Molecular Structure of Gaseous 1,7-Dichloro-1,7-dicarba-*closo*-dodecaborane(12), 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$, as studied by Electron Diffraction and *Ab Initio* Calculations

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Gas-phase electron diffraction (GED) data for 1,7-dichloro-1,7-dicarba-*closo*-dodecaborane(12), 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$, were fitted by a structure possessing overall C_{2v} symmetry. Not all of the independent parameters could be refined, and some differences between C–B and B–B bond lengths were fixed at values calculated *ab initio*. Assumption of local C_{5v} symmetry for the CB_5 pentagonal pyramids led to the same GED fit (R_G = 0.065) as with a model in which the B_5 rings adjacent to the carbon atoms were not quite regular, as found by *ab initio* optimisations [HF/6-31G* and MP2(fc)/6-31G*]. Nearest-neighbour C–B and B–B separations do not deviate significantly from normal values, and distortion of the cage from regular icosahedral symmetry is small. The C–Cl bond length, 175.9(9) pm, [MP2/6-31G* 174.9 pm], is shorter than in C(sp^3)–Cl systems and longer than in C(sp^2)–Cl systems. The geometrical parameters calculated at the MP2(fc)/6-31G* level, as well as ^{11}B NMR chemical shifts, calculated by the individual gauge for localised orbitals method, are in satisfactory agreement with the experimental observations.

There have been few experimental studies of the structures of gaseous *closo*-carbadodecaboranes and related heteroboranes. Bohn and Bohn[1] reported the gas-phase structures of the 1,2, 1,7 and 1,12 isomers of dicarba-*closo*-dodecaborane(12), $C_2B_{10}H_{12}$. Only the structure of the most symmetrical (D_{5d}) 1,12 isomer was established at a high level of accuracy and those of the less symmetrical (C_{2v}) 1,2 and 1,7 isomers could not be determined unambiguously. The D_{5d} C_2B_{10} cage has also been investigated as the 1,12-diiodo[2] and -dimethyl[3] derivatives. An electron-diffraction study of 1,7-I_2-1,7-$C_2B_{10}H_{10}$ was unsuccessful[4] and no substituted 1,2-dicarbadodecaboranes have been examined.

Considerable progress in determining accurate structures of relatively large boranes has recently been achieved using the combined *ab initio*-IGLO[5] (individual gauge for localised orbitals)-NMR[6] method. In addition to predicting the structures of many boranes and heteroboranes,[7] this approach has been used successfully to facilitate analyses of electron-diffraction data.[8] Highly correlated parameters defining the molecular geometry of clusters are rarely resolved by gas-phase electron-diffraction (GED) analysis alone, and so the technique is complemented by the ability of high-quality *ab initio* calculations to predict differences between similar bond lengths quite reliably. The computed differences between such distances may then be used as constraints during the GED refinements. Absolute values of parameters obtained by calculations which allow for electron correlation (*e.g.* MP2) may also be used. Furthermore, the calculated ^{11}B NMR chemical shifts for a particular experimental geometry and its energy relative to that of the structure calculated *ab initio* are invaluable in selecting the most probable structure on occasions when several fit the experimental scattering intensities comparably well.

In order to extend the knowledge of structural variations in the family of 12-vertex boron clusters, we have undertaken an electron-diffraction study of 1,7-dichloro-1,7-dicarba-*closo*-dodecaborane(12), 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ **1**. One of the purposes of the present work was to determine how the chlorine substituents on the carbon atoms influence the extent of the deformation from regular icosahedral symmetry on going from $B_{12}H_{12}{}^{2-}$ towards the assumed C_{2v} symmetry of the present cluster. In addition, because chlorine has a greater electron-scattering ability than does hydrogen, compound **1** is a better subject for studying the 1,7-C_2B_{10} cage than is the parent 1,7-$C_2B_{10}H_{12}$, the MP2/6-31G* geometry of which is also reported in this paper. Geometry optimisation at this level has also been carried out for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$, so that theoretical differences in C–B and B–B bond lengths could be used in the refinements. The final electron-diffraction geometry was verified by IGLO–^{11}B NMR chemical shift (DZ//GED and II′//GED levels) and single-point (MP2/6-31G* level) energy calculations.

