo-C*=N distances vary (1.490(2)–1.345(4) Å i.e. 0.15 Å), because the former are fractional-order bonds becoming progressively weaker as the table is descended, whereas the latter



Fig. 6. Preferred orientations in RCb^oNHR'' systems. The cage acts as a π -acceptor.



Fig. 7. Preferred orientation in RCb^oN=Z systems (Z = O, NR'). The cage *may* act as a π -donor.

Table 1

X-ray-determined trends: the optimum torsion angle C(2)-C(1)-N(1)-Z/R'' to align the p-orbital lone pair of sp^2 -hybridised nitrogen with the cage C(1)-C(2) bond is 90° for compounds RCb°NHR'', and to align the sp^2 -orbital lone pair of sp^2 -hybridised nitrogen with the cage C(1)-C(2) bond is 180° for compounds RCb°N=Z. HMPA = OP(NMe_2)_3.

Х		C(1)–C(2) (Å)	C(1)-N(1) (Å)	C(2)-C(1)-	•N(1) (°)	C(1)-N(1)-Z/R'' (°) C(2)-C(1)-N(1)	−Z/R′′ (°)	C(1)-C(2)-C(Ph)-C(Ph) (°)	Reference
PhCb ^o X										
NO		1.677(2)	1.490(2)	112.1(2)		113.0(2)	164.7		82.4	[14]
N=NC ₆ H ₄ Me		1.694(2)	1.443(2)	111.3(1)		112.8(2)	178.2		75.5	This work
NHOH		1.737(3)	1.423(3)	115.7(2)		110.7(2)	101.6		86.5	This work
$NH_{2}(4)$	Α	1.745(3)	1.391(3)	119.3(2)					69.9	[8]
	В	1.765(3)	1.403(3)	115.9(2)					91.2	
	С	1.774(3)	1.404(3)	119.8(2)					64.1	
	D	1.785(3)	1.392(2)	118.5(2)					76.7	
NHNHC ₆ H ₄ Me		1.778(3)	1.401(2)	115.2(2)		116.4(2)	105.9		83.4	This work
NHCb⁰Ph		1.794(3)	1.404(2)	117.3(2)		132.0(2)	92.4		70.1	[14]
		1.799(3)	1.404(2)	116.9(2)			97.6		73.9	
$NH_2 \cdot HMPA(2)$	Α	1.818(8)	1.360(8)	116.1(6)					59.3	[8]
	В	1.853(8)	1.363(9)	114.9(5)					81.8	
[NCb ^o Ph] ⁻		1.980(3)	1.355(4)	118.8(2)		127.0(2)	90.3		53.6	[14]
		1.995(3)	1.345(4)	118.8(2)			89.0		53.2	
	С	(1)–C(2) (Å)	C(1)–N(1) (Å	Å) C	C(2)-C(1)-	·N(1) (°)	C(1)–N(1)–Z/R'' (°)	C(2	2)-C(1)-N(1)-Z/R'' (°)	Reference
MeCb°X	_									
NHCb⁰Me	1	.748(4)	1.409(4)	1	17.3(2)		131.1(2)	95	.0	[14]
	1	.752(4)	1.410(4)	1	17.0(2)		131.1(2)	94	.7	
NHNHPh	1	.770(2)	1.388(2)	1	15.9(1)		118.8(1)	10	4.1	This work

Table 2

Observed bond distances (Å) and calculated bond orders.

Х	C(1)-C(2)	Bond order	C(1)-N(1)	Bond order	π -Bond order
PhCb⁰X					
NO	1.677(2)	0.605	1.490(2)	0.921	0.056
N=NAr	1.694(2)	0.590	1.444(2)	0.998	0.070
NHOH	1.737(3)	0.539	1.423(3)	1.025	0.073
NHNHAr	1.778(3)	0.485	1.401(2)	1.044	0.104
NHCb⁰Ph	1.798(3)	0.453	1.404(2)	1.038	0.124
$NH_2(C)$	1.774(3)	0.456	1.404(3)	1.102	0.143
NH ₂ ·HMPA (av)	1.835(8)	0.396	1.362(8)	1.146	0.185
[NCb ^o Ph] ⁻	1.987(3)	0.235	1.350(4)	1.295	0.357
MeCb°X					
NHCb ^o Me (av)	1.750(4)	0.506	1.410(4)	1.026	0.113
NHNHPh	1.770(2)	0.486	1.387(2)	1.057	0.128

range in bond order from single to multiple. To aid comparison within the series, AM1 calculations have been carried out using the atomic coordinates determined by X-ray diffraction, without further optimisation. Selected bond distances and orders, with corresponding σ and π contributions, are given in Table 2.

The data in Table 2 show the correlation between the cage C(1)-C(2) and *exo*-C(1)-N(1) bond orders expected from their lengths. The bond orders of the cage $C \cdots C$ bonds decrease as those of the exo-C(1)-N(1) bonds increase. The range over which the C(1)-C(2) bond orders vary (from 0.61 in PhCb^oNO to 0.24 in the anion $(PhCb^{o})_{2}N^{-}$) is comparable to that over which the *exo*-C(1)–N bond orders vary (from 0.92 to 1.30), and is itself worthy of comment. Because icosahedral carborane clusters are held together by only 13 skeletal electron pairs spread around their 30 edge 'bonds', the average cage edge bond order will be 0.43 (13/30). The cage carbon-carbon bond in ortho-carborane HCb^oH itself has an order some 50% in excess of this because the carbon atoms are more electronegative than their boron neighbours and so attract a greater share of the electrons available. The data in Table 2 show that the cage C(1)-C(2) bond order has been reduced to about this average icosahedral value of 0.43 in the amine PhCb^oNH₂, and to roughly half this value in the anion $(PhCb^{o})_{2}N^{-}$.

