

Tetraborane(10), B₄H₁₀: structures in gaseous and crystalline phases†

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Supplementing gas-phase electron-diffraction data with restraints derived from a graded series of *ab initio* calculations makes possible refinement of all geometrical parameters and amplitudes of vibration. By avoiding the need to fix some parameters, this technique yields structures which are more completely refined and thus have more reliable standard deviations than procedures used previously. It has been applied to the gas-phase structure of the *arachno* boron hydride tetraborane(10), B₄H₁₀. Salient structural parameters (*r_a* structure) were found to be: *r*[B(1)–B(2)] 186.6(2), *r*[B(1)–B(3)] 173.7(5), *r*[B(1)–H(1,2)] 123.0(15), *r*[B(2)–H(1,2)] 141.7(8), *r*[B(1)–H(1)] 119.8(8), *r*[B(2)–H(2)]_{endo} 121.0(8) and *r*[B(2)–H(2)]_{exo} 120.5(8) pm; butterfly angle 117.2(4)°. The crystal structure was also redetermined at 100 K. All gas-phase, crystallographic and *ab initio* structural parameters were found to be in good agreement.

We have recently described a methodology for determining gas-phase electron-diffraction (GED) structures by supplementing GED data with information derived from a series of *ab initio* calculations.¹ This so-called SARACEN method (structure analysis restrained by *ab initio* calculations for electron diffraction) normally allows all geometric parameters and all significant amplitudes of vibration to refine, thereby giving structures which are as accurate as possible and have realistic estimated standard deviations of parameters.

The last decade has seen major improvements in the field of computational chemistry. Rapid developments in both computer technology and software have allowed much more sophisticated calculations to be performed than were previously possible. It is now routine to perform reliable *ab initio* calculations, including treatment of electron correlation, on moderately large systems, making the method particularly attractive for experimentalists working in the gas phase. Recent work in our laboratory has aimed to exploit these developments by combining calculations of molecular structures with experiment to obtain molecular structures of maximum reliability.

In the analysis of GED data it is frequently the case that certain parameters need to be fixed at assumed values;² often the positions of light atoms (normally hydrogen) are poorly defined due to their low electron-scattering ability, and parameters defining similar interatomic distances can be strongly correlated. In a procedure described as molecular orbital constrained electron diffraction (MOCED),³ the parameters (usually differences between related bond lengths or angles) are fixed at values obtained by *ab initio* calculations. However, this practice of fixing parameters is not ideal. It can result in unrealistically low estimated standard deviations for refining parameters, particularly if they are strongly correlated with other parameters; the effects of the correlation are concealed, however, by fixing these other parameters. Merely multiplying standard deviations by a factor of two or three is unsatisfactory; in some cases this factor may not be large enough, while in others it may be unnecessarily discarding hard-won precision.

In one approach to overcoming this problem electron-diffraction data are often supplemented with data from other experimental techniques, such as rotation constants obtained by microwave spectroscopy and/or direct coupling constants derived from liquid-crystal NMR (LCNMR) spectra. These

extra data are used in the GED refinements as additional observations with their estimated uncertainties‡ used to weight the data. The recent refinement of the structure of perfluorocyclopropene, C₃F₄,⁴ serves as a good example of this procedure. This is the ideal approach, as the resulting structure is based entirely on experiment. However, sufficient experimental data are not always available. Bartell *et al.*⁵ demonstrated that it was also possible to incorporate estimates of geometrical parameters with their uncertainties (so-called predicate observations) in the same way. These estimates could come from any appropriate source of structural information, but assignment of uncertainties must necessarily be to some extent subjective.

In essence the SARACEN method is the combination of the MOCED³ and predicate observation⁵ methodologies, with *ab initio* data being used to construct the predicate observations necessary to complete the refinement. Clearly there is no standard deviation associated with a single *ab initio* result, since the calculation will be exact within the constraints of the basis set and level of theory used. However, the uncertainty can be estimated by performing a series of calculations in which the basis set and level of theory are systematically improved, or it can be based on a knowledge of how reliable the highest-level *ab initio* calculations are for similar types of systems. The value for the *ab initio* predicate observation (termed restraint§) is normally taken from the highest-level calculation.

It should be noted that the use of restraints is not confined purely to the independent geometrical parameters used to describe the molecular structure. They can be applied equally well to dependent bond distances or angles, or to any other quantity which is a function of the geometrical parameters. Restraints can also be applied to vibration (*u*) required for the amplitudes of GED refinement, with values derived from a scaled *ab initio* force field. A restraint can be applied either directly to a vibrational amplitude, which would otherwise fail to refine satisfactorily, or, for amplitudes to be refined in a tied group, to the ratio or ratios of the amplitudes. Since *ab initio* force fields calculate the ratios of vibrational amplitudes more

‡ We use the term 'uncertainty' for the estimated possible error in a supplementary observation, and 'estimated standard deviation' for the error in a parameter derived in the least-squares refinements. The uncertainties, which give the weights assigned to additional observations, are, in the case of additional experimental data, the estimated standard deviations of those data.

§ 'Restraint' is used for any additional information which is applied flexibly, 'constraint' for one which is applied rigidly, such as a fixed parameter or molecular symmetry.

† Non-SI unit employed: Hartree, E_h ≈ 4.36 × 10⁻¹⁸ J.

accurately than their absolute values, for the latter method we suggest that as a general rule an uncertainty of 5% is appropriate for weighting a ratio, as opposed to 10% if the restraint is applied directly to a particular amplitude. However, the uncertainties chosen must depend on an assessment of the specific circumstances, and never produced automatically or without careful consideration.

