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FULL PAPER

Synthesis and molecular structure of 1,12-dicarba-*closo*-dodecaborane(12)-1,12-dithiol, 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$, in the gaseous phase, determined by electron diffraction and *ab initio* calculations; geometrical consequences of three-dimensional aromaticity in carbaboranes 1,12-X_2-1,12-$C_2B_{10}H_{10}$ †

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The molecular structure of 1,12-dicarba-*closo*-dodecaborane(12)-1,12-dithiol, 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$, prepared by means of an improved synthesis, has been determined by gas-phase electron diffraction restrained by *ab initio* calculations. The carbaborane core, shown by calculations at the MP2(fc)/6-31G* level to be very close to D_{5d} symmetry, gave good agreement between theoretical and experimental ^{11}B NMR chemical shifts. A model of the entire molecule in overall C_2 symmetry led to an experimental geometry ($R_G = 0.077$), in good agreement with the theoretical findings. The substituents do not distort the cage significantly. The well determined parameters, the C–B, B(2)–B(3), and B(2)–B(7) distances, 170.6(4), 177.5(3) and 176.5(9) pm respectively (r_a), are consistent with the analogous parameters established experimentally for other 1,12-disubstituted 1,12-dicarbadodecaboranes. Whereas the C–B and B–B distances are found to be relatively constant in the MP2(fc)/6-31G* geometries of a series of carbaboranes 1,12-X_2-1,12-$C_2B_{10}H_{10}$ (in addition to SH, X = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, OH, F and Cl) the C(1)···C(12) distances and B(2)–C(1)–C(12) angles are appreciably sensitive to the nature of X, in a similar manner to the *para*-disubstituted benzene derivatives, 2 × B(2)–C(1)–C(12) being viewed as an analogue of the *ipso* angle in the latter.

Introduction

Analyses of gas-phase electron diffraction (GED) data in conjunction with geometries, energies and NMR chemical shifts calculated at adequately high *ab initio*[2] levels of theory, such as MP2(fc)/6-31G* (fc is omitted in the following for the simplicity), have resulted in considerable progress in the structural chemistry of boron compounds.[3] Of the *n*-vertex boranes and heteroboranes ($n \geq 10$) studied recently using the combined (*ab initio* + GED)/IGLO (individual gauge for localised orbitals)[4]/NMR[5] method, the systems in which the hydrogen atoms within a cluster are substituted have been studied to a smaller extent than the unsubstituted parent compounds.

One example which has been studied is 1,7-dichloro-1,7-dicarba-*closo*-dodecaborane(12).[1] It has C_{2v} symmetry, and the study revealed that the small distortion from the ideal $[B_{12}H_{12}]^{2-}$ icosahedral symmetry primarily involves a reduction in the height of the CB_5 pyramids. The recently introduced SARACEN (structure analysis restrained by *ab initio* calculations for electron diffraction) method[6] in combination with the *ab initio* + GED/IGLO/NMR tool during the analysis of the diffraction patterns has improved the reliability of the structural parameters determined for 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12)[7] considerably, despite a number of assumptions made to simplify the problem, such as the assumption of C_{2v} symmetry for the carbaborane moiety. The structures of the parent 1,7- and 1,2-$C_2B_{10}H_{12}$ compounds, both having C_{2v} symmetry, have also been investigated by GED, but the accuracy was not high.[8] In contrast, the structural parameters of the more highly symmetrical 1,12-$C_2B_{10}H_{12}$ isomer were determined precisely. The structures of the D_{5d} C_2B_{10} cage in the 1,12-diiodo[9] and dimethyl derivatives[10] have also been reported. Methyl and iodo substitution do not change the C(1)···C(12) separations significantly with respect to that of the parent 1,12-$C_2B_{10}H_{12}$ carbaborane, a three-dimensional aromatic system.[11] In contrast, the C(1)···C(4) ring-diagonal distance in *para*-disubstituted benzene derivatives, 1,4-X_2-C_6H_4, is strongly influenced by the substituents. For example, in the gas phase this distance is *ca.* 10 pm shorter in the *p*-dihalogen than in the *p*-dimethyl derivatives.[12] Such deformations resulting from the electronic perturbations of substituents attached to two-dimensional aromatic rings contrast with the smaller deformations of the more rigid cages of the spherically aromatic icosahedral dicarbadodecaboranes whose structures have been determined.