In our discussion of bond lengths and bond order so far, we have concentrated on the cage C(1)-C(2) and exo-C(1)-N(1) bonds. This is because these are the only bonds in these systems PhCb^oX whose lengths and orders change significantly and systematically with X,

as illustrated by the data in Table 3, which lists the experimental lengths of all the 2-centre links in the immediate environment of C(1); Fig. 8 illustrates that pentagonal pyramidal environment. From Table 3 it is clear that, although there are minor variations between compounds in the measured lengths of C(1)–B(3/6), C(1)–B(4,5), C(2)–B(3,6), B(3,6)–B(4,5) and B(4)–B(5), these variations cannot be regarded as systematic or significant.

However, on closer inspection, the C1–C2 bond lengths determined cannot simply be explained by the orientation of the π -donating groups. For example, the two compounds **2** and **3** contain similar C1–C2 bond lengths of *ca*. 1.77 Å even though it is generally accepted that the phenyl group lengthens the bond by *ca*. 0.03–0.05 Å compared to the methyl group due to the steric and/or electronic effect(s) of the former [24,25]. The difference of 0.04 Å for the C1–C2 bond lengths in **2** and **4** is significant even though the orientations of the nitrogen groups are similar. There are six distinct PhCb^oNH₂ molecular geometries experimentally determined, with C1–C2 bond lengths ranging from 1.745 to 1.853 Å (see Table 1) – a difference of 0.11 Å, which cannot be explained solely by the orientation of the amine group.

2.4. Structural aspects: computational studies

Optimised geometries of carboranes at the MP2/6-31G^{*} level of theory have been shown to be in excellent agreement with experimental geometries determined by gas-phase electron diffraction

interationic distances (A) for compounds Fireb A.								
Х	C1-C2	C1-N	C1-B3/6	C1-B4/5	C2-B3/6	B3/6-B4/5		
H [26,27]	1.643(1)		1.713(1)	1.695(1)	1.733(1)	1.776(1)		
NO	1.677(2)	1.490(2)	1.706(2)	1.703(2)	1.740(2)	1.786(3)		
NNAr	1.694(2)	1.443(2)	1.716(3)	1.703(3)	1.738(3)	1.780(3)		
NHOH	1.737(3)	1.423(3)	1.721(3)	1.701(3)	1.732(3)	1.779(3)		
NHNHAr	1.778(3)	1.401(2)	1.719(3)	1.708(3)	1.736(3)	1.786(3)		
NH ₂ (av)	1.767(3)	1.396(3)	1.715(4)	1.698(4)	1.722(4)	1.780(4)		

 Table 3

 Interatomic distances (Å) for compounds PhCb°X.

[28–30] and X-ray crystallography [8,12,20,31,32]. Earlier, we had carried out computations on model geometries of HCb^oX with π -donor groups (X = OH, NH⁻, NH₂ and CH₂⁻) to investigate the effect of orientation of these groups on the C1–C2 bond length; in these computations a planar configuration (*sp*²) was assumed for NH₂ [8]. The effect of a pyramidal form (*sp*³) at a nitrogen π -donor group on the C1–C2 bond or the effect of π -acceptor groups on the cage geometry had not been investigated previously. Here, data for the systems HCb^oX where X = N=O, N=NH, NHOH, NH₂ and NHNH₂ in various possible orientations (indicated by their torsion angles) are listed in Table 4. The pyramidal or planar configura-



Fig. 8. The pentagonal pyramidal environment about C1.

tions of the nitrogen atom N1 attached to C1 for NHR" groups were also examined.

B4-B5

1.781(1)

1.779(3)

1.784(3)

1.781(3) 1.784(3) 1.775(4)

The model carboranes with Π -acceptor groups, NO and NNH, prefer to be oriented in plane (0° and 180°) with the C1–C2 bond, as opposed to being oriented perpendicular to the C1–C2 bond, with an energy difference of *ca.* 4 kcal mol⁻¹ (Fig. 8). The reasons for a slight preference for 0° orientations over 180° orientations in these models are cage C–H···X bond interactions [12]. Energetically, the hydroxylamino (NHOH) group clearly favours the pyramidal form (sp^3 N) over the planar form (sp^2 N) irrespective of the orientation. There is no strong preference for one orientation over another for the NHOH group. The substituents NO, NNH and NHOH (with sp^3 N) have little orientational influence on the *ortho*-carborane cage geometry.

By contrast, the models containing the NH₂ groups are similar in energy irrespective of whether the nitrogen atom N1 is planar (sp^2) or pyramidal (sp^3) in configuration (Fig. 7). However, the 90° orientations are energetically favourable and are expected for a π -donor group –NHR" to be oriented to align the donor p-orbital with the C1–C2 bond for maximum overlap. The model HCb^oNH₂ has four geometries within a range of 2.9 kcal mol⁻¹ in energy but their C1–C2 bond distances vary from 1.623 to 1.713 Å, a difference of 0.09 Å, attributable to the orientations and the sp^2 or sp^3 configuration about the nitrogen atom. Similar observations are found for the model carborane containing the NHNH₂ group.

Table 4

Selected bond lengths (Å) and energies of MP2-optimised geometries of HCb^oX where torsion angles for C2–C1–N–Z/R^{''} are fixed at 0, 90 and 180° (a = N–H away from C1, t = N–H towards C1).