In the SARACEN method all geometric parameters and all significant amplitudes of vibration should be allowed to refine as a matter of principle, although for more complex systems this may not yet be practicable. With more parameters refining, the standard deviations obtained for parameters reflect more fully the interparameter correlations and should therefore be larger. The resulting structure will be the best obtainable based on both experimental and theoretical information. A fuller account of this method, including a series of guidelines for deriving restraints from *ab initio* data, has been given recently.¹

In the light of these improvements, we have decided to review our earlier study⁶ of the gas-phase structure of tetraborane(10), B₄H₁₀. The importance of the boron hydrides in chemistry is well established; studies of these compounds continue to contribute enormously to modern concepts of structure and bonding.⁷ Lipscomb's pioneering work in the 1950s led to the experimental determination of the structures of numerous boron hydrides in the solid phase, including B₄H₁₀ in 1953.⁸ With improved methods of data collection and refinement, it is now possible, in principle, to determine crystal structures with much greater precision than was possible in these early studies. Thus, in addition to the gas-phase study, we have redetermined the crystal structure of B₄H₁₀.

The results of the graded series of *ab initio* calculations carried out on tetraborane(10) are discussed first. The limited structural information available using only the GED data is then reported, and results of a refinement improved by the inclusion of nine rotation constants are presented. The final refinement of GED data, rotation constants and restraints derived from *ab initio* calculations, is then discussed. With all structural parameters refining with realistic estimated standard deviations, a new, more reliable gas-phase structure has been obtained. The new crystal structure is also reported, the differences between the gas- and solid-phase structures are discussed, and the experimental structures are compared with that computed *ab initio*.

Experimental

(a) *Ab initio* calculations

Theoretical methods. *Ab initio* molecular orbital calculations were performed on a Dec Alpha APX1000 workstation using GAUSSIAN 92.⁹ Optimised geometrical parameters and a theoretical harmonic vibrational force field were computed as detailed below with estimates of vibrational amplitudes being obtained using the program ASYM 40.¹⁰

Some geometry calculations for tetraborane(10) had been carried out previously,¹¹ at the SCF/3-21G*, SCF/6-31G*, MP2/6-31G* and MP2/6-31G** levels. The current work extended the range to include two larger basis sets and two higher levels of theory. These additional basis sets were 6-31 + G*^{12,13} (to gauge the effects of diffuse functions on the boron atoms) and a triple- ζ plus polarisation (TZP)¹⁵ basis set with the contraction scheme [62111/411/1] for boron and [311/1] for hydrogen. The latter consisted of Dunning's TZ basis augmented with one set of d-polarisation functions on B (exponent 0.386) and one set of p-polarisation functions on H (exponent 0.75). The two higher levels of theory employed were MP3 and CCSD(T), both used with the TZP basis set (Table 1).

The vibrational-frequency calculation was performed at the MP2/6-31G* level, verifying that tetraborane(10) has C_{2v} sym-

metry. Cartesian force constants obtained from this calculation were transformed to those described by a set of symmetry coordinates using ASYM40. Since the tentative vibrational assignments derived from the infrared and Raman spectra of B₄H₁₀¹⁶ were not found to be consistent with those from the theoretical study, it was not possible to scale the *ab initio* force constants using the experimental frequencies. Instead, as the best alternative, the force constants were scaled using scaling factors of the order of 0.9 for bond stretches, angle bends and torsions.[†] Scaling the force field was found to have only a small effect on the vibrational amplitude values; in general the scaled values increased in magnitude by the order of 10%, compared to the unscaled values.

(b) Gas-phase electron diffraction (GED)

GED data. The new GED refinements reported in this paper are derived from the original data set.⁶

GED model. Assuming C_{2v} symmetry, twelve independent parameters are required to define the structure completely (Table 2). They were chosen to be the average B–B bond distance (p_1), the difference between the two distinct B–B distances (p_2), the average B–H bond distance (p_3), the difference between the average bridge and terminal B–H distances (p_4), the difference between the outer and inner B–H bridge distances (p_5), the difference between the central and average wing B–H distances (p_6), the difference between the *endo* and *exo* wing B–H distances (p_7), the angle H(2)_{endo}–B(2)–H(2)_{exo} (p_8), the angle H(1)–B(1)–B(3) (p_9), the butterfly angle (p_{10}), describing the angle between the two planes BBB, the angle H_b dip (p_{11}), describing the elevation of the bridging-hydrogen atoms from the BBB plane, *i.e.* the angle between the planes B(1)B(2)B(3) and B(1)B(2)H(1,2), and finally a parameter describing the tilt of the BH₂ wing unit in the B(2)B(4)H(4)_{endo}H(4)_{exo} plane (p_{12}). This parameter was defined as the angle between the bisector of the H–B–H angle and the BBB plane, a positive angle representing an *endo* tilt.

(c) Crystallography

Crystal data. B₄H₁₀, $M = 53.22$, monoclinic, space group $P2_1/n$, $a = 5.7917(11)$, $b = 10.145(2)$, $c = 8.699(2)$ Å, $\beta = 106.03(2)^\circ$, $U = 491.3$ Å³ (from 75 reflections, $30 \leq 2\theta \leq 44^\circ$, measured at $\pm\omega$, $\lambda = 1.54184$ Å), $Z = 4$, $D_c = 0.721$ g cm⁻³, $F(000) = 120$, $T = 100$ K, colourless column $0.8 \times 0.15 \times 0.15$ mm, $\mu(\text{Cu-K}\alpha) = 0.140$ mm⁻¹.