B_{12} compounds with sulfur-containing substituents, such as the $[B_{12}H_{11}SH]^{2-}$ anion, are important in boron neutron capture therapy (BNCT).[13] The solid state structure of 1,12-$(SMe_2)_2$-1,12-$B_{12}H_{10}$ has been published recently.[14] We report

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Table 1 Flexible restraints for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$

Restrained parameter	Value/pm or °	Uncertainty/pm or °
p_6	95.0	4.0
p_8	43.3	10.0
p_9	1.8	1.0

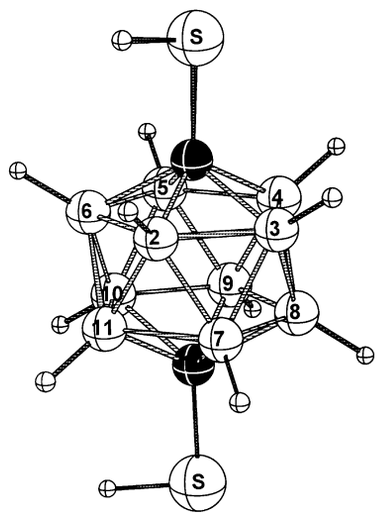

Fig. 1 Molecular structure of 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$.

here the gas-phase molecular structure of 1,12-dicarba-*closo*-dodecaborane(12)-1,12-dithiol, 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$ **1**, Fig. 1, as determined by electron diffraction. Sulfur has a greater electron-scattering ability than hydrogen and carbon in the parent 1,12-$C_2B_{10}H_{12}$ compound and its dimethyl derivative, and so the cage geometry of the sulfur derivative is expected to be defined more accurately. In connection with the proposed concept of three-dimensional aromaticity, we also performed geometry optimisations of a series of compounds 1,12-X_2-1,12-$C_2B_{10}H_{10}$, including the limiting electropositive Li and electronegative F derivatives, to examine in detail whether cage parameters are influenced by the nature of X.

Molecular model and refinement of the structure

The overall symmetry of 1,12-dicarba-*closo*-dodecaborane(12)-1,12-dithiol was assumed to be C_2, as revealed by the MP2 computations. Local D_{5d} symmetry was assumed for the $C_2B_{10}H_{10}$ core during the GED analysis. This was based on the computed geometry fully optimised in C_2 symmetry which showed only marginal deviations of the $C_2B_{10}H_{10}$ core from idealised D_{5d} symmetry. For example, the maximum deviation of the BBB bond angles in the pentagons girdling the C atoms was computed to be only 0.4° away from the average value of 108°. In general, the distortions of the geometry of the CB_5 groups from C_5 symmetry are *much* smaller than those in the cages of 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ (for which two models were considered)[1] or of the 1-phenyl derivative.[7]

With these assumptions, the structure of compound **1** was modelled using nine independent geometrical parameters. These included the C–B (p_1), mean B–B (p_2), and B–H (p_4) bond lengths, the C–S (p_3) and S–H (p_5) bond distances and the mean values of the C–B–H bond angles (p_7), the C–S–H angle (p_6), and the H–S(1)–C(1)–B(5) dihedral angle (p_8). The final parameter was the difference between the longitudinal, *r*[B(2)–B(3)], and latitudinal, *r*[B(2)–B(7)], B–B bond lengths, p_9.

Refinements of all these nine parameters proceeded smoothly, although some of them (p_6, p_8, p_9) were subject to flexible restraints (Table 1), the uncertainty values of which were chosen so that the refined parameters did not depart significantly from the MP2 values. In the final stage 13 amplitudes of vibration or tied groups of amplitudes were refined simultaneously. Those that were not refined were fixed at values consistent with those obtained for equivalent distances in related molecules.

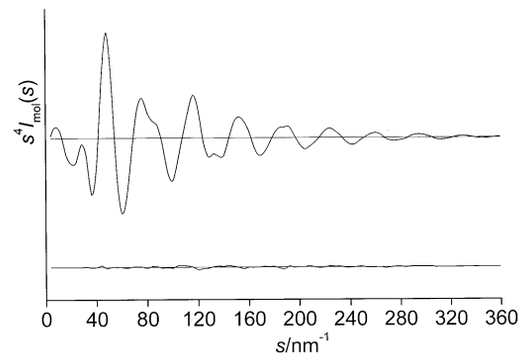

Fig. 2 Combined experimental and final weighted difference (experimental − theoretical) molecular-scattering intensities for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$.