Х		N1-Z/R''	C1-N1	C1-C2	C1-B3/6	C1-B4/5	Energy (au)	Relative E (kcal mol ⁻¹)
NO	0	1.230	1.491	1.621	1.713	1.691	-459.79796	0.0
	90	1.227	1.514	1.618	1.716	1.689	-459.79160	4.1
	180	1.228	1.493	1.617	1.711	1.692	-459.79740	0.2
NNH	0	1.265	1.455	1.634	1.716	1.694	-439.98786	0.0
	90	1.265	1.468	1.621	1.725	1.693	-439.98075	4.7
	180	1.265	1.457	1.624	1.715	1.698	-439.98616	1.1
NHOH(sp ³)	0	1.445	1.450	1.631	1.712	1.693	-460.99182	0.0
	90(a)	1.440	1.441	1.635	1.727	1.699	-460.99040	0.1
	90(t)	1.437	1.434	1.665	1.723	1.697	-460.98922	1.7
	180	1.441	1.452	1.620	1.731	1.699	-460.98794	2.6
NHOH(sp ²)	0	1.396	1.397	1.609	1.749	1.704	-460.97107	13.0
	90	1.397	1.377	1.739	1.720	1.700	-460.97564	10.0
	180	1.394	1.396	1.607	1.756	1.706	-460.96728	15.6
NH ₂ (sp ³)	0	1.019	1.430	1.640	1.731	1.700	-386.01371	4.1
	90(a)	1.017	1.422	1.651	1.722	1.702	-386.01982	0.0
	90(t)	1.015	1.412	1.675	1.725	1.700	-386.01982	0.0
	180	1.020	1.434	1.623	1.732	1.701	-386.01650	2.2
$NH_2(sp^2)$	0	1.007	1.396	1.612	1.752	1.705	-386.00656	8.9
	90	1.008	1.383	1.713	1.718	1.703	-386.01552	2.9
NHNH ₂ (sp ³)	0	1.417	1.442	1.636	1.728	1.701	-441.16414	3.9
	90(a)	1.420	1.429	1.654	1.725	1.701	-441.16998	0.0
	90(t)	1.416	1.414	1.703	1.724	1.699	-441.16752	1.6
	180	1.428	1.445	1.623	1.736	1.701	-441.16800	1.3
NHNH ₂ (sp ²)	0	1.389	1.406	1.612	1.748	1.705	-441.15795	8.0
	90	1.399	1.386	1.731	1.721	1.701	-441.16639	2.4
	180	1.395	1.403	1.611	1.755	1.706	-441.15887	7.4



Fig. 9. Preferred orientations in PhNHR" and PhN=Z systems.

There are parallels here between carborane chemistry and aromatic ring chemistry, where substituents that can act as π -donors or π -acceptors adopt orientations that maximise interaction with the π -system of the aromatic ring (Fig. 9) provided that steric factors do not rule out the preferred orientations of substituents NO, NNH, NHOH, NH₂ and NHNH₂ when attached to a benzene ring. Selected bond distances and relative energies from computational data on these benzene derivatives for the two orientations, planar (0°) and perpendicular (90°) , at the MP2/6-31G^{*} level of theory are listed in Table 5. For the acceptor groups NO and NNH, the coplanar form is energetically preferred over the perpendicular form by 8.9 and 5.1 kcal mol⁻¹, respectively, but the orientation has little influence on the ring geometries [33]. The NHOH group strongly favours the pyramidal (sp^3) configuration over the planar (sp^2) form energetically, but small energy and geometry differences between the two orientations are found for the sp^3 form. The amino NH₂ group does not have a strong energetic preference for the sp^2 or sp^3 form but has a notable orientational effect on the C–N bond, with distances of 1.381 Å for the sp^2 N geometry in plane with the C1–C2 bond (0°) and 1.435 Å for the sp^3 N geometry perpendicular to the C1–C2 bond (90°) [34]. The ring geometry, however, remains largely unaffected by the C-N bond variations. The orientation of the NHNH₂ group has a similar effect on the geometry and energies as the orientation of the NH₂ group. Preferred orientations determined computationally for PhNNH and PhNHNH₂ are in accord with the orientations of the aromatic rings in the experimental structures for 1, 2 and 3.

Table 5

Selected bond lengths (Å) and energies of MP2-optimised geometries of PhX where torsion angles for C2–C1–N–Z/R^{$\prime\prime$} are fixed at 0 and 90°.

Х		N1-Z/R''	C1-N1	C1-C2	Relative energy (kcal mol ⁻¹)
NO	0	1.244	1.443	1.399	0.0
	90	1.243	1.460	1.394	8.9
NNH	0	1.272	1.433	1.399	0.0
	90	1.270	1.441	1.395	5.1
NHOH(sp ³)	0	1.440	1.432	1.399	0.0
	90	1.465	1.434	1.398	1.5
NHOH(sp ²)	0	1.395	1.378	1.403	7.5
	90	1.412	1.408	1.403	16.9
$NH_2(sp^3)$	0	1.014	1.409	1.403	0.0
	90	1.019	1.435	1.401	2.4
$NH_2(sp^2)$	0	1.007	1.381	1.405	1.2
	90	1.005	1.416	1.403	9.2
NHNH ₂ (sp ³)	0	1.410	1.404	1.404	0.0
	90	1.449	1.432	1.401	1.8
NHNH ₂ (sp ²)	0	1.396	1.386	1.404	2.4
	90	1.403	1.415	1.402	12.4

The geometries of PhCb^oX and MeCb^oX were also computed at the MP2/6-31G^{*} level of theory. Comparisons shown in Table 6 reveal very good agreements between the selected geometric parameters for optimised and experimental geometries in all cases. The NHR" groups, as discussed for the model carboranes, are particularly intriguing: the sp^3 N form is more stable than the sp^2 N form in these groups. However, for the NH₂ group the energy difference between the geometries containing sp^3 N and sp^2 N groups is small (less than 3 kcal mol⁻¹), which indicates that both forms could coexist in the solid and solution states where intermolecular interactions come into play. The computed C1–C2 distances of 1.743 and 1.813 Å for the sp^3 N and sp^2 N PhCb^oNH₂ geometries, respectively, and their energies, are in broad agreement with the observation of six distinct PhCb^oNH₂ molecules with C(1)–C(2) bond distances of 1.745–1.853 Å (see Table 1) in the crystal structure.

