The Molecular Structure of Tetraborane(10) in the Gas Phase as determined by a Joint Analysis of Electron-diffraction and Microwave Data

By **C. John Dain** and **Anthony J. Downs,*** Department of Inorganic Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR
Graham S. Laurenson and **David W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The structure of the gaseous tetraborane(10) molecule, B_4H_{10}, has been redetermined by electron diffraction. The new analysis confirms not only that the structure comprises a folded diamond of boron atoms bridged by four hydrogen atoms, but also (*i*) that the B–H–B bridges are unsymmetrical, the H_2B-H_b distance being 17 pm longer than the $HB-H_b$ distance, and (*ii*) that the bridging hydrogen atoms are situated 5.6 pm above the plane defined by the three boron atoms of each $H_2B(HB)_2$ moiety to fall within the fold of the tetraboron framework. Other salient parameters are (distances correspond to r_a; figures in parentheses are the estimated standard deviations of the last digits): r[B(1)–B(2)] 185.6(0.4), r[B(1)–B(3)] 170.5(1.2), r[B(1)–H$_t$] 122.1(1.4), r[B(2)–H$_t$] 119.4(0.7), r[B(1)–H$_b$] 131.5(0.9), r[B(2)–H$_b$] 148.4(0.9) pm; H$_t$–B(2)–H$_t'$ 122.7(3.5), H$_t''$–B(1)–B(3) 111.2(3.5), and the dihedral angle between the two planes B(1)B(2)B(3) and B(1)B(3)B(4) 117.1(0.7)° (t = terminal, b = bridging).

SINCE its discovery in 1912 by Stock and Massenez,[1] tetraborane(10) has attracted much attention; indeed its isolation and characterization marked the beginning of systematic studies of the boron hydrides. To date, however, there has been no accurate determination of the structure of the gaseous molecule. The results of X-ray diffraction studies on single crystals at low temperature [2] and of electron-diffraction studies on the vapour,[3] published simultaneously, have shown that the skeleton of the B_4H_{10} molecule consists of a folded diamond of boron atoms linked by four hydrogen bridges. The structure of the molecule in the crystalline state has been further refined [4,5] but, in common with other structure determinations using X-ray methods, the analysis gives unrealistic results, particularly for the distances between the boron and terminal hydrogen atoms.[6] The electron-diffraction investigation [3] failed to locate accurately the positions of the bridging hydrogen atoms which are a primary feature of the structure. Many theoretical calculations involving the B_4H_{10} molecule have been ventured; these have been based mainly on the molecular dimensions deduced from the crystal structure, with appropriate corrections to the positions of the hydrogen atoms.[7]

We have reinvestigated the structure of the gaseous tetraborane(10) molecule by electron diffraction. In this we have had two principal aims: (*i*) the accurate definition of the positions of as many atoms as possible, (*ii*) the exploration of the relationship between the structure of the B_4H_{10} molecule and molecules like $MMe_2(B_3H_8)$ (M = Al or Ga) [8] formally derived from tetraborane(10). During our investigations, we were acquainted with the results of a microwave study of the gaseous B_4H_{10} molecule; [9] in this study the r_s structure of the boron skeleton had been determined with fair precision, but the hydrogen atoms had not been located. We found that the results agreed well with the parameters deduced from our early calculations based on the electron-scattering pattern of the B_4H_{10} molecule; we have made use of the rotational constants calculated from the microwave spectrum as additional data for our final refinement calculations.

EXPERIMENTAL

The synthesis and manipulation of tetraborane(10) were achieved using a conventional high-vacuum line having stopcocks and ground-glass joints lubricated with Apiezon L grease. The reaction between polyphosphoric acid (B.D.H.) and tetramethylammonium octahydridotriborate (Strem Chemicals Inc.) gave a yield of *ca.* 40% of tetraborane(10) [10] which could be separated from the other higher boranes produced by fractional distillation *in vacuo*. The purity of the resulting tetraborane(10) was checked by measuring the vapour pressure of the liquid at 0 °C [11] and the i.r. spectrum of the vapour.[12]

Electron-scattering patterns were recorded photographically on Kodak Electron Image plates using the Edinburgh/Cornell gas diffraction apparatus.[13,14] The sample was held at 209 K (corresponding to an equilibrium vapour pressure of *ca.* 10 mmHg †) in an ampoule closed by a greased stopcock and gained access to the nozzle of the diffraction apparatus *via* a greased glass taper joint and a stainless steel needle valve. Six plates were exposed at a nozzle-to-plate distance of 128 mm and three at a nozzle-to-plate distance of 285 mm. With an electron wavelength of *ca.* 5.12 pm determined from the scattering pattern given by benzene vapour, these distances gave a range of 28—356 nm^{-1} in the scattering variable s. The intensity measurements were recorded digitally using a modified Jarrell–Ash microdensitometer: [15] this gave for its output *ca.* 800 data points spaced at equal intervals across the diameter of a plate which was rotated continuously about its centre.

Calculations were performed on an ICL 2970 computer at the Edinburgh Regional Computing Centre with the aid of the programs for data reduction [14] and least-squares refinement [16] previously described. The complex scattering factors listed by Schäfer *et al.*[17] were used throughout. The weighting functions applied to setting up the off-diagonal weight matrix are given in Table 1 together with the appropriate scale factors, correlation parameters, and electron wavelengths. Each of the data sets (two corre-

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

sponding to three plates each of the six exposed at a nozzle-to-plate distance of 128 mm and one corresponding to three plates exposed at a distance of 285 mm) was assigned an appropriate scale factor which was itself separately refined.

been refined on this basis by full-matrix least-squares analysis. We have not been in a position to apply shrinkage corrections in any of our refinements although the analysis points to some relatively large amplitudes of vibration.