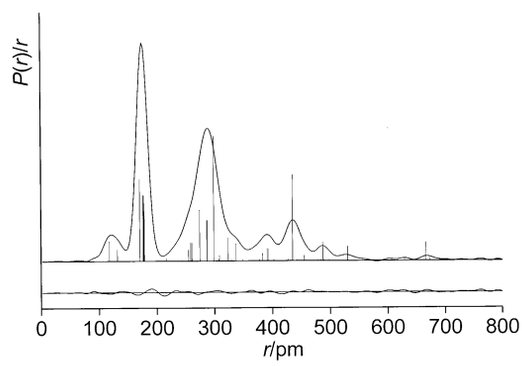

Fig. 3 Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$. Before Fourier inversion the data were multiplied by $s \times \exp(-0.00002s^2)/(Z_B - f_B)(Z_S - f_S)$.

The parameters obtained in the final refinement, for which $R_G = 0.077$ ($R_D = 0.070$), together with the corresponding values computed at the MP2/6-31G* level are provided in Table 2. Interatomic distances and amplitudes of vibration are listed in Table 3 and the most important elements of the least-squares correlation matrix in Table 4. Molecular scattering intensities and the radial-distribution (RD) curves are shown in Figs. 2 and 3 respectively. Atomic coordinates for the experimental and computer structures are listed in Table 5.

Discussion

As expected, the structural information in the radial-distribution curve for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$ is appreciably richer than that of the parent 1,12-$C_2B_{10}H_{12}$,[8] even though the S–C bond distance is similar to the B–B bond distances (Tables 1, 2). There are distinct features in the radial-distribution curve at *ca.* 435 and 490 pm associated with the S···B(7) and S···C separations, respectively, which contribute to the reliable determination of the S–C, C–B, and B–B bond lengths, even though they are not distinct in the RD curve. The assignment of a small peak at *ca.* 670 pm to the S(1)–C(1)···C(12)–S(2) distance provides support for the accuracy of these experimental determinations. The S–C bond length refined to 178.5(10) pm (MP2/6-31G*, 180.2 pm), which may be compared with the MP2/6-31G* S–C distances of 181.6 pm for CH_3SH and 179.0 pm for C_6H_5SH (benzenethiol).[15] The experimental C–B and B–B lengths of **1** are very similar to the GED values determined for the parent compound

Table 2 Molecular parameters (r_a, distances/pm, angles/°) for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$ (overall C_2 symmetry)[a] as obtained by electron diffraction and *ab initio* calculations

	Parameter	GED[b]	MP2/6-31G*[c]
p_1	r(C–B)	170.6(4)	171.2
p_2	r(B–B)	177.0(4)	177.9
p_3	r(C–S)	178.5(10)	180.2
p_4	r(B–H)	118.0(6)	118.7
p_5	r(S–H)	131.9(33)	134.2
p_6	C–S–H	92.8(30)[d]	95.0
p_7	C–B–H	123.1(10)	119.0
p_8	φ[H–S(1)–C(1)–B(5)]	44.8(98)[d]	43.3
p_9	$\Delta r[(B–B)_{longitudinal} - r(B–B)_{latitudinal}]$	1.0(9)[d]	1.8
p_{10}	$r(B–B)_{longitudinal}$	177.5(3)[e]	177.9
p_{11}	$r(B–B)_{latitudinal}$	176.5(9)[e]	176.1
p_{12}	φ[H(1)–S(1)···S(2)–H(2)]	55.2(65)[e]	48.7

[a] Least-squares standard deviations in the last digit are given in parentheses. [b] D_{5d} of the $C_2B_{10}H_{10}$ core assumed. [c] The $C_2B_{10}H_{10}$ core was computed to be very close to D_{5d} symmetry; mean values of parameters are given. [d] Flexibly restrained. [e] Dependent parameter.