For compounds with NHNHR' groups, **2** and **3**, the relative energies between their sp^3 N and sp^2 N geometries are slightly larger at *ca.* 4.0 kcal mol⁻¹, but comparison of the bond parameters of experimental geometries with sp^3 N optimised geometries are poor. The experimental geometry for **3** is in much better agreement with the sp^2 N optimised geometry of MeCb⁰NHNHPh, whereas the experimental geometry for **2** lies between the two optimised geometries $(sp^2$ N and sp^3 N) of PhCb⁰NHNHC₆H₄Me. As for PhCb⁰NH₂, these geometries depend on intermolecular interactions such as crystal packing forces. This subtle difference in the sp^2/sp^3 N character results in similar C1–C2 bond distances found experimentally for **2** and **3**. The pyramidal sp^3 N form is clearly favoured in energy for the PhCb⁰NHOH geometry and in accord with the experimental geometry found for **4**.

The optimised and experimental geometries for the dicarboranylamines (PhCb^o)₂NH and (MeCb^o)₂NH are in excellent agreement and their planar nitrogen atoms are clearly sp^2 in character. Optimised geometries for some methyl analogues, where no experimental structures were determined, reveal geometries and trends similar to the experimental and optimised geometries for the phenyl analogues.

2.5. Experimental and computed NMR trends

The ¹¹B NMR spectra of polyhedral borane clusters such as carboranes provide a rich source of information provided that signals can be assigned with confidence. At the simplest level, the number of different boron sites in a molecule, deduced from the number of resonances, helps identify isomers. Of more importance in the present context is the 'antipodal effect' in icosahedral carborane chemistry [35-39], whereby the NMR shift of the boron atom directly opposite a substituted cage carbon atom is sensitive to the nature of the substituent. In ortho-carborane derivatives RCbºX, bearing substituents X and R on carbon atoms 1 and 2, respectively, the resonances of the atoms opposite (B12 and B9, respectively) respond to the corresponding substituent, particularly if that substituent is a π -donor [2,8]. For the present series of compounds RCb^oX, where X is a nitrogen π -donor, the antipodal shift is expected to be related to the degree of *exo* π -bonding, and hence to exo-C1-N1 and cage C1-C2 bond lengths.

For such a comparison to be made the ¹¹B NMR shift for the antipodal atom (¹¹B δ -B12) must be reliably assigned. Although the two peaks corresponding to B9 and B12 are readily identified from the peak intensities it is impossible to assign each unambiguously without assumptions being made. One of these peaks appears at approximately the same shift in all compounds. This therefore can be assigned to B9, antipodal to the Ph or Me group in PhCb^oX and MeCb^oX, respectively. This peak would be expected to change little in these series of compounds as the substituent on C2, i.e. the Me or Ph group, remains unchanged. ¹¹B NMR shifts for B9 and B12 have been assigned on this basis (see Table 7).

Table 6

Comparison of selected computed and experimental geometric parameters (Å and °) for RCb^oX systems. Experimental values are shown in italics.

х		C1-C2	C1-N1	C2-C1-N1	C1-N1-X/R''	Angle sum at N	Relative energy (kcal mol ⁻¹)
PhCb ^o X							
н		1.636					
NO		1.671	1.490	112.1	111.6		
N=NC ₆ H ₄ Me		1.677(2) 1.679	1.490(2) 1.441	112.1(2) 111.1	113.0(2) 111.3		
NUOU	3	1.694(2)	1.444(2)	111.3(1)	112.8(2)	222.4	0.0
NHUH	sp ²	1.828	1.367	113.5 116.2 115.7(2)	110.6 120.9 110.7(2)	322.4 360.0 324.7	8.3
NHCb⁰Ph		1.790	1.401	115.9 117 3(2)	132.3	360.0 360.0	
NHNHC ₆ H ₄ Me	sp ³ sp ²	1.727 1.830	1.424 1.379	116.4 119.1	117.4 120.5	335.4 360.0	0.0 4.2
NH ₂	sp ³	1.778(3) 1.743	1.401(2) 1.411	115.2(2) 114.5	116.4(2)	342.4 332.7	0.0
	sp ²	1.813 1.767(3)	1.374 1.396(3)	117.0 118.4(2)		360.0 344.3	2.6
[NCb ^o Ph] ⁻		1.977 1.987(3)	1.353 1.355(4)	118.7 118.8(2)	126.2 127.0		
MeCb ^o X							
H		1.630	1 400	112 5	111.0		
NU N=NPh		1.638	1.400	112.5	110.9		
NHOH	sp ³ sp ²	1.696	1.427	115.4 118.2	113.2 120.7		0.0 6.0
NHCb⁰Me	1	1.748 1.750(4)	1.406 1.410(4)	117.3 117.2(2)	132.3 131.1(2)	360.0 359.8	
NHNHPh	sp ³ sp ²	1.737 1.764	1.448 1.384	114.5 117.9	119.9 121.6	338.9 360.0	0.0 3.8
NU	cm ³	1.770(2)	1.387(2)	115.9(1) 114.9	118.8(1)	355.4	0.0
11112	sp sp ²	1.770	1.379	114.5		360.0	2.7
[NCbºMe] [_]		1.886	1.358	118.7	126.2		

Table 7

Comparison of selected experimental (in CDCl₃) and computed NMR shifts (ppm) for RCb^oX systems. Calculated values are in italics.

δ(B12)		δ(B12H)		δ(C1)		δ(C2)	
-1.2	-1.2	2.46	3.09	60.1	57.7	76.5	78.5
-2.0	0.2	2.67	3.34	114.1	125.1	81.3	84.1
-4.2	-2.4	2.57	3.18	98.8	103.8	81.7	83.0
-5.5	-4.5	2.38	3.00	98.4	101.0	86.5	87.8
-5.8	-5.1	2.28	2.86	94.4	95.7	90.3	92.5
-6.8	-6.0	2.32	2.85	102.3	105.3	90.0	91.3
-8.3	-7.8	2.18	2.80	96.3	98.1	87.7	92.2
-12.6	-13.6	1.72	2.08	129.5	125.4	89.8	95.5
-1.7	0.0	2.31	3.05	61.5	58.6	70.4	70.5
-2.4	0.4	2.50	3.29	111.4	120.2	73.3	74.6
-4.2	-2.6	2.40	3.07	95.7	97.9	73.9	73.8
-6.1	-5.8	2.24	2.83	94.5	96.6	78.6	81.8
-6.4	-6.0	2.22	2.78	90.9	93.0	81.8	84.0
-7.1	-6.5	2.16	2.81	96.7	98.9	80.9	82.2
-9.4	-8.4	1.98	2.90	91.1	92.5	78.9	81.0
-13.7	-14.4	1.59	1.99	120.0	119.1	87.0	90.8
	$\begin{array}{c} \delta(\text{B12}) \\ \\ -1.2 \\ -2.0 \\ -4.2 \\ -5.5 \\ -5.8 \\ -6.8 \\ -8.3 \\ -12.6 \\ \\ \\ -1.7 \\ -2.4 \\ -4.2 \\ -6.1 \\ -6.4 \\ -7.1 \\ -9.4 \\ -13.7 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					

^a Computed shifts for *sp*³ geometry.