Data collection and processing. Stöe Stadi-4 diffractometer equipped with an Oxford Cryosystems variable-temperature device;¹⁷ ω – 2θ mode on-line profile learning,¹⁸ graphite-monochromated Cu-K α radiation, 1268 reflections measured ($-6 \leq h \leq 6$, $-5 \leq k \leq 11$, $0 \leq l \leq 9$, $5 \leq 2\theta \leq 120^\circ$), 727 unique ($R_{\text{int}} = 0.0571$). No absorption correction was applied.

Structure analysis and refinement. For the boron-atom positions the structure was solved by direct methods.¹⁹ Hydrogen-atom positions were clearly visible in a ΔF synthesis, and the structure was refined²⁰ against F^2 with anisotropic displacement parameters for the B and H atoms being fully refined with isotropic displacement parameters. At convergence, $R1$ [based on F and 504 data with $F > 4\sigma(F)$] was 0.0666 and $wR2$ (based on F^2 and 721 data) was 0.2039 for 78 parameters. The final ΔF synthesis showed no feature outwith $+0.15$ to -0.15 e Å⁻³.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors,

[†] Varying scaling factors over the range 0.85–0.95 was found to have little effect on vibrational amplitudes and correctional values.

Table 1 *Ab initio* molecular geometries and energies for B₄H₁₀

Parameter*	Level of theory/basis set					
	SCF/6-31G*	MP2(FC)/6-31G*	MP2(FC)/6-31+G*	MP2(FC)/TZP	MP3(FC)/TZP	CCSD(T)(FULL)/TZP
Bond length/pm						
$r[B(1)-B(3)]$	174.1	171.8	171.9	173.1	173.7	173.4
$r[B(1)-B(2)]$	189.3	184.0	184.0	185.6	186.9	186.5
$r[B(1)-H(1,2)]$	124.7	125.3	125.3	125.6	125.6	125.5
$r[B(2)-H(1,2)]$	142.3	141.2	141.2	142.0	142.1	141.8
$r[B(1)-H(1)]$	118.1	118.6	118.6	118.2	118.3	118.3
$r[B(2)-H(2)_{endo}]$	118.8	119.7	119.8	119.5	119.4	119.5
$r[B(2)-H(2)_{exo}]$	118.4	119.2	119.3	119.0	119.0	119.0
Angle/°						
B(1)-B(2)-B(3)	54.8	55.7	55.7	55.6	55.4	55.4
B(2)-B(1)-B(3)	62.6	62.2	62.2	62.2	62.3	62.3
H(2) _{endo} -B(2)-H(2) _{exo}	120.2	118.7	118.6	119.6	119.7	119.6
H(1)-B(1)-B(3)	115.6	115.0	114.9	114.8	115.0	115.0
BH ₂ tilt	1.3	-2.2	-2.2	-1.7	-1.8	-1.6
Torsion/°						
Butterfly angle	116.9	117.4	117.4	116.6	116.3	116.0
H _b dip	7.6	8.8	8.7	8.4	7.8	7.4
<i>E</i> /Hartree	-104.457 02	-104.843 58	-104.847 77	-104.953 22	-105.008 27	-105.106 06

* For definitions of parameters, see the text.

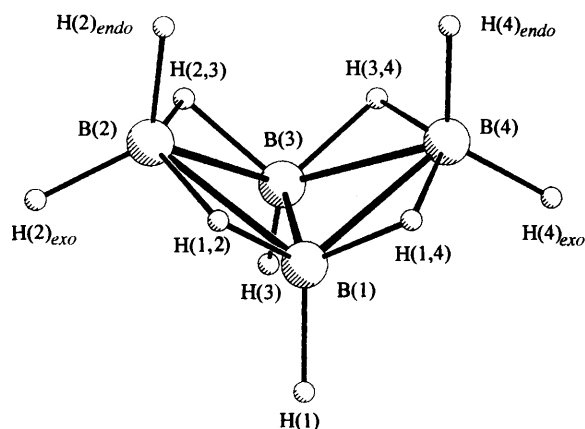


Fig. 1 Structure of B₄H₁₀ from the optimum refinement of the GED data

J. Chem. Soc., Dalton Trans., 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/272.

Results

(a) *Ab initio* calculations

The results of the geometry-optimisation calculations, which demonstrate the effects of improving the basis set and level of theory, are given in Table 1; atom numbering is as in Fig. 1.

$r(B-B)$. The B(1)-B(3) and B(1)-B(2) bond distances were found to be slightly sensitive to the quality of basis set used and to the level of theory. Improving the basis set from 6-31G* to TZP at the MP2 level led to increases in these bond lengths of about 2 pm. Diffuse functions (6-31+G* basis) were found to be less important, resulting in a 0.5 pm increase in both bond distances, relative to the MP2/6-31G* results. The level of theory was also found to be important; when electron-correlation effects were included (*i.e.* MP2 level and above) both distances shortened, the change being most noticeable from the SCF (self-consistent field) to the MP2 (second-order Moeller-

Plesset perturbation) level where the distances shortened by 2.7 and 5.8 pm for B(1)-B(3) and B(1)-B(2), respectively. Higher levels of theory caused the bond distances to lengthen slightly, with the final, highest-level calculation at CCSD(T)/TZP predicting distances of 173.4 pm for B(1)-B(3) and 186.5 pm for B(1)-B(2).