Experimental

A sample of compound **1** was prepared by the standard method.[9] Its purity was checked by TLC and ^{11}B NMR spectroscopy. The NMR spectrum was recorded using a Bruker WH360 spectrometer and assigned using two-dimensional correlation spectroscopy (COSY) and established empirical rules.[10]

The electron-diffraction patterns were recorded on Kodak Electron Image plates using the Edinburgh diffraction apparatus.[11] The sample was held at 372 K and the nozzle at 405 K during the experiments. The electron beam was accelerated by a voltage of *ca.* 44.5 kV and the electron wavelength and nozzle-to-plate distances were calibrated using the scattering pattern of benzene as a reference. The electron-scattering patterns were converted into digital form using a computer-controlled Joyce–Löebl MDM6 microdensitometer at the SERC laboratory, Daresbury.[12] The data reduction[12] and least-squares refinements[13] used standard programs and complex scattering factors.[14] The weighting points used in setting up the off-diagonal weight matrices, *s* ranges, scale factors, correlation parameters and electron wavelengths are all given in Table 1.

The geometry was fully optimised in C_{2v} symmetry both at the Hartree–Fock level (standard basis sets 3-21G, 6-31G*[15]) and by employing second-order Möller–Plesset (MP) perturbation theory in the frozen-core (fc) approximation (denoted as MP2/6-31G*; fc is normally omitted) with the GAUSSIAN 92 program.[16] The optimised geometries for $1,7\text{-}X_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ (X = Cl or H) are summarised in Table 2.

The ^{11}B NMR chemical shifts were calculated with the IGLO program[15] using the following Huzinaga basis sets:[17] DZ, *i.e.* (10s6p) contracted to [511111, 3111] for Cl, (7s3p) contracted to [4111, 21] for C and B and (3s) contracted to [21] for H; II′, *i.e.* (11s7p2d) contracted to [5111111, 211111, 11] for Cl, (9s5p1d) contracted to [51111, 2111, 1] for C and B (d components: 0.4, 1.6 for Cl, 1.0 for C and 0.7 for B), and (3s) contracted to [21] for H. (In this nomenclature [511111] implies that five of the S type functions are contracted, the remaining five being treated independently.) The DZ results were obtained with an IGLO lobe version, whereas for II′ calculations the direct IGLO program (DIGLO)[5d] was used.

Molecular Model and Structure Refinement

The symmetry of the 1,7-dichloro-1,7-dicarba-*closo*-dodecaborane(12) molecule was assumed to be C_{2v} (Fig. 1). Although in principle there are three different B–C and seven different B–B bond distances, at first (model A) these were represented by just three distances: r_{1A}, which is a single value for all the B–B bonds forming the pentagonal belts adjacent to the carbon atoms, these belts being regular and planar in this approximation; r_{2A}, corresponding to the three kinds of B–C bonds and, finally, r_{3A}, representing the remaining B–B bonds, B(9)–B(10), B(4)–B(8) and B(5)–B(9). The distances r_{1A}, r_{2A} and r_{3A} were then related to the following independent refinable parameters: $p_{1A} = (9r_{1A} + 7r_{3A})/16$, $p_{2A} = r_{2A}$, and $p_{3A} = r_{1A} - r_{3A}$. Further parameters, which together defined the positions of the terminal atoms, were the C–Cl bond length, p_{4A}, the B–H bond length (all were assumed to be equal), p_{5A}, the C(1)–B(4)–H and C(1)–B(5)–H angles, p_{6A}, and the B(2)–B(3)–H and B(9)–B(10)–H angles, p_{7A}. Finally, a dip angle, p_{8A}, allowing the C–Cl bonds to deviate from the assumed local C_5 axes, was included.