^b Computed shifts averaged for both *sp*² and *sp*³ geometries.

^c Observed values in CD₃CN.

The antipodal shift increases as π -bonding increases, displayed by the graph of the B12 shift vs experimental C–N bond lengths (Fig. 10). This is in agreement with previous work showing that such shifts are related to electron donation to the cluster. Hence the ¹¹B NMR data give an indication of degree of *exo* π -bonding and this can be used to assess such effects in compounds which have not been structurally characterised. The shifts of the BH protons revealed by ${}^{1}H{{}^{11}B}$ NMR can be assigned using ${}^{1}H{-}^{11}B$ HETCOR or ${}^{1}H{{}^{11}B}$ selective} experiments. The ${}^{1}H$ shifts of the hydrogen atoms bonded to the antipodal boron show the same relationship with the C–N bond length as the ${}^{11}B$ shifts of B12, decreasing frequency of the antipodal hydrogen with increased π -bonding to the cage suggesting increased shielding. The ${}^{13}C$ shifts of the cage carbon atoms C1 and C2, however, are



Fig. 10. Correlation between the observed ¹¹B shift of B12 (ppm) and the experimental C(1)–N(1) bond length (Å).

not simply related to the *exo*-C–N π -bonding effects. Calculated NMR chemical shifts on MP2-optimised geometries are in very good agreement with observed shifts and trends as shown in Table 7.

3. Conclusions

In this paper we have reported the crystallographically derived molecular structures and ¹¹B, ¹³C and ¹H NMR spectra of four new ortho-carboranyl-nitrogen compounds PhCb^oN=N(p-tolyl) (1), PhCb^oNHNH(p-tolyl) (2), MeCb^oNHNHPh (3) and PhCb^oNHOH (4) $(Cb^{o} = 1, 2-C_{2}B_{10}H_{10})$. Together with other carboranyl-nitrogen systems RCb^oX reported earlier, these provide a useful data bank from which the general structural, bonding and NMR characteristics of such systems can be discerned. Their structures show how dative exo-C=N p-bonding from the substituent to the cage is reflected in shortening of the exo-C-N bond (as it gains multiple character) and lengthening of the cage C1-C2 bond (as it loses bond order) to an extent that reflects the π -donor power of the substituent, the orientation of the CN group and the sp^2 or sp^3 character of the nitrogen atom for the NHR" group, which are seen from computational studies to be important. The ¹¹B NMR chemical shift of the boron atom antipodal to the substituent also provides a guide to the π -donor power of X.

4. Experimental

All air-sensitive manipulations were carried out under dry, oxygen-free N₂. Stirring refers to use of a magnetic stirrer. Hexanes were distilled over Na. 1,2-Dimethoxyethane (DME) was dried by reflux and distillation over potassium; ether refers to diethyl ether dried, where appropriate, over sodium. Ether solutions were dried over magnesium sulfate and evaporated near room temperature. 1-Methyl-ortho-carborane [41] and 1-phenyl-ortho-carborane [42] were prepared by literature methods and dried by sublimation at 0.01 mm Hg. 1-Nitroso-2-methyl-ortho-carborane and 1-nitroso-2-phenyl-ortho-carborane were made as described elsewhere [14]. Benzenediazonium tetrafluoroborate and 4-methylbenzenediazonium tetrafluoroborate salts were made using a general literature method [43].

Melting points were measured in capillary tubes with an Electrothermal 9200 heating block. Infrared spectra were recorded from KBr discs on Perkin-Elmer 1600 series FTIR or Perkin-Elmer 1720X FTIR spectrometers and ultraviolet spectra with a Shimadzu UV 1201. Elemental carbon, hydrogen and nitrogen analyses were performed using Exeter Analytical CE-440 or Carlo Erba Strumentazione EA Model 1106 instruments. Mass spectra (MS) were recorded on a VG Micromass 7070E instrument under EI conditions at 70 eV. Values of M show the isotope range ${}^{10}B_n$ to ${}^{11}B_n$ including a ¹³C contribution if observed. NMR spectra were measured using Varian Unity-300 (¹H, ¹¹B, ¹³C), Bruker AM250 (¹H, ¹³C), Bruker Avance 400 (¹H, ¹¹B, ¹³C) and/or Varian Inova 500 (¹H, ¹¹B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ¹H NMR spectra were referenced to residual protio impurity in the solvent (CDCl₃, 7.26 ppm). ¹³C NMR spectra were referenced to the solvent resonance (CDCl₃, 77.0 ppm). ¹¹B NMR spectra were referenced externally to $Et_2O \cdot BF_3$, $\delta = 0.0$ ppm. Peak assignments of cage boron and hydrogen atoms were determined with the aid of 2D $^{11}B\{^1H\}-^{11}B\{^1H\}$ COSY, selective $^1H\{^{11}B\}$ and ¹H–¹¹B correlation spectra.