$r(B-H_b)$. In contrast to $r(B-B)$, the bridging B-H bond distances were found to be less sensitive to the details of the basis set and level of treatment. Improving the basis set from 6-31G* to TZP at the MP2 level resulted in the bridging distances B(1)-H(1,2) and B(2)-H(1,2) lengthening by 0.4 and 1 pm, respectively. Diffuse functions were again found to be less important, with both bond distances lengthening by no more than 0.2 pm relative to the MP2/6-31G* values. Improving the level of theory from SCF to MP2 using the 6-31G* basis set resulted in an increase of 0.5 pm for $r[B(1)-H(1,2)]$ and a decrease of 1.3 pm for $r[B(2)-H(1,2)]$. At higher levels, using the TZP basis set resulted in changes no greater than 0.1 pm for $r[B(1)-H(1,2)]$ and 0.2 pm for $r[B(2)-H(1,2)]$. The final calculation at CCSD(T)/TZP predicted bond distances of 125.5 pm and 141.8 pm for $r[B(1)-H(1,2)]$ and $r[B(2)-H(1,2)]$, respectively.

$r(B-H_t)$. The terminal B-H bond distances were found similarly to be largely insensitive to both the basis set used and the level of theory. At the MP2 level, improving the basis set from 6-31G* to TZP resulted in a shortening of 0.3 pm for the $r[B(1)-H(1)]$ distance and 0.1 pm for both B(2)-H(2) distances. Diffuse functions increased the distances by no more than 0.2 pm relative to the MP2/6-31G* results. Improving the level of theory from SCF to MP2 using the 6-31G* basis set resulted in increases of 0.4, 0.8 and 0.7 pm for the three distances. Further improvements in the level of theory using the TZP basis set gave rise to changes no greater than 0.1 pm for all three bond distances, with final values at CCSD(T)/TZP calculated to be 118.3 pm for $r[B(1)-H(1)]$, 119.5 pm for $r[B(2)-H(2)_{endo}]$ and 119.0 pm for $r[B(2)-H(2)_{exo}]$.

For the series of calculations detailed in Table 1 it is clear that the B-H distances have effectively converged whilst further changes in B-B distances should be no more than a few tenths of a picometre.

Table 2 Geometrical parameters for the GED structures (r_a^0) of B_4H_{10} (r /pm, angles in $^\circ$)

Parameter	Results ^a		
	GED data alone	GED + rotation constants	GED + rotation constants + restraints
Independent^b			
p_1 av. $r(B-B)$	184.2(2)	183.5(3)	184.0(2)
p_2 diff. $r(B-B)$	11.7(11)	13.3(7)	12.9(6)
p_3 av. $r(B-H)$	127.0(3)	128.0(4)	127.3(3)
p_4 av. $r(B-H)$ bridge – av. $r(B-H)$ terminal	10.5(19)	13.7(12)	12.0(17)
p_5 diff. $r(B-H)$ bridge	19.3(23)	18.5(14)	18.7(16)
p_6 cent. $r(B-H)$ – av. $r(B-H)$ wing	–1.0 (f)	–1.0 (f)	–1.0(3)
p_7 diff. $r(B-H)$ wing	0.5 (f)	0.5 (f)	0.5(1)
p_8 $H(2)_{exo}-B(2)-H(2)_{endo}$	119.6 (f)	119.6 (f)	119.6(13)
p_9 $H(1)-B(1)-B(3)$	115.0 (f)	114.5(17)	115.0(16)
p_{10} Butterfly angle	120.2(13)	117.0(5)	117.2(4)
p_{11} H_b dip	7.4 (f)	7.4 (f)	6.2(5)
p_{12} BH_2 tilt	0.8 (f)	–0.4(13)	1.2(12)
p_{13} diff. $r(^{10}B-^{11}B) - (^{11}B-^{11}B)$	—	0.02(3)	0.06(2)
Dependent			
$r[B(1)-B(3)]$	174.9(9)	172.8(7)	173.7(5)
$r[B(1)-B(2)]$	186.5(3)	186.1(2)	186.6(2)
$r[B(1)-H(1,2)]$	121.9(19)	124.6(12)	123.0(15)
$r[B(2)-H(1,2)]$	141.2(9)	143.1(8)	141.7(8)
$r[B(1)-H(1)]$	120.0(8)	119.5(7)	119.8(8)
$r[B(2)-H(2)_{endo}]$	121.6(11)	120.7(7)	121.0(8)
$r[B(2)-H(2)_{exo}]$	121.1(11)	120.2(7)	120.5(8)
$B(1)-B(2)-B(3)$	55.9(4)	55.3(2)	55.5(2)

^a Estimated standard deviations (e.s.d.s), obtained in the least-squares refinement, are given in parentheses. f = Fixed at the value obtained from the CCSD(T)/TZP *ab initio* calculation. ^b For definitions of parameters, see the text.

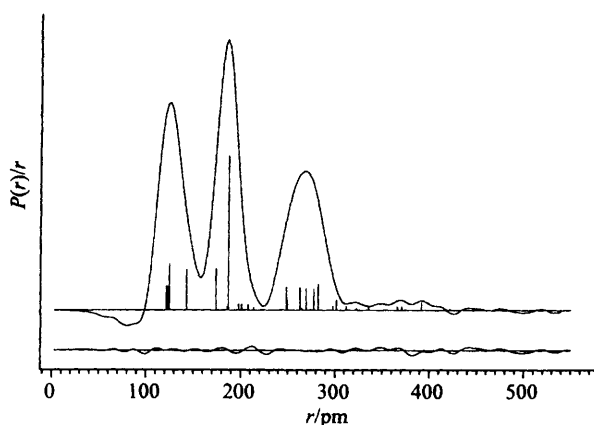


Fig. 2 Observed and final difference radial-distribution curves for B_4H_{10} . Before Fourier inversion the data were multiplied by $s.\exp(-0.000\ 02s^2)/(Z_B - f_B)^2$

(b) Gas-phase electron-diffraction

(i) **GED data alone.** The r_a^0 structural parameters determined from the GED data alone are given in Table 2. Only six of the twelve geometric parameters (*viz.* p_{1-5} and p_{10}) could be refined at this stage, together with the vibrational amplitudes $u_1[B(1)-B(3)]$, $u_2[B(1)-H(1,2)]$, $u_4[B(2)-H(1,2)]$, $u_7[B(1)\cdots B(2)]$, $u_{20}[B(1)\cdots H(4)_{exo}]$ and $u_{27}[B(2)\cdots B(4)]$. The R_G factor for this refinement was 0.076, indicating that the data are of good quality.