Refinement of the parameters, p_{1A}–p_{7A}, for model A proceeded smoothly, giving an R_G factor of 0.065 (R_D = 0.046), with p_{8A} fixed at zero. All attempts to refine this last parameter were unsuccessful, leading to divergence of the refinements. However, the assumption that the value of this parameter is zero is in agreement with the theoretical dimensions: the Cl–C–X angle, where X is the midpoint of the B_5 belt adjacent to a carbon atom, was calculated to be 179.9°. A further problem was encountered with amplitudes of vibration for the cluster

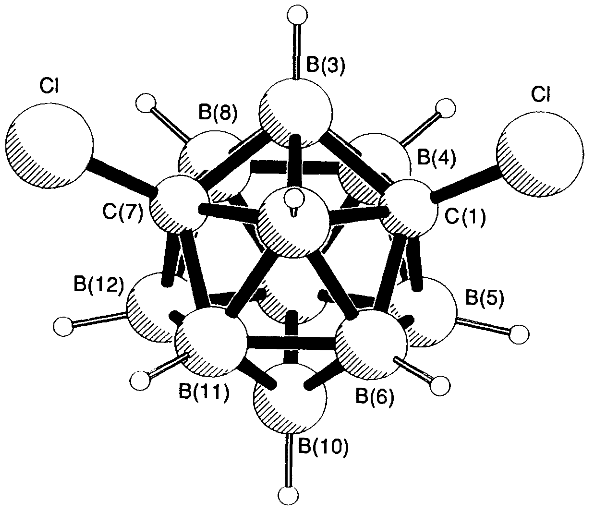

Fig. 1 View of the refined $1,7\text{-}Cl_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ structure based on electron-diffraction data constrained by certain MP2/6-31G* bond-length differences, model B. The atomic numbering of the carbaborane framework is shown

Table 1 Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors and electron wavelengths

Nozzle-to-plate distance/mm	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor[a] k	Electron wavelength[b]/pm
	nm^{-1}							
259.46	2	20	40	140	164	0.4314	0.877(8)	5.681
93.78	4	80	100	304	356	0.4435	0.809(18)	5.689

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

Table 2 *Ab initio* optimised nearest-neighbour separations (pm) for $1,7\text{-}X_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ (X = H or Cl) compared with GED data

	X = Cl			X = H	
	HF/6-31G*	MP2/6-31G*	GED (model B)	MP2/6-31G*	GED[a]
C(1)–B(2)	169.9	169.4	168.5(6)	168.8	172.0(2)
C(1)–B(4)	172.5	171.4	170.5(6)	170.9	
C(1)–B(5)	172.1	170.9	171.2(17)	170.6	
B(2)–B(3)	180.9	178.7	179.5(13)	178.0	183.5(16)
B(2)–B(6)	177.1	176.7	177.5(13)	176.5	177.1(8)
B(5)–B(6)	179.3	178.0	179.5(7)	177.8	180.3(8)
B(4)–B(8)	177.4	176.3	177.2(13)	176.6	181.8(3)
B(5)–B(9)	178.3	177.3	178.8(7)	177.3	
B(9)–B(10)	180.3	178.8	179.6(13)	178.9	
B(4)–B(9)	178.7	177.1	179.5(30)	177.5	
C–X	175.3	174.9	175.9(9)	108.7	115.0[b]
B–H	117.6[c]	118.6[c]	117.7(9)	118.7[d]	121.6[b]

[a] A five-parameter model in ref. 1. [b] Assumed. [c] Only an average value is given. The four kinds of MP2/6-31G* (HF/6-31G*) B–H distances are as follows: B(2)–H 118.3 (117.2); B(4)–H 118.6 (117.6); B(5)–H 118.6 (117.7); B(9)–H 118.9 (118.1) pm. [d] Average value: B(2)–H 118.5; B(4)–H 118.7; B(5)–H 118.8; B(9)–H 118.9 pm.

Table 3 Molecular parameters (distances/pm, angles/°) for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ (C_{2v} symmetry)[a]

Model A			Model B		
p_{1A}[b]	r(B–B)	179.4(3)	p_{1B}[b]	r(B–B)[(2–3) + (9–10) + 4(2–6) + 2(4–8)]/8	177.9(13)
p_{2A}[b]	r(C–B)	169.8(4)	p_{2B}[b]	r(C–B)[(1–2) + (1–6)]/2	169.5(6)
p_{3A}[b]	Δr(B–B)	−1.6(7)	p_{3B}[b]	Δr[B(2)–B(3)] − [B(9)–B(10)]	−0.1[c]
p_4	r(C–Cl)	174.8(7)	p_4	r(C–Cl)	175.9(9)
p_5	r(B–H)	117.0(7)	p_5	r(B–H)	117.7(9)
p_6	C–B–H	113.8(15)	p_6	C–B–H	110.6(19)
p_7	B–B–H	126.8(37)	p_7	B–B–H	124.7(64)
p_8	dip	0.0[d]	p_8	dip	0.0[d]
			p_{9B}	r(B–B)[(5–9) − (5–6)]/2	179.2(7)
			p_{10B}	B(3)–B(2)–B(6)	108.2(4)
			p_{11B}	Δr[B(4)–B(8)] − [B(2)–B(6)]	−0.3[c]
			p_{12B}	Δr[B(9)–B(10)] − [B(2)–B(6)]	2.1[c]
			p_{13B}	Δr[C(1)–B(6)] − [C(1)–B(2)]	2.0[c]
			p_{14B}	Δr[B(5)–B(6)] − [B(5)–B(9)]	0.7[c]