Table 3 Final interatomic distances (r_a/pm)[a] and mean amplitudes of vibration (u/pm) for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$

Atom pair	r_a[b]	u_a[b]
d_1 C(1)–B(2)	170.6(4)	6.1(10)
d_2 B(2)–B(3)	177.5(3)	7.1(9)
d_3 B(2)–B(7)	176.5(7)	7.1 tied to u_2
d_4 S(1)–C(1)	178.5(10)	4.0(21)
d_5 B(2)–H(2)	118.0(6)	7.7(12)
d_6 S(1)–H(1)	131.9(33)	7.5[c]
d_7 (C,B···B)[d]	274.4–287.2	7.6, 8.4(12)
d_8 C(1)···C(12)	308.5(15)	10.0[c]
d_9 B(2)···B(10)	337.1(5)	12.0[c]
d_{10} S(1)···B(2)	298.8(8)	10.8(8)
d_{11} S(1)···B(7)	434.7(4)	13.0(4)
d_{12} S(1)···C(12)	487.0(9)	9.2(12)
d_{13} S(1)···S(2)	665.5(11)	30.7(69)
d_{14} C(1)···H(1)	216.8(56)	10.0[c]
d_{15} (C,B···H[–B])[d]	255.0–261.2	12.6(12)
d_{16} (C,B···H[–B])[e]	383.0–392.4	12.2(8)
d_{17} B(2)···H(10)	455.0(6)	12.0[c]
d_{18} B(2–6)···H(1)	260.3–377.7	12.0–14.0[c]
d_{19} B(7–11)···H(1)	402.5–486.7	13.0[c]
d_{20} C(1)···H(2)	498.4(66)	14.0[c]
d_{21} S(1)···H[–B(2,6)]	323.6(20)	10.9(17)
d_{22} S(1)···H[–B(7,11)]	530.0(14)	16.4(24)
d_{23} S(1)···H(2)	672.2(66)	30.0[c]

[a] The H···H distances were included in the refinement, but are not listed. Their vibrational parameters were fixed at 15 pm. [b] Least-squares standard deviations in the least significant digit are given in parentheses. [c] Fixed. [d] Two bonds between atoms. [e] Three bonds between atoms.

Table 4 Portion of the least-squares correlation matrix for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$ showing all elements >50%

	p_5	p_9	u_1	u_7	u_{10}
p_1		69			
p_2		−71		69	78
p_3			−74	−71	
u_2			−65		
u_4			84		
u_5	−68				
u_7		−74			
u_{10}		−51		81	
u_{15}				62	
u_{21}					55

Table 5 Atomic coordinates for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$[a]

	x	y	z
(a) GED			
C(1,12)	0.0	0.0	+/−154.25
B(2,3)	−/+88.76	−122.17	74.91
B(4,6)	+/−143.62	46.66	74.91
B(5)	0.00	151.01	74.91
B(7,9)	−/+143.62	−46.66	−74.91
B(8)	0.0	−151.01	−74.91
B(10,11)	+/−88.76	122.17	−74.91
H(2,3)	−/+149.31	−205.51	132.37
H(4,6)	+/−241.59	78.50	132.37
H(5)	0.00	254.02	132.37
H(7,9)	−/+241.59	−78.50	−132.37
H(8)	0.0	−254.02	−132.37
H(10,11)	+/−149.31	205.51	−132.37
S(1,2)	0.0	0.0	+/−332.77
H(1,2)	116.7	−/+61.07	+/−326.41
(b) MP2/6-31G*[b]			
C(1,12)	−/+135.53	−/+74.26	−0.39
B(2,7)	−/+43.55	−/+77.05	−143.86
B(3,11)	−/+123.83	+/−72.54	−89.62
B(4,10)	−/+124.88	+/−71.19	87.75
B(5,9)	−/+42.35	−/+77.08	143.11
B(6,8)	+/−7.69	−/+168.94	−0.29
H(2,7)	−/+84.41	−/+134.12	−239.63
H(3,11)	−/+218.26	+/−112.62	−149.09
H(4,10)	−/+219.27	+/−111.78	147.29
H(5,9)	−/+82.53	−/+134.44	238.97
H(6,8)	0.0	−/+287.26	0.18
S(1,2)	−/+292.03	−/+163.34	−6.01
H(1,2)	−/+332.67	−/+123.12	115.38

[a] The H and S atoms are numbered in the order of the skeletal atoms to which they are attached. H atoms bonded to S have the same number as the corresponding S atoms. [b] The computed total energy at that level is −126.1123585 hartrees.