Parameters 1 and 2, the mean and difference B–B distances, both refined well, giving well determined individual distances: $r[B(1)-B(2)] = 186.5(3)$ pm and $r[B(1)-B(3)] = 174.9(9)$ pm. The smaller standard deviation for the former distance reflects its multiplicity of four, as compared to one for $r[B(1)-B(3)]$. The

non-bonded $B(2)\cdots B(4)$ distance then defines the butterfly dihedral angle, which refined to $120.2(13)^\circ$.

The average B–H distance also refined well to $127.0(3)$ pm, but since all of the B–H bonded distances fall under the first peak in the radial-distribution curve (Fig. 2), the five independent parameters defining them would be expected to be strongly correlated with one another on simultaneous refinement. Of the parameters p_{4-7} , which describe differences between various B–H distances, only two could be refined. These were p_5 , describing the difference between the two bridging B–H distances, which refined to $19.3(23)$ pm (indicating a very asymmetric bridge), and p_4 , defining the difference between the average bridge and terminal B–H distances, which refined to $10.5(19)$ pm. Parameters 6 and 7, and the angles describing the H atom positions, $p_{8,9,11,12}$, could not be refined freely and were fixed at their *ab initio*, CCSD(T)/TZP level, values.

Using the GED data alone, only the geometrical parameters defining the heavy-atom cage structure, together with the average B–H bond distance, could be refined to a high degree of accuracy. It will be shown in the next two sections that the addition of non-GED data improves the definition of the structure considerably.

(ii) **Combined analysis of GED data and rotation constants.** Nine rotation constants, measured by Simmons *et al.*,²¹ were introduced into the refinement. These comprised three sets; the first corresponded to a boron cage composed of ^{11}B only, the second to molecules containing one ^{10}B atom at a hinge position, and the third to molecules with one ^{10}B atom at a wing position. The original refinement² included the first set of rotation constants only, but since no force field for B_4H_{10} was available at that time the vibrational corrections, needed to convert these data from B_0 into B_z values (which are appropriate to the r_a^0 structure type given in the GED refinement) could not be obtained. With the scaled force field now available the required vibrational corrections have been obtained. The B_z

Table 3 Rotation constants (B /MHz) for B_4H_{10} as used in the GED study

Species	Axis	Observed ^a		Calculated ^b B_z	Difference B_z (Obs. – Calc.)	Uncertainty
		B_0	B_z			
¹¹ B(1–4)	<i>a</i>	11 013.388(19)	11 008.505	11 008.154	0.351	0.52
	<i>b</i>	6 198.643(23)	6 197.392	6 197.443	–0.051	0.20
	<i>c</i>	5 592.817(21)	5 586.325	5 586.214	0.109	0.68
¹⁰ B(1) ¹¹ B(2–4)	<i>a</i>	11 248.386(15)	11 243.492	11 243.842	–0.350	0.51
	<i>b</i>	6 215.416(20)	6 214.195	6 214.342	–0.147	0.23
	<i>c</i>	5 638.440(20)	5 631.908	5 632.323	–0.415	0.68
¹⁰ B(2) ¹¹ B(1,3,4)	<i>a</i>	11 055.969(17)	11 051.075	11 051.062	0.013	0.52
	<i>b</i>	6 368.152(20)	6 366.946	6 366.890	0.056	0.23
	<i>c</i>	5 718.786(18)	5 712.254	5 711.987	0.276	0.68

^a Taken from ref. 21. ^b For the final GED refinement.

Table 4 Derivation of geometrical parameter restraints for the GED study (r /pm, angles in °)

Parameter*	SCF/6-31G*	MP2/6-31G*	MP2/6-31+G*	MP2/TZP	MP3/TZP	CCSD(T)/TZP	Value used
p_6 cent. r (B–H) – av. r (B–H) wing	–0.5	–0.8	–0.9	–1.1	–0.9	–1.0	–1.0(2)
p_7 diff. r (B–H) wing	0.4	0.5	0.5	0.5	0.4	0.5	0.5(1)
p_8 $H(2)_{endo}$ –B(2)–(2) _{exo}	120.2	118.7	118.6	119.6	119.7	119.6	119.6(10)
p_{11} H_b dip	7.6	8.8	8.7	8.4	7.8	7.4	7.4(15)

* For definitions of parameters, see the text.

rotation constants, along with the original B_0 data and the calculated values for the final new structure (given in the next section), are reported in Table 3. The uncertainty for each constant quoted in this table was derived from the sum of the standard deviation of the experimental B_0 value and an assumed 10% uncertainty in the vibrational correction. It can be seen that for each rotation constant the calculated value lies well within the uncertainty limit, verifying that the structural information contained within the rotation constants was in good agreement with the GED results obtained. The R_G factor recorded for this combined analysis refinement rose slightly to 0.083.

With the introduction of the rotation constants for the isotopically substituted molecules, an additional parameter had to be included in the model to account for the minute increase in the B–B bond distance that occurs when one ¹¹B atom is substituted by ¹⁰B. Parameter 13 was defined as the difference $r(^{10}\text{B}–^{11}\text{B}) – r(^{11}\text{B}–^{11}\text{B})$. This was assumed to be constant for all substituted B–B bonds, and was allowed to refine. A value of 0.02(3) pm was returned.