[a] Least-squares standard deviations in the last digit are given in parentheses. [b] For the different meanings of model A and model B parameters see text. [c] Fixed at the MP2/6-31G* value. [d] Fixed.

C–B and B–B bonds. These amplitudes of vibration were refined as a group, with fixed ratios, and a single refinable amplitude parameter representing the whole group. However, even with this constraint, the refined values were rather small, *ca.* 4 pm, for this class of compound and so they were subsequently fixed at reasonable values[8] (Table 4).

The r_e parameters obtained from *ab initio* optimisations (HF/6-31G* and MP2/6-31G* levels, Table 2) revealed that the assumption that there is local C_5 symmetry of the CB_5 group is not valid, although the calculations still indicate the planarity of the B_5 rings adjacent to carbon atoms. For example, there are significant differences between the C–B bond distances. Consequently, the restrictions which had been imposed on these pentagonal pyramids in model A were relaxed both by introducing some new parameters and by changing the meaning of some of p_{1A}–p_{8A}. The overall C_{2v} symmetry was retained. In the new model (model B) p_{1B} was the mean value of the B(2)–B(3), B(9)–B(10), B(2)–B(6) and B(4)–B(8) bond lengths, p_{2B} the average of the C(1)–B(2) and C(1)–B(6) bond lengths and p_{3B} represented the difference r[B(2)–B(3)] − r[B(9)–B(10)]. Parameters p_{4B}–p_{8B} were identical to the corresponding parameters in model A. In addition, six extra parameters, p_{9B}–p_{14B}, were considered in this model. However, none of the bond length differences included in this model was refined: instead they were fixed at the values obtained in the MP2/6-31G* calculations as shown in Table 3. Again, the refinement was straightforward, leading to R factors of 0.065 (R_G) and 0.046 (R_D). The problem of refining the vibrational amplitudes for nearest-neighbour atom pairs, as found in refinement A, recurred, and so they were fixed at the same values as in refinement A. The parameters obtained in both refinements are given in Table 3. Interatomic distances, together with the associated amplitudes of vibration, are listed in Table 4, and Table 5 lists those elements of the least-squares correlation matrix which exceed 50%. Table 6 gives the atomic coordinates for the experimental and MP2/6-31G* geometries. Molecular scattering intensities and the radial-distribution curves are shown in Figs. 2 and 3 respectively.

Table 4 Final interatomic distances (r_a/pm)[a] and mean amplitudes of vibration (u/pm) of 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ as obtained in refinement B