{1,12-$C_2B_{10}H_{12}$ (pm): r(C–B) = 171.0(11), r[B(2)–B(3)] = 179.2(7), r[B(2)–B(7)] = 177.2(13) pm},[8] for the 1,12-dimethyl derivative of 1,12-$C_2B_{10}H_{12}$[10] [171.6(13), 177.7(7), and 176.6(20) pm] and for 1,12-I_2-1,12-$C_2B_{10}H_{10}$ [170.8(8), 177.7(8), and 177.5(11) pm].[9]

In order to provide support for the experimental and computed structures of **1**, we calculated the ^{11}B NMR chemical shifts, as for many other boron clusters investigated earlier.[1,3,7] The IGLO/DZ method was applied to both the MP2/6-31G* and GED geometries. With C_2 molecular symmetry there are five different chemical shifts. The calculated average value was δ −14.9 for the MP2 geometry and −14.5 for the GED geometry, the maximum deviation of an individual ^{11}B signal from the average values being *ca.* 2 ppm. The experimental value (which, due to rapid rotations of the SH groups, is an average) is lower than both, but in reasonable accord (δ −11.4). This last value compares well with δ −13.9 determined for the boron atoms bonded to hydrogen in 1,12-$(SMe)_2$-1,12-$B_{12}H_{10}$.[14] The GED geometry was computed to lie only 21.8 kJ mol^{-1} higher in energy (MP2/6-31G* single point) than the optimised theoretical structure. Such so-called "excess energy" is one of the smallest we have determined, and is well within the range normally calculated for "accurate" experimental structures of boranes and heteroboranes.[1,3,7] A major part of this 21.8 kJ mol^{-1} energy difference is due to the hydrogen positions, which are relatively poorly refined experimentally. The energy difference was reduced to 2.5 kJ mol^{-1} when the GED geometry of the heavy-atom core was kept fixed and the hydrogen placements were optimised at the MP2/6-31G* level. Both this energy criterion and the NMR fit indicate that a quite high level of accuracy has been achieved in the determination of the experimental geometry of compound **1**.

The 1,12-$C_2B_{10}H_{12}$ molecule and the other *closo*-dicarbaboranes, $C_nB_{n-2}H_n$, for which several positional isomers exist

Table 6 Salient computed cluster parameters for the compounds 1,12-X_2-1,12-$C_2B_{10}H_{10}$

X	PG[a]	d(C–B)[b]/pm	d(B–B)$^b_{long.}$/pm	d(B–B)$^b_{lat.}$/pm	2α[b]/°	d[C(1)···C(12)]/pm
H	D_{5d}	170.3	178.1	176.2	125.7	304.7
Li	D_{5d}	171.3	176.2	177.2	122.0	317.1
BeH	D_{5d}	171.5	177.7	176.4	123.7	311.4
F	D_{5d}	170.3	178.5	175.8	126.0	303.1
Cl	D_{5d}	170.8	178.3	175.9	125.2	306.0
CN	D_{5d}	171.6	179.0	175.8	125.1	306.7
CH_3	C_{2h}	171.2	177.3	176.0	123.6	311.2
SiH_3	C_{2h}	171.2	177.8	176.2	124.0	310.2
OH	C_2	171.2	177.9	175.8	124.2	308.9
SH	C_2	171.2	177.9	176.1	124.3	309.1
NH_2	C_2	171.5	177.5	175.9	123.3	312.0
BH_2[c]	C_s	171.6	178.2	176.2	124.2	309.8

[a] Point group characterising the minimum on the respective potential energy hypersurface. [b] Average values if not D_{5d} symmetric. [c] C(1) and C(12) are not related by symmetry and the parameters are therefore averages.