The geometrical parameters obtained from this new refinement are given in Table 2. Small changes in the boron cage were observed, such that the average B–B distance (p_1) shortened by 0.7 pm to 183.5(3) pm and the difference between the two different B–B distances (p_2) increased by 1.6 pm to 13.3(7) pm. The butterfly angle (p_{10}) also changed, decreasing by 3.2° to 117.0(5)°. For p_2 and p_{10} the estimated standard deviations were significantly lower than for the refinement using GED data alone. The dependent B–B distances were shortened, from 174.9(9) to 172.8(7) pm for B(1)–B(3) and 186.5(3) to 186.1(2) pm for B(1)–B(2).

For the H-atom positions, two additional geometrical parameters, p_9 and p_{12} , describing angles could be refined. The angle H(1)B(1)B(3), previously held fixed at 115.0°, refined to 114.5(17)°. Parameter 12, describing the tilt of the BH₂ wing unit in the symmetry plane, refined to –0.4(13)°, the tiny negative value indicating that the tilt is *exo* in character. With a standard deviation of over 1°, the refined value is not significantly different from the theoretical value of –1.6°.

The main effect observed on introducing the rotation constants was that two additional parameters could be refined. Subsequently, the structure is better defined, although four

geometrical parameters remain fixed. It will be demonstrated in the next section, however, that the introduction of *ab initio*-based restraints allows all parameters and significant amplitudes of vibration to be refined, yielding sensible values with realistic estimated standard deviations.

(iii) **Combined analysis of GED and rotation constant data with *ab initio* restraints: the SARACEN method.** The introduction of ten restraints, four for geometrical parameters (Table 4) and six for vibrational amplitudes (Table 5), allowed all geometric parameters and all significant amplitudes of vibration to refine. In the case of the four geometric parameters, values for restraints were taken from the highest-level calculation, *i.e.* CCSD(T)/TZP, and uncertainties chosen that reflect, to some extent, our experience of the reliability of such calculations for small boranes. In the refinement based on GED data alone discussed above only seven amplitudes of vibration could be refined freely. However, with the inclusion of six restraints applied to the various ratios of amplitudes, the thirteen most significant amplitudes of vibration, associated with the bond distances giving rise to peaks greater than 10% of the most intense component peak in the radial-distribution curve, could be refined freely. The values obtained for all refining amplitudes were in good agreement with those obtained from the scaled theoretical force field.

The results obtained from the final refinement are given in Table 2. In general the structural parameters varied little when the restraints were introduced, with all dependent bond distances and angles agreeing with those obtained in the previous refinement within one or two standard deviations. A final R_G value of 0.078 was recorded.

Of particular interest are the four additional geometrical parameters, $p_{6-8,11}$, now refining. Parameter 6 refined to a value of –1.0(3) pm, compared to its restraint of –1.0(2) pm, and p_7 refined to 0.5(1) pm, in exact agreement with its restraint. The two angles requiring restraints, p_8 and p_{11} , refined to 119.6(13) and 6.2(5)° respectively, compared to their restraints of 119.6(10) and 7.4(15)°. These results demonstrate an important principle behind the SARACEN method; if a parameter refines to give a value and standard deviation in exact agreement with its restraint, then clearly no information regarding this parameter is contained within the GED data, as observed for p_7 . If,

however, some information is contained in the GED data contrary to the *ab initio* restraint then, since the restraint is flexible, a value and standard deviation different from the restraint would be expected to be returned in the refinement. In other words, the GED result for this parameter agrees with the *ab initio* result to a certain extent, but was not forced to accept the *ab initio* prediction as law. This was noted in the case of p_{11} . Alternatively, if the information contained within the GED is in exact agreement with the restraint, the same value and a lower standard deviation would be expected (since the same information is effectively recorded twice and the overall standard deviation will be the square root of the sum of the squares of the two uncertainties).

A complete list of interatomic distances (r_a) and amplitudes of vibration (u) determined in this final refinement are given in

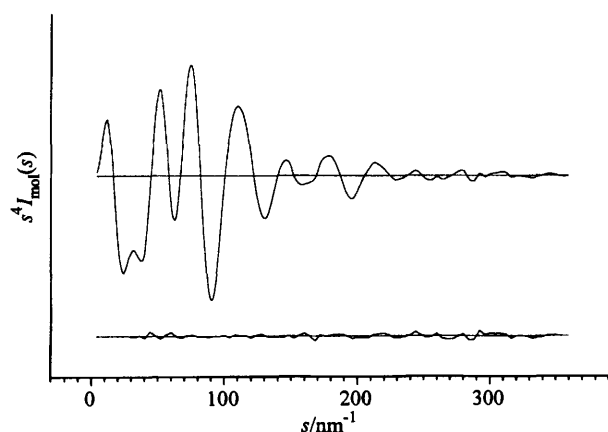


Fig. 3 Observed and final difference combined molecular scattering curves for B_4H_{10} . Theoretical data were used in the range 0–20 nm^{-1} for which no experimental data are available

Table 5 Derivation of vibrational amplitude restraints for the GED study

Amplitude ratio	Value ^a	Uncertainty ^b
$u_2[B(1)-H(1)]/u_3[B(1)-H(1,2)]$	0.906	0.045
$u_5[B(2)-H(2)_{endo}]/u_3$	0.921	0.046
$u_6[B(2)-H(2)_{exo}]/u_3$	0.912	0.046
$u_{17}[B(4)\cdots H(1)]/u_{20}[B(1)\cdots H(4)_{exo}]$	0.946	0.047
$u_{18}[B(4)\cdots H(1,2)]/u_{20}$	1.012	0.051
$u_{19}[B(1)\cdots H(4)_{endo}]/u_{20}$	0.982	0.049

^a Taken from the scaled MP2/6-31G* force field. ^b 5% of the amplitude ratio.