Atom pair	r_a[b]	u[b]
d_1 C(1)–B(2)	168.5(6)	5.5[c]
d_2 C(1)–B(4)	170.5(6)	5.5[c]
d_3 C(1)–B(5)	171.2(17)[d]	5.5[c]
d_4 B(2)–B(3)	179.5(13)	5.8[c]
d_5 B(2)–B(6)	177.5(13)	5.8[c]
d_6 B(5)–B(6)	179.5(7)	5.8[c]
d_7 B(4)–B(8)	177.2(13)	5.8[c]
d_8 B(5)–B(9)	178.8(7)	5.8[c]
d_9 B(9)–B(10)	179.6(13)	5.8[c]
d_{10} B(4)–B(9)	179.5(30)[d]	5.8[c]
d_{11} C(1)–Cl	175.9(9)	4.7(15)
d_{12} (B–H), single	117.7(9)	11.3(16)
d_{13} C···C	255.9(12)[d]	6.7(2)
d_{14} (C···B)[e]	272.8–275.2[d]	8.8 (tied to u_{13})
d_{15} (B···B)[e]	288.3–290.4[d]	9.3 (tied to u_{13})
d_{16} (C···B)[f]	321.1(13)[d]	7.4(18)
d_{17} (B···B)[g]	340.0–340.7[d]	8.3 (tied to u_{16})
d_{18} (B···Cl)[e]	293.2–294.8[d]	10.3 (tied to u_{13})
d_{19} (B, C···Cl)[f]	415.9–432.2[d]	10.6–13.3(4)
d_{20} B(12)···Cl[h]	496.9(10)[d]	8.0[c]
d_{21}Cl···Cl	555.2(11)[d]	17.6(23)
d_{22} (C···H)[e]	238.9–257.9[d]	7.9 (tied to u_{13})
d_{23} (B···H)[e]	252.0–274.6[d]	7.9 (tied to u_{13})
d_{24} (C···H)[f]	380.3–381.4[d]	11.3(12)
d_{25} (B···H)[f]	379.9–403.5[d]	11.3 (tied to u_{24})
d_{26} (C···H)[h]	435.1(13)[d]	10.6 (tied to u_{19})
d_{27} (B···H)[h]	454.0–458.3[d]	10.6 (tied to u_{19})
d_{28} (Cl···H)[f]	293.9–325.9[d]	11.0–12.0[c]
d_{29} (Cl···H)[i]	523.9–525.7[d]	16.9(37)
d_{30} (Cl···H)[h]	610.6(12)[d]	6.0[c]

[a] The H···H distances were included in the refinement, but they are not listed. Their vibrational amplitudes were fixed at 15 pm. [b] Least-squares standard deviations in the least significant digit are given in parentheses. [c] Fixed. [d] Dependent distance. [e] Atoms separated by two bonds. [f] Atoms separated by three bonds. [g] Body diagonal. [h] Diametrically opposite. [i] Atoms separated by four bonds.

Discussion

As anticipated the radial-distribution curve for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ is significantly richer than that of the parent 1,7-$C_2B_{10}H_{12}$,[1] even though the C–Cl bond distance lies within the range of the C–B and B–B bond lengths (Tables 3 and 4). The eight-parameter model A gives the same R factors as does the fourteen-parameter model B. Similar results were found in the GED study of 1,7-$C_2B_{10}H_{12}$,[1] in which there was no significant difference in the R factors for two-parameter (with just one B–C and one B–B bond distance) and six-parameter models. Of course the constraints described in Table 3 are not unique, but the ten distinct nearest-neighbour separations, d_1–d_{10} (Table 4), assuming C_{2v} symmetry, cannot be distinguished unambiguously by GED. The following discussion is based on the results in refinement B.

The angle between the planes of the two pentagonal B_5 belts, each surrounding one carbon atom, and linked by the common edge B(2)–B(3), is 63.4(2)° in the experimental structure, and is

Table 5 Portion of the least-squares correlation matrix for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ showing all elements > 50% (model B)

p_2	p_5	p_6	p_7	p_9	p_{10}	u_{11}	u_{13}	u_{19}	u_{29}	
73		−68		−86	−81	86		50		p_1
				−57		65				p_2
	52			−54			−56			p_4
				−57						p_5
			68	59		−61				p_6
						−80	59			p_9
					68	−74				p_{10}
								50		u_{11}
									69	u_{21}

Table 6 Atomic coordinates (pm) for 1,7-X_2-1,7-$C_2B_{10}H_{10}$[a]

	Electron-diffraction (model B) (X = Cl)			*Ab initio* (MP2/6-31G*) (X = H)			*Ab initio* (MP2/6-31G*) (X = Cl)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C(1,7)	0.0	(±)127.9	−63.0	0.0	(±)129.9	−79.8	0.0	(±)130.3	−26.3
B(2,3)	(±)89.7	0.0	0.0	(±)89.0	0.0	−140.7	(±)89.4	0.0	−87.2
B(4,6,8,11)	(∓)145.1	(±)88.6	−143.5	(∓)144.2	(±)88.3	1.8	(∓)144.5	(±)88.2	55.7
B(5,12)	0.6	(±)144.2	−233.5	0.0	(±)142.7	90.3	0.0	(±)142.9	144.2
B(9,10)	(∓)89.8	0.0	−289.5	(∓)89.4	0.0	145.7	(∓)89.4	0.0	199.1
X(13,19)	0.0	(±)277.6	29.4	0.0	(±)221.5	−138.3	0.0	(±)277.0	−121.4
H(14,15)	(±)156.8	0.0	96.8	(±)142.6	0.0	−246.4	(±)141.6	0.0	−193.4
H(16,18,20,23)	(∓)226.8	(±)171.1	−124.2	(∓)239.5	(±)158.4	−8.4	(∓)239.0	(±)158.9	44.2
H(17,24)	0.0	(±)257.8	−264.3	0.0	(±)250.7	139.9	0.0	(±)251.3	192.3
H(21,22)	(∓)156.9	0.0	−386.3	(∓)153.2	0.0	246.1	(∓)153.2	0.0	299.4