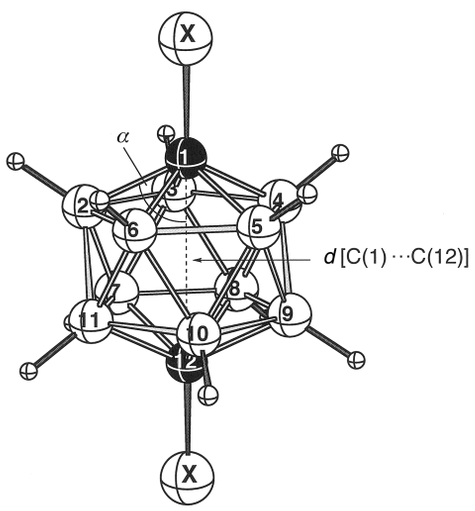

Fig. 4 Definition of the α and d[C(1)···C(12)] parameters for the series of compounds 1,12-X_2-1,12-$C_2B_{10}H_{10}$.

for a given cluster nuclearity, were claimed to exhibit three-dimensional aromaticity[11] or even to be superaromatic,[13,16] according to several different criteria. For example, the stability of *closo*-$C_nB_{n-2}H_n$ generally increases with increasing cluster size from 5 to 12 vertices.[11] The rather large nucleus-independent chemical shifts (NICS)[11,17] and the magnetic susceptibilities[11] also support the aromatic behaviour of *closo*-carbaboranes. Benzene-like reactions of *closo*-carbaboranes, such as electrophilic substitutions,[18] resulting for example in 2-X-1,12-$C_2B_{12}H_{11}$, and nucleophilic substitutions[18] (very rare for aromatics), yielding for example 1-X-1,12-$C_2B_{12}H_{11}$ or 1,12-X_2-1,12-$C_2B_{12}H_{10}$, are consistent with this concept. Geometric criteria of aromaticity, *e.g.* differences between the longest and shortest bond lengths, have also been examined in this class of compounds.[11,19]

As with two-dimensional aromatic compounds, substitutions of hydrogen cause considerable ring deformations. For example, in the series of compounds 1,4-$X_2C_6H_4$, there are appreciable variations in the C(1)···C(4) distances, accompanied by simultaneous narrowing or widening of the C(2)–C(1)–C(6) angles (*i.e.* at the *ipso* positions).[12] These geometrical changes were ascribed to inductive effects of the substituents, as demonstrated *e.g.* by analysis of the regression of the values of the *ipso* angles against the inductive parameters σ_I.[20]

We have studied whether such trends also exist for the 1,12-disubstituted 1,12-dicarbadodecaboranes. A positive result would provide an additional criterion by which three-dimensional aromaticity could be recognised. As just three such compounds have been studied in the gas phase (X = CH_3, I or SH), we also performed MP2/6-31G* optimisations of the structures of 1,12-X_2-1,12-$C_2B_{10}H_{10}$ for a series of compounds (Table 6), to provide a consistent single source of structural data. Fig. 4 shows two parameters that can be used to represent the strength of the cross-cage interaction. Note that they are analogous to C(2)–C(1)–C(6) (strictly speaking 2α is equivalent to the *ipso* angle) and d[C(1)···C(4)] in 1,4-X_2-C_6H_4.

We have then studied the correlation of various substitution constants,[20a] quantifying both inductive and resonance effects, with the C(1)···C(12) distance. Regression analysis of the angular parameter 2α and body diagonals C(1)···C(12) against the inductive constants σ_I and the resonance constants σ_R reveals that the relatively large changes in the body diagonal lengths (maximum difference 14 pm, Table 6) and smaller, but significant, changes of 2α (Table 6) are controlled primarily by the inductive effect of the substituents. The quality of the correlations is shown in Fig. 5. So that the σ_I constants could be perfectly comparable, their computed values[20b] were used as no experimental values are available for some substituents. The importance of the choice of these constants is marginal, given that the experimental values of σ_I may differ considerably, depending on which of the different approaches is used.[20] The points corresponding to unsubstituted 1,12-$C_2B_{10}H_{12}$ depart significantly from the regression line. This may be a consequence of the zero electron core of hydrogen.