Table 6 Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) for the GED structure of B_4H_{10} ^a

<i>i</i>	Atom pair	Distance	Amplitude ^b	<i>i</i>	Atom pair	Distance	Amplitude ^b
1	B(1)–B(3)	173.6(5)	6.8(8)	17	B(4) \cdots H(1)	277.2(8)	11.2(9)
2	B(1)–H(1)	121.1(9)	8.5(5)	18	B(4) \cdots H(1,2)	268.5(9)	12.0(9)
3	B(1)–H(1,2)	124.0(15)	9.4(4)	19	B(1) \cdots H(4) _{endo}	262.9(9)	11.7(9)
4	B(2)–H(1,2)	142.6(8)	9.7(8)	20	B(1) \cdots H(4) _{exo}	262.5(9)	11.9(8)
5	B(2)–H(2) _{endo}	122.5(9)	8.6(5)	21	H(3) \cdots H(1,4)	335.3(12)	15.1 (f)
6	B(2)–H(2) _{exo}	122.0(9)	8.6(5)	22	H(2,3) \cdots H(1,4)	321.8(20)	15.4 (f)
7	B(1) \cdots B(2)	186.5(2)	7.7(3)	23	H(4) _{endo} \cdots H(1)	370.6(12)	14.0 (f)
8	B(1) \cdots H(3)	249.3(18)	13.1 tied to u_{13}	24	H(4) _{endo} \cdots H(1,2)	297.0(9)	22.9 (f)
9	H(1) \cdots H(1,2)	200.3(14)	14.1 (f)	25	H(4) _{exo} \cdots H(1)	312.0(12)	21.6 (f)
10	H(1,2) \cdots H(2) _{endo}	197.5(12)	15.8 (f)	26	H(4) _{exo} \cdots H(1,2)	365.5(6)	14.6 (f)
11	H(1,2) \cdots H(2) _{exo}	207.7(8)	15.8 (f)	27	B(2) \cdots B(4)	281.7(5)	9.4(10)
12	H(1,2) \cdots H(2,3)	263.8(19)	16.7 (f)	28	B(2) \cdots H(4) _{endo}	301.2(12)	20.6 (f)
13	B(1) \cdots H(2,3)	247.6(13)	9.6(8)	29	B(2) \cdots H(4) _{exo}	391.4(6)	11.6 (f)
14	H(1,2) \cdots H(1,4)	184.9(15)	15.6 (f)	30	H(2) _{endo} \cdots H(4) _{endo}	269(3)	31.3 (f)
15	H(2) _{endo} \cdots H(2) _{exo}	213(3)	13.2(f)	31	H(2) _{exo} \cdots H(4) _{exo}	491.8(17)	15.1 (f)
16	H(1) \cdots H(3)	275(5)	20.4 (f)	32	H(4) _{endo} \cdots H(2) _{exo}	421.8(14)	21.4 (f)

^a Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses. ^b f = Fixed at the value derived from the scaled MP2/6-31G* force field.

Table 6. The final least-squares correlation matrix is presented in Table 7 and the combined molecular scattering intensities and final differences are shown in Fig. 3.

(c) Crystal structure

Molecules of B_4H_{10} occupy general positions in the crystal structure, but are not distorted significantly from C_{2v} symmetry (Table 8). There appear to be no particularly significant intermolecular interactions in the solid state; the crystal-packing arrangement is shown in Fig. 4.

Direct comparison with Lipscomb's results is not valid since displacement parameters were refined isotropically in the earlier work.⁴ Subsequently, we have also refined the structure using the original intensity data, but using exactly the same scheme as reported above, *i.e.* with anisotropic displacement parameters for the boron atoms. Details are given as part of the Supplementary Material. A comparison of the resulting parameters reveals that although our current e.s.d.s are slightly smaller, the absolute values do not differ significantly from those refined from data recorded more than 43 years ago. Such a comparison bears witness once again to the quality of the work undertaken by Lipscomb.

Discussion

The final results for the molecular structure of B_4H_{10} determined by gas-phase electron diffraction (supplemented with rotation constants and *ab initio*-based restraints), and X-ray crystallography, and predicted by *ab initio* calculations, are summarised in Table 9, where values of parameters related by C_{2v} symmetry have been averaged.

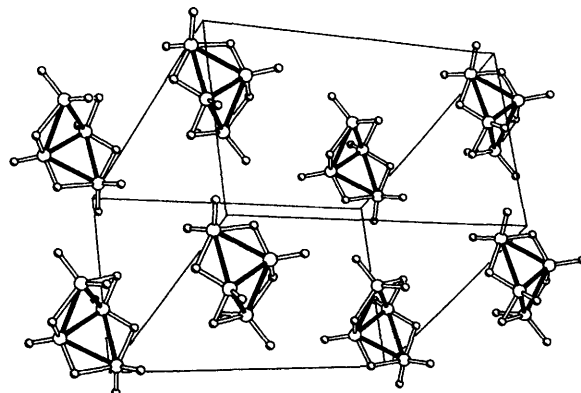


Fig. 4 Crystal packing of B_4H_{10}

Table 7 Least-squares correlation matrix ($\times 100$) for the GED study of $B_4H_{10}^*$