4.1. Preparation of azocarboranes (modification of a reported [17] method)

A solution of the substituted lithiocarborane was prepared by the addition of butyllithium (5.05 ml, 2.5 M in hexanes) to a solution of the starting carborane (0.0127 mol) in diethyl ether (100 ml) at 0 °C. The solution was warmed to ambient temperature with stirring for 30 min. The diazonium salt was added as a solid over a period of 30 min and stirred overnight to give a cloudy red solution. Water was added and the organic layer was separated and washed with water. The organic layer was dried and evaporated to leave a brown residue. This was recrystallised from hexane to give orange crystals of the azocarborane.

1-Methyl-2-phenylazo-ortho-carborane, 1.78 g (50%), M.p. 122.5–123.5 °C (lit. [17] 121–122 °C). Anal. Calc. for $C_9H_{18}B_{10}N_2$: C, 41.2; H, 6.9; N, 10.7. Found: C, 41.1; H, 7.0; N, 10.6%. IR v_{max} (KBr) [cm⁻¹]: 3062w (aryl CH), 2926w (methyl CH), 2640m, 2615s, 2582s, 2574s, 2550s (BH), 1497s, 1451s, 1205s, 1157s, 1072s, 1019s, 768s, 728s, 683s, 419s. ¹H{¹¹B} NMR (CDCl₃), δ :

7.81 (d, 2H, ortho-phenyl CH), 7.58 (t, 1H, para-phenyl CH), 7.52 (d, 2H, meta-phenyl CH), 2.50 (s, 2H, H8,10), 2.40 (s, 5H, BH including H12), 2.30 (s, 3H, CH₃), 2.20 (s, 3H, BH); ¹¹B{¹H} NMR (CDCl₃), δ : -4.2 (1B, B12), -6.4 (1B, B9), -10.6 (8B); ¹³C NMR (CDCl₃), δ : 151.2 (C_6H_5 ipso), 133.5 (d of t, ¹ J_{CH} 161 Hz, ² J_{CH} 8 Hz, C_6H_5 para), 129.4 (d of d, ¹ J_{CH} 161 Hz, ² J_{CH} 8 Hz, C_6H_5 meta), 95.7 (C1), 73.9 (C2), 22.5 (q, ¹ J_{CH} 132 Hz, CH₃).

1-Phenyl-2-(4-methylphenyl)azo-ortho-carborane, 2.77 g (82%), M.p. 90–91 °C. Anal. Calc. for $C_{15}H_{22}B_{10}N_2$: C, 53.3; H, 6.5; N, 8.3. Found: C, 53.1; H, 6.8; N, 8.1%. MS (El⁺, *m/z*) 91 (C₆H₄Me); 216– 221 [PhCb]⁺; IR v_{max} (KBr) [cm⁻¹]: 3052w (aryl CH), 2922w (methyl CH), 2642m, 2603s, 2566s (BH), 1600s, 1500s, 1489s, 1472s, 1446s, 1157s, 1071s, 1026s, 827s, 810s, 802s, 752s, 688s. ¹H{¹¹B} NMR (CDCl₃), δ : 7.70 (d, 2H, ortho C₆H₅), 7.42 (t, ³*J*_{HH} 8 Hz, 1H, *para* C₆H₅), 7.34 (t, ³*J*_{HH} 8 Hz, 2H, *meta* C₆H₅), 7.35 (d, ³*J*_{HH} 8 Hz, 2H, *meta* C₆H₄Me), 7.17 (d, ³*J*_{HH} 8 Hz, 2H, ortho C₆H₄Me), 3.00 (s, 2H, BH), 2.63 (s, 2H, BH), 2.57 (s, 3H, BH), 2.44 (s, 1H, BH), 2.37 (s, 3H, CH₃), 2.34 (s, 2H, H9,12); ¹¹B{¹H} NMR (CDCl₃), δ : -4.2 (2B, B9,12), -11.0 (8B); ¹³C NMR (CDCl₃), δ : 149.1 (C–N), 144.4 (C–CH₃), 131.1 (*ortho* C₆H₅), 130.5 (*ipso* C₆H₅), 130.2 (*para* C₆H₅), 129.8, 128.2 (aryl CH); 123.5 (CHCN), 98.8 (C1), 81.7 (C2), 21.6 (CH₃).

4.2. Preparation of hydrazocarboranes

Lithium aluminium hydride, LiAlH₄, (0.3 g, 8 mmol), was added to a solution of 1-methyl-2-phenylazo-ortho-carborane (0.50 g, 1.91 mmol) in diethyl ether (20 ml) and the mixture stirred for 20 h. Wet diethyl ether was added, followed by water (10 ml) and dilute HCl until the cloudy solution became clear. The organic layer was washed with water $(2 \times 50 \text{ ml})$, dried and evaporated to leave a pale yellow solid. This was recrystallised from hot hexane to yield colourless crystals of 1-methyl-2-phenylhydrazo-orthocarborane (0.41 g, 82%). M.p. 142-144 °C (lit. [17] 143-144 °C). Anal. Calc. for C₉H₂₀B₁₀N₂: C, 40.9; H, 7.6; N, 10.3. Found: C, 40.7; H, 7.8; N, 10.3%. MS (EI⁺, m/z) [M]⁺ 260–267; 264 (100); IR v_{max} (KBr) [cm⁻¹]: 3360, 3322 (NH), 3125 (phenyl CH), 2933 (methyl CH), 2615s, 2580s, 2559s (BH), 1601, 1497, 1454m, 1251m, 1019m, 754s, 696 m. ¹H{¹¹B} NMR (CDCl₃), δ: 7.24 (t, ³J_{HH} 7 Hz, 2H, meta C₆H₅), 6.90 (t, ${}^{3}J_{HH}$ 7 Hz, 1H, para C₆H₅), 6.85 (d, ${}^{3}J_{HH}$ 8 Hz, 2H, ortho C₆H₅), 5.68 (s, 1H, NH), 4.89 (s, 1H, NH), 2.52 (s, 2H, H8,10), 2.23 (s, 3H, BH), 2.16 (s, 3H, BH), 2.09 (s, 3H, CH₃), 2.05 (s, 2H, BH); ${}^{11}B{}^{1}H{}$ NMR (CDCl₃), δ : -6.1 (1B, B9), -7.1 (1B, B12), -11.0 (4B), -11.8 (4B); ¹³C NMR (CDCl₃), δ: 147.3 (C₆H₅ ipso), 129.3 (d, ¹J_{CH} 158 Hz, C₆H₅), 121.0 (d, ¹J_{CH} 160 Hz, C₆H₅), 113.0 (d of t, ¹*J*_{CH} 156 Hz, C₆H₅), 96.7 (C1), 80.9 (C2), 22.1 (q, ¹*J*_{CH} 130 Hz, CH₃).