[a] The terminal atoms X = H or Cl are numbered in the order of the heavy atoms to which they are attached: thus X(*n* + 12) is bonded to B(*n*).

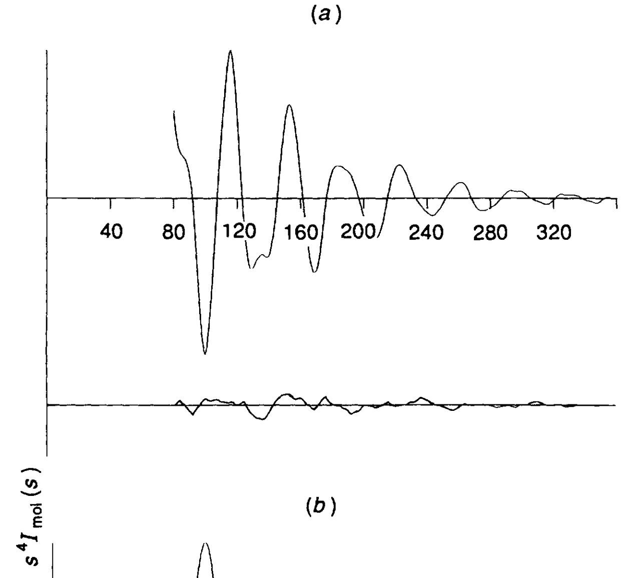

Fig. 2 Final experimental molecular-scattering intensities for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ at nozzle-to-plane distances of (*a*) 94 and (*b*) 260 mm. The weighted difference curves (experimental − theoretical) are also shown

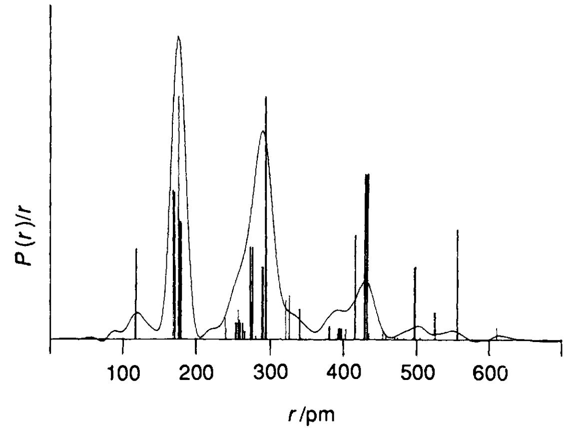

Fig. 3 Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, for 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$ vapour; before Fourier inversion, the data were multiplied by $s\cdot\exp(-0.000\,02s^2)/(Z_c - f_c)(Z_B - f_B)$

also calculated to be 63.4° at the MP2/6-31G* level. It is thus the same as the corresponding angle in the regular icosahedral $B_{12}H_{12}^{2-}$. The corresponding angle in 1,7-$C_2B_{10}H_{10}$ is also 63.4° in both the MP2/6-31G* geometry and the structure based on electron-diffraction data.[1] The B_5 rings at the bases of the CB_5 pentagonal pyramids are planar and almost regular: the angle B(3)–B(2)–B(6) refined to 108.2(4)°, the same value as obtained in the *ab initio* calculations. The distortion of the 1,7-C_2B_{10} cage from a regular icosahedral structure is thus small, and can be represented primarily by a reduction in the height of the CB_5 pyramids.