Table 6 and Fig. 5 show that a substantial part of the variance of the cage parameters arises from a concerted change of 2α and d[C(1)···C(12)]. The gradual decrease of the former from 126° for X = F to 122° for X = Li is accompanied by a simultaneous increase of d[C(1)···C(12)] from 303 to 317 pm. The two cage parameters are linearly related (Fig. 6) with a correlation coefficient $r = -0.996$. (For 1,4-X_2-C_6H_4 this coefficient is -0.997.)[12] The linearity of Fig. 6 has a clear physical meaning. While some substituents (F, CN) have the ability to distort the cage by pushing C(1) and C(12) towards the centre of the icosahedron, others such as Li have the opposite geometrical effect. The much smaller variation of the C–B bond lengths and of both kinds of B–B bond lengths (Table 6), compared with d[C(1)···C(12)], indicates that the quite large distortion of the cage that takes place along the body diagonal is accompanied by only small changes in the lengths of the B–B bonds, the C–B bonds being affected to an even lesser extent (Table 6). More electropositive substituents push electron density towards C and generate a more carbanion-like structure, accompanied by a move towards a more pyramidal geometry (*cf.* the structure of CH_3^-). On the other hand, more electronegative substituents pull electron density from the radial ("p_z" orbital, causing a more carbacation-like structure (*cf.* CH_3^+). This tendency towards a planar arrangement brings the carbon atoms closer. This is the σ inductive effect that is responsible for such changes.

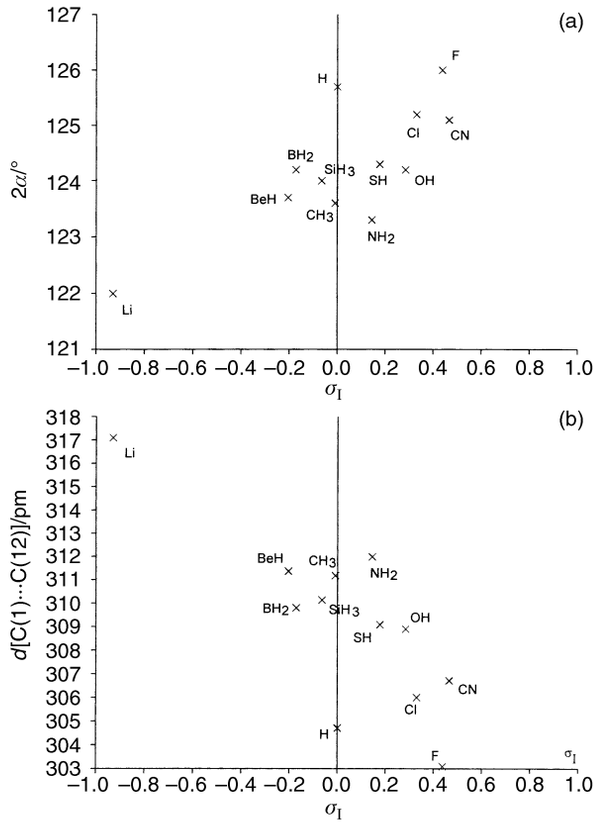

Fig. 5 (*a*) Plot of the angles 2*α* (symmetrised where there is strictly no C_5 axis, see *e.g.* Table 6) against the theoretically calculated (MP2/6-31G*) inductive parameters σ_I for 1,12-disubstituted 1,12-dicarbadodecaboranes. Also depicted is the reference point of the parent 1,12-$C_2B_{10}H_{12}$. The correlation coefficient $r = 0.857$ (excluding H, see text). (*b*) Plot of the body diagonals *d*[C(1)···C(12)] against the theoretically calculated (MP2/6-31G*) inductive parameters σ_I for 1,12-disubstituted 1,12-dicarbaboranes. The correlation coefficient $r = -0.883$ (excluding H, see text).

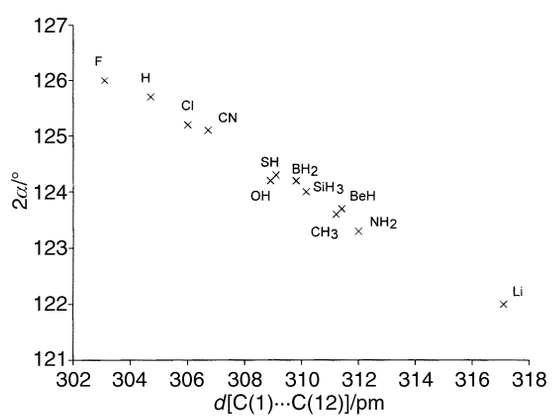

Fig. 6 Correlation between the angles 2*α* and the distances *d*[C(1)···C(12)] in 1,12-disubstituted 1,12-dicarbadodecaboranes. Structures were computed at the MP2/6-31G* level.