The compound 1-phenyl-2-(4-methylphenyl)azo-ortho-carborane (0.73 g) was dissolved in 20 ml of ethanol. Zinc dust (3.5 g) was added and 20 ml conc HCl added dropwise. The solution was stirred overnight, becoming colourless. It was poured into water (200 ml), giving a white precipitate. The solid was extracted with diethyl ether $(3 \times 50 \text{ ml})$. The organic layer was washed with water, dried and evaporated. The residue was recrystallised from hexane to give pale yellow crystals of 1-phenyl-2-(4-methylphenyl)hydrazo-ortho-carborane (0.65 g, 89%). M.p. 148-149.5 °C. Anal. Calc. for C₁₅H₂₄B₁₀N₂: C, 52.8; H, 7.0; N, 8.2. Found: C, 53.0; H, 7.0; N, 8.1%. MS (EI⁺, m/z) [M]⁺ 336–343; 340 (100); IR v_{max} (KBr) [cm⁻¹]: 3312s (NH), 3120, 3105 (aryl CH), 2950 (methyl CH), 2663s, 2628s, 2550s (BH), 1514s, 1262m, 814s, 689s. ¹H{¹¹B} NMR (CDCl₃), δ : 7.69 (d, ³J_{HH} 8 Hz, 2H, ortho C₆H₅), 7.53 (t, ³J_{HH} 8 Hz, 1H, para C₆H₅), 7.40 (t, ³J_{HH} 8 Hz, 2H, meta C₆H₅), 6.82 (d, ³J_{HH} 8 Hz, 2H, meta C₆H₄Me), 6.17 (d, ³J_{HH} 8 Hz, 2H, ortho C₆H₄Me), 5.28 (br,s, 1H, NH), 4.83 (s, 1H, NHAr), 2.83 (s, 2H, H3,6), 2.59 (s, 2H, BH), 2.41 (s, 3H, BH incl H9), 2.32 (s, 1H, H12), 2.21 (s, 3H, CH₃), 2.14 (s, 2H, H8,10); ${}^{11}B{}^{1}H{}$ NMR (CDCl₃), δ :

-3.9 (1B, B9), -6.8 (1B, B12), -10.6 (4B), -12.6 (4B); $^{13}C{^{1}H}$ NMR (CDCl₃), δ : 144.9 (C-CH₃), 131.8, 129.5, 128.8 (aryl CH); 131.0 (*ipso* C₆H₅), 130.5 (*para* C₆H₅), 130.1 (C-N), 112.5 (CHCN), 102.3 (C1), 90.0 (C2), 20.4 (CH₃).

4.3. Preparation of carboranylhydroxylamines

The methyl nitrosocarborane (0.22 g) was dissolved in 10 ml of *p*-dioxane, 5% Pd/C (40 mg) added and the solution degassed by a freeze-pump–thaw process. Hydrogen was admitted and its uptake measured using a standard hydrogenation apparatus. Twenty-five milliliters of hydrogen was consumed over a period of 6 h. The solution was filtered and evaporated to leave a white solid (210 mg, 95%), M.p. 253–255 °C (lit. [19] 256–258 °C). *Anal.* Calc. for C₁₅H₂₄B₁₀N₂: C, 19.1; H, 7.9; N, 7.4. Found: C, 19.4; H, 8.1; N, 6.2%. MS (EI⁺, *m/z*) [M]⁺ 185–192; 189 (100); IR ν_{max} (KBr) [cm⁻¹]: 3340, 3290 (NH,OH), 2914 (methyl CH), 2579s (BH), 1254s, 1116s, 1080m, 870s. ¹H{¹¹B} NMR (CDCl₃), δ : 5.94 (s, 1H, NH), 5.39 (s, 1H, OH), 2.46 (s, 2H, H3,6), 2.24 (s, 3H, BH), 2.22 (s, 1H, BH), 2.18 (s, 2H, BH), 2.05 (s, 2H, H8,10), 2.02 (s, 3H, CH₃); ¹¹B{¹H} NMR (CDCl₃), δ : -6.1 (2B, B9,12), -10.9 (4B), -11.7 (4B); ¹³C{¹H} NMR (CDCl₃), δ : 94.5 (C1), 78.6 (C2), 21.6 (CH₃).

A larger-scale preparation was used for the phenyl analogue to afford 3.37 g (87%) from 3.86 g of the nitroso compound, M.p. 95–96 °C, (lit. [18] 98–99 °C). *Anal.* Calc. for $C_{15}H_{24}B_{10}N_2$: C, 38.2; H, 7.2; N, 5.4. Found: C, 38.3; H, 6.8; N, 5.6%. MS (El⁺, *m/z*) [M]⁺ 247–255; 251 (100); IR v_{max} (KBr) [cm⁻¹]: 3532, 3463, 3280 (NH,OH), 3061 (phenyl CH), 2574s (BH), 1493m, 1446s, 1071s, 1003s, 689s. ¹H{¹¹B} NMR (CDCl₃), δ : 7.70 (d, 2H, *ortho* C₆H₅), 7.47 (t, 1H, *para* C₆H₅), 7.40 (t, 2H, *meta* C₆H₅), 5.69 (s, 1H, NH), 5.09 (s, 1H, OH), 2.83 (s, 2H, H3,6), 2.53 (s, 2H, BH), 2.42 (s, 3H, BH), 2.38 (s, 1H, H12), 2.17 (s, 2H, H8,10); ¹¹B{¹H} NMR (CDCl₃), δ : -3.8 (1B, B9), -5.7 (1B, B12), -10.6 (4B), -12.1 (4B); ¹³C{¹H} NMR (CDCl₃), δ : 131.3, 130.8 (para C), 130.0 (ipso C), 129.1, 98.4 (C1), 86.5 (C2).