	Geometrical parameter						Vibrational amplitude					Scale factor			
	p_4	p_5	p_9	p_{10}	p_{11}	p_{12}	p_{13}	u_1	u_7	u_{13}	u_{19}	u_{20}	k_1	k_2	k_3
p_1						63	70								
p_2		-63	81	-88				-51	-63						
p_3			-72							60	51	58	53		
p_4					78						51	55			
p_5	-76			73	-58			55	57						
p_8						-55									
p_9				-82					-52	-56					
p_{10}						65	52		58						
p_{11}											55				
p_{12}							62								
u_1								81					61	57	52
u_7													76	71	66
u_{17}												66			
u_{18}												59			
u_{19}												61			
u_{20}													52		
k_1														78	71
k_2															65

* Only off-diagonal elements with absolute values $> 50\%$ are shown.**Table 8** Structural parameters from the crystal structure of B_4H_{10}

Bond length/pm	
$r[B(1)-B(2)]$, $r[B(2)-B(3)]$, $r[B(3)-B(4)]$, $r[B(1)-B(4)]$	185.2(4), 185.1(4), 185.3(4), 185.0(4)
$r[B(1)-B(3)]$	171.7(4)
$r[B(1)-H(1,2)]$, $r[B(1)-H(1,4)]$, $r[B(3)-H(2,3)]$, $r[B(3)-H(3,4)]$	117(3), 119(2), 121(3), 110(3)
$r[B(2)-H(1,2)]$, $r[B(4)-H(1,4)]$, $r[B(2)-H(2,3)]$, $r[B(4)-H(3,4)]$	142(2), 138(3), 143(3), 135(3)
$r[B(1)-H(1)]$, $r[B(3)-H(3)]$	105(3), 107(3)
$r[B(2)-H(2)_{endo}]$, $r[B(4)-H(4)_{endo}]$	112(3), 111(3)
$r[B(2)-H(2)_{exo}]$, $r[B(4)-H(4)_{exo}]$	112(3), 110(3)
Angle/ $^\circ$	
Butterfly ^a	118.2(2)
$H_b(1,2)$ dip, $H_b(2,3)$ dip, $H_b(1,4)$ dip, $H_b(3,4)$ dip ^b	10.2(19), 6.2(25), 7.0(5), 9.9(10)
$B(3)-B(1)-H(1)$, $B(1)-B(3)-H(3)$	116(2), 117(2)
$H(2)_{endo}-B(2)-H(2)_{exo}$, $H(4)_{endo}-B(4)-H(4)_{exo}$	121(2), 117(2)

^a Angle between planes $B(1)B(2)B(3)$ and $B(1)B(4)B(3)$. ^b Angle between planes $B(1)H(1,2)B(4)$ and $B(1)B(4)B(3)$, etc.**Table 9** Comparison of the geometrical parameters for B_4H_{10} from diffraction and theoretical methods

Geometrical parameter ^a	Method		
	GED + rotation constants + restraints (r_σ^b)	CCSD(T)/TZP (r_e)	Crystal structure (average values) ^b
Bond length/pm			
$r[B(1)-B(2)]$	186.6(2)	186.5	185.2(1)
$r[B(1)-B(3)]$	173.7(5)	173.4	171.7(4)
$r[B(1)-H(1,2)]$	123.0(15)	125.5	116(5)
$r[B(2)-H(1,2)]$	141.7(8)	141.8	140(4)
$r[B(1)-H(1)]$	119.8(8)	118.3	106(1)
$r[B(2)-H(2)_{endo}]$	121.0(8)	119.5	111(1)
$r[B(2)-H(2)_{exo}]$	120.5(8)	119.0	111(1)
Angles/ $^\circ$			
Butterfly	117.2(4)	116.0	118.2(2)
H_b dip	6.2(5)	7.4	8(2)
H-B-H	119.6(13)	119.6	119(3)
H-B-B	115.0(16)	115.0	116(1)
BH_2 tilt	1.2(12)	-1.6	—

^a For definitions of parameters, see the text. ^b Figures in parentheses represent uncertainties on average structure, quoted to 1σ .

Gas-phase electron-diffraction and *ab initio* computations both give discrete molecular structures. In other words, the results should be directly comparable. Some differences are to be expected, however, since the two techniques are based on different structural definitions. *Ab initio* calculates a static equilibrium structure, which is completely free from the vibrational averaging effects experienced in the dynamic GED experiment.

Since there is no large vibrational motion associated with the B_4H_{10} molecule (as judged from the vibrational spectra¹⁶), such differences are small and the *ab initio* and GED parameters were found to be in excellent agreement (Table 9). All values of the GED parameters lie within one standard deviation of the *ab initio* value, with the exceptions of the butterfly angle, the H dip angle, the BH_2 tilt angle and the bridging distance $r[B(2)-$

H(1,2)], which agree with the *ab initio* values within three standard deviations.

The absolute values recorded for parameters in the gas and solid phases differed; this would be expected since the two techniques measure different types of distances; X-ray diffraction locates the centres of highest electron density whereas electron diffraction measures internuclear distances. This distinction is most clearly evident in distances involving H. In general, however, the same structural trends were observed in the two phases. The average B(1)–B(2) distance, for example, was found to be *ca.* 13 pm longer than the B(1)–B(3) distance in both phases. The asymmetry of the B–H bridge was conserved, with the average inner bridge distance 24(5) pm shorter than the average outer distance in the crystal structure, a slightly but not significantly larger value than that of 18.7(16) pm measured in the GED experiment. A similar value was found for the H dip angle in both phases: 6.2(5)°, GED; vs. 8(2)°, X-ray.

The final results for tetraborane(10) thus show how state-of-the-art techniques for gas-phase structure determination, for the low-temperature X-ray crystallography and for *ab initio* calculations yield data which are fully consistent with one another.

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