Experimental

Synthesis

The literature synthesis[21] was modified to improve the yield of compound **1**. To a solution of 3.6 g (25 mmol) of 1,12-$C_2B_{10}H_{12}$ in 50 ml of water-free diethyl ether, 24 ml (60 mmol) of a 2.5 M solution of butyllithium in hexane were added. The mixture was stirred for one hour at room temperature, and then 2 g (62.5 mmol) of elemental sulfur were added. After a further one hour stirring at room temperature 50 ml of water were added. The organic layer was separated and then extracted by 50 ml of 10% aqueous NaOH. The aqueous layer was combined with the extract and the mixture acidified with HCl to a pH of *ca.* 1. The product was extracted twice with 30 ml of hexane; the hexane was then evaporated *in vacuo.* The crude product was purified by column chromatography in hexane using silica gel (Silpearl, Kavalier). The fraction with $R_f = 0.35$ (in hexane) was collected. The process was repeated several times, and the combined fractions were then evaporated *in vacuo* and solid residue was sublimed *in vacuo* at 80 °C. 3.0 g of **1** were obtained, a yield of 57.7% with respect to the starting 1,12-$C_2B_{10}H_{12}$. The purity was further checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil) and by ^1H-{^{11}B} and ^{11}B-{^1H} NMR spectra recorded on a Varian Unity-500 instrument in $CDCl_3$ solution.

Electron diffraction

Electron-scattering intensities for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$ **1** were recorded on Kodak Electron Image photographic plates using the Edinburgh gas diffraction apparatus[22] operating at *ca.* 44.5 kV. The sample and nozzle were kept at 430 and 451 K respectively during the experiments. The electron wavelength and nozzle-to-plate distances were calibrated using diffraction data for benzene as reference. Experimental data were obtained in digital form using a computer-controlled Joyce-Loebl Microdensitometer 6 at the E.P.S.R.C. Daresbury Laboratory.[23] In the subsequent analysis of the data, established data reduction[22] and least-squares refinement programs[24] and complex scattering factors[25] were employed. The weighting points used in setting up the off-diagonal weight matrix, *s* ranges, scale factors, correlation parameters, and electron wavelengths are all presented in Table 7.

Computational details

The r_e geometry of compound **1** was optimised using standard *ab initio* methods[2] starting at the SCF level. Analytical frequency calculations with the 3-21G(*) basis set showed the structure with C_{2h} symmetry to be a transition state for rotation about the S–C bond. The corresponding minimum has C_2 symmetry. The other 1,12-X_2-1,12-$C_2B_{10}H_{10}$ derivatives were computed in D_{5d} symmetry for X = H, Li, BeH, F, Cl and CN, in C_{2h} for X = CH_3 and SiH_3 and in C_2 for X = OH and NH_2. The two boryl groups for X = BH_2 (C_s symmetry) are twisted by 90°, one eclipsing the C(1)–B(2) bond. These chosen conformations are minima at the HF/6-31G* level of theory (no imaginary frequencies). The final level of optimisation employed second-order Møller–Plesset (MP2) perturbation theory in the frozen-core approximation (MP2(fc)/6-31G*) and was carried out with GAUSSIAN 94.[26]

Chemical shieldings of compound **1** were computed with the IGLO program[4] using the Huzinaga DZ basis set,[27] *i.e.* (10s6p) contracted to [511111, 3111] for S, (7s3p) contracted to [4111,21] for C, B and (3s) contracted to [21] for H. B_2H_6 served as the primary reference and the calculated δ values were converted into the experimental scale using the δ (BF_3·OEt_2) gas-phase value of 16.6 ppm.[28]

The inductive and resonance constants were calculated according to the formulas given in ref. 20(*b*) using GAUSSIAN 94.[26]

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Table 7 Electron-diffraction experimental data for 1,12-$(SH)_2$-1,12-$C_2B_{10}H_{10}$

Camera distance/mm	Weighting function/nm^{-1}					Correlation parameter	Scale factor k[a]	Electron wavelength[b]/pm
	Δs	s_{min}	sw_1	sw_2	s_{max}			
259.91	2	30	50	140	164	0.4951	0.706(8)	5.681
94.95	4	80	100	284	336	0.0522	0.716(18)	5.716

[a] Figures in parentheses are estimated standard deviations of the least significant digits. [b] Determined by reference to the scattering pattern of benzene vapour.

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