4.4. Preparation of methyl-ortho-carboranyl amine

The compound 1-nitroso-2-methyl-ortho-carborane (1.50 g) was dissolved in dimethoxyethane (25 ml) and tin powder (1.50 g) was added. Concentrated HCl (25 ml) was added dropwise and the solution stirred for 15 min, after which time the blue colour had disappeared. The solution was heated to reflux for 3 h, cooled to room temperature and diluted with diethyl ether (100 ml). The solution was washed with water $(3 \times 50 \text{ ml})$, dried and evaporated. The white residue was sublimed to yield 1-amino-2-methyl-ortho-carborane (1.10 g, 79%), M.p. 301-302 °C (lit. [19] 302-303 °C). Anal. Calc. for C3H15B10N: C, 20.8; H, 8.7; N, 8.1. Found C, 20.9; H, 9.0; N, 7.1%. MS (EI): M, 169–176 ($C_3H_{15}B_{10}N = 173$). I.R. (cm^{-1}): 3306, 3219br (NH), 2939w (methyl CH), 2671s, 2634s, 2602s, 2580s (BH), 1491m, 1451m, 1221m, 1079s, 1026m, 1002m, 864m, 809m, 764s, 700s. ¹H{¹¹B} NMR (CDCl₃): 3.00 (2H, s, H4,5), 2.99 (2H, NH₂), 2.41 (2H, H7,11), 2.20 (1H, H9), 2.04 (3H, CH₃), 2.02 (2H, H3,6), 1.98 (1H, H12), 1.95 (2H, H8,10), ¹¹B NMR (CDCl₃): -5.5 (1B, d, B9), -9.4 (1B, d, B12), -9.8 (2B, d, B4,5), -10.6 (4B, d, B3,6,7,11), -12.5 (2B, d, B8,10). ¹³C{¹H} NMR (CDCl₃): 91.1 (C1), 78.9 (C2), 21.1 (CH₃).

4.5. Crystal structure determinations

Crystals of the compounds **1–4** were examined on Bruker SMART (**3**) and Stoe STADI4 (**1**, **2**, **4**) diffractometers with Mo K α radiation ($\lambda = 0.71073$ Å; Cu K α with $\lambda = 1.54184$ Å for **1**) at 160 K. Crystal data and other information are given in Table 8. Standard methods and software were employed, including refine-

Table 8					
Crystal data and	refinement	information	for com	pounds	1-4.

Compound	1	2	3	4
Formula	$C_{15}H_{22}B_{10}N_2$	$C_{15}H_{24}B_{10}N_2$	$C_9H_{20}B_{10}N_2$	C ₈ H ₁₇ B ₁₀ NO·½C ₄ H ₈ O ₂
Μ	338.5	340.5	264.4	295.38
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	28.695(6)	11.753(6)	8.6912(11)	12.394(1)
b (Å)	7.071(2)	7.617(4)	15.568(2)	6.714(1)
c (Å)	19.008(5)	21.899(13)	11.5680(15)	19.498(2)
β (°)	96.34(3)	104.74(6)	96.576(3)	94.30(2)
V (Å ³)	3833.2(17)	1895.9(18)	1554.9(3)	1617.9(3)
Ζ	8	4	4	4
Data collected	6424	4051	8134	4131
Unique data	2992	3329	3099	2846
R _{int}	0.046	0.049	0.056	0.031
Refined parameters	246	252	271	217
R (on $F, F^2 > 2\sigma$)	0.053	0.049	0.049	0.048
$R_{\rm w}$ (on F^2 , all data)	0.154	0.137	0.126	0.134
Minimum, maximum electron density (e $Å^{-3}$)	0.25, -0.23	0.24, -0.21	0.23, -0.20	0.25, -0.21

ment on all F^2 values [44]; no absorption corrections were applied, and no structural disorder was found.

5. Computational

AM1 [45,46] calculations were carried out on crystallographically determined geometries using MOPAC2002 (Version 2.40) within the CACHE 6.1 program for Windows [47]. Ab initio computations were carried out with the GAUSSIAN 03 package [48]. All model geometries of HCb°X and PhX with fixed torsion angles for C2-C1-N-R/X listed in Tables 4 and 5, respectively, were optimised initially at the HF/6-31G^{*} level of theory followed by the MP2/6-31G^{*} level of theory. The geometries of PhCb^oX and MeCb^oX listed in Table 6 were optimised at the HF/6-31G^{*} level of theory either with no symmetry constraints (and confirmed by frequency calculations to be a true minimum) or with the nitrogen atom N1 constrained to a planar configuration. These geometries were then optimised at the MP2/6-31G^{*} level of theory.

Calculated NMR shifts at the GIAO-B3LYP/6-311G^{*} level were obtained from these MP2-optimised geometries. Theoretical ¹¹B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level were referenced to B_2H_6 (16.6 ppm [49]) and converted to the usual BF₃·OEt₂ scale: $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. The ¹³C and ¹H chemical shifts were referenced to TMS: $\delta(^{13}C) = 179.81 - \sigma(^{13}C)$; $\delta({}^{1}\text{H}) = 32.28 - \sigma({}^{1}\text{H})$. Agreements between observed and calculated (B3LYP/6-311G*//MP2/6-31G* level) ¹¹B and ¹³C NMR shifts generated from optimised geometries are generally very good for carboranes [50-54]. Agreements between observed and calculated ¹H NMR shifts in carboranes are often not as good due to a narrow ppm range (*ca.* 12 ppm) and substantial solvent effects on ¹H shift measurements [40].

Supplementary data

CCDC 704893, 704894, 704895 and 704896 contain the supplementary crystallographic data for 1, 2, 3 and 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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