The C–Cl bond length refined to 175.9(9) pm (MP2/6-31G*, 174.9 pm). This is shorter than the C(sp^3)–Cl bond lengths in other monohalogenated C(sp^3) systems such as $CClH_3$, for which r_g is 178.3(2) pm.[18] On the other hand, C(sp^2)–Cl bond lengths for systems in which the carbon atom bears no other halogen are shorter, as, for example, in CH_2=CHCl [r_g 173.0(4) pm][18] and C_6H_5Cl [r_a 173.9(2) pm].[19]

The ^{11}B NMR chemical shifts of B(2) and B(4) in 1,7-Cl_2-1,7-

Table 7 The IGLO results for 1,7-X_2-1,7-$C_2B_{10}H_{10}$ (X = H or Cl)

X	Level of theory// geometry	δ (^{11}B)[a] B(2,3)	B(4,6,8,11)	B(5,12)	B(9,10)	Relative energy[b]/kJ mol^{-1}
Cl	DZ//HF/6-31G*	−11.7	−14.0	−3.2	−18.1	
	DZ//MP2/6-31G*	−12.1	−14.5	−4.2	−18.7	
	DZ//GED	−12.0	−14.2	−5.5	−20.7	36.0
	DZ//GED (H relaxed)[c]	−13.8	−14.4	−4.1	−17.8	
	II′//MP2/6-31G*	−12.7	−12.7	−5.6	−15.5	
	II′//GED	−12.7	−12.3	−6.9	−17.5	43.7
	II′//GED (H relaxed)[c]	−14.7	−12.5	−5.2	−14.1	
	Experimental[d]	−11.0	−9.7	−7.2	−11.0	
H	DZ//HF/6-31G*	−18.2	−17.2	−4.5	−17.1	
	DZ//MP2/6-31G*	−18.3	−17.6	−5.1	−17.8	
	II′//MP2/6-31G*	−18.1	−15.4	−5.8	−13.8	
	Experimental[e]	−18.1	−14.3	−7.7	−11.6	
	Experimental[f]	−16.4	−12.5	−5.7	−9.4	
	Experimental[g]	−16.3	−12.9	−6.6	−10.4	

[a] Relative to BF_3·OEt_2. [b] Energy of the GED structure with respect to that of the MP2/6-31G* geometry, computed at SCF levels employing DZ and II′ basis sets; the more refined MP2/6-31G* value is 40.5 kJ mol^{-1} (*i.e.* MP2/6-31G*//GED *vs.* MP2/6-31G*//MP2/6-31G*). [c] Partially optimised GED structure (model B) at the MP2/6-31G* level in which the C_2B_{10} skeleton remained fixed and only the locations of the hydrogen atoms were optimised. [d] This work. [e] Ref. 10. [f] Ref. 20. [g] Ref. 21.

$C_2B_{10}H_{10}$ are shifted to high frequency relative to those of the parent molecule, with that for B(2) being more pronounced (Table 7). This has been called the *ortho* effect.[10] On the other hand, the antipodal shift to high frequency[6d,8a,22] of B(5) with respect to $B_{12}H_{12}^{2-}$, for which δ(^{11}B) is −15.3,[23] is practically unchanged for both 1,7-X_2-1,7-$C_2B_{10}H_{10}$ molecules (X = H or Cl) (for X = Cl, an unexpected shift to low frequency is countered by the *ortho* shift to high frequency). The IGLO calculations (II′ and DZ basis sets) with both the theoretical (HF/6-31G*, MP2/6-31G*) and the experimental (GED) geometries show reasonable agreement with experimental findings: as expected, the larger II′ basis set performs better.

The GED geometry of compound **1** was computed to lie only 40.5 kJ mol^{-1} higher in energy (MP2/6-31G* single point) than the theoretical structure optimised at the same level. Such an energy difference is typical for GED structures of boranes and heteroboranes established recently.[8] When the heavy-atom structure of **1** was fixed at its GED geometry and the hydrogen positions were optimised at the MP2/6-31G* level the relative energy of the so-called 'hydrogen-relaxed' structure was only 4.9 kJ mol^{-1}. This indicates that the 'excess energy' may be almost completely attributed to the hydrogen atom placements, which are poorly determined in the electron-diffraction experiments. A reasonable NMR fit further supports the conclusion that model B affords a good representation of the experimental geometry of 1,7-Cl_2-1,7-$C_2B_{10}H_{10}$.

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