TABLE 1

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

Nozzle-to-plate distance/ mm	Δs/ nm^{-1}	$s_{\min.}$/ nm^{-1}	sw_1/ nm^{-1}	sw_2/ nm^{-1}	$s_{\max.}$/ nm^{-1}	Correlation, p/h	Scale factor, k *	Electron wavelength/ pm
128.5	4	60	80	300	356	0.1361	1.003(30)	5.120
128.4	4	60	80	300	356	0.3644	0.945(30)	5.134
284.6	2	28	44	134	164	0.4871	0.913(27)	5.120

* Figures in parentheses are the estimated standard deviations of the last digits.

STRUCTURE ANALYSIS

Previous studies based on the crystal structure at low temperature and on the electron-diffraction pattern of the vapour imply that the tetraborane(10) molecule conforms to C_{2v} symmetry. On this basis an attempt has been made to interpret the vibrational spectra of the species $^{10}B_4H_{10}$, $^{11}B_4H_{10}$, $^{10}B_4D_{10}$, and $^{11}B_4D_{10}$.[12] In our analysis we have adopted a structural model consistent with this symmetry and admitted a total of ten independent geometrical parameters. With reference to the numbering scheme of Figure 1, these parameters are the two distances B(1)–B(2) and B(1)–B(3), an average B–H distance, the difference Δ_1 between the average B–H_b and B–H_t distances, the difference Δ_2 between the middle B(1)–H_t'' and the apical B(2)–H_t distances, the difference Δ_3 between the inner B(1)–H_b and the outer B(2)–H_b distances, the two angles H_t–B(2)–H_t' and H_t''–B(1)–B(3), the dihedral angle α between the two planes B(1)B(2)B(3) and B(1)B(3)B(4), and an angle β describing the orientation of the plane B(1)H_bB(2) with respect to the plane B(1)B(2)B(3) (t = terminal, b = bridging). The inclusion of this last parameter has enabled us to explore the departure from planarity of the five-membered ring B(1)H_bB(2)H_b'B(3) discernible in the crystal structures of tetraborane(10)[4] and the related compound beryllium bis(octahydridotriborate), Be$(B_3H_8)_2$.[18] It was not practicable to use a model where the mutual orientation of the planes B(1)B(3)H_bH_b' and B(2)H_bH_b' is defined by an independent parameter but this angle γ has been calculated as a dependent parameter in our refinements.

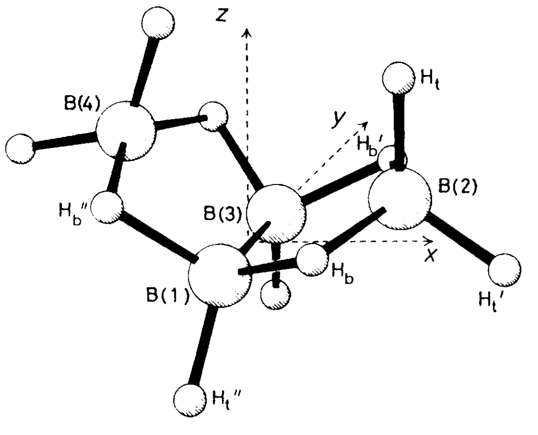

FIGURE 1 Perspective view of the tetraborane(10) molecule

Molecular-scattering intensities have been calculated by established procedures[19] and the molecular structure has

Unfortunately the vibrational spectra ascribed to the different isotopic versions of the tetraborane(10) molecule[12] do not lend themselves to detailed vibrational analysis: thus product-rule calculations reveal inconsistencies in the assignments which militate against any calculations designed to elicit even a crude force field. In the absence of more definitive information about the vibrational properties of the molecule, there is little prospect of gaining a clearer picture of the amplitudes of vibration. We infer, however, that any effects of shrinkage will be within the limits of error defined by the estimated standard deviations. Such deviations as quoted take into account the effects of correlation between molecular parameters and have been augmented to allow for systematic errors in the electron wavelength, nozzle-to-plate distance, *etc.*

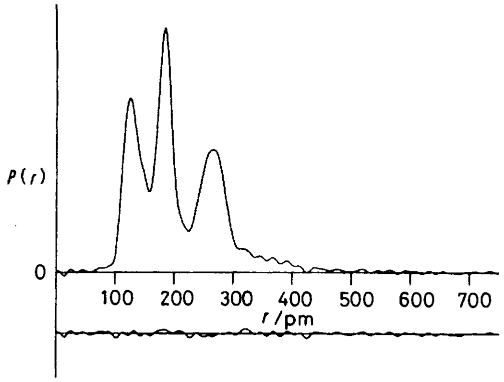

FIGURE 2 Observed and difference radial-distribution curves, $P(r)$ *versus* r, for tetraborane(10). Before Fourier inversion the data were multiplied by $s\,.\,\exp[(-0.000\,015\,s^2)/(z_B-f_B)(z_H-f_H)]$

Combination of the scaled experimental data sets yields, after Fourier inversion, the radial-distribution curve $P(r)/r$ shown in Figure 2. The three prominent peaks correspond to scattering from various groups of atom pairs: that at *ca.* 120 pm originates in all the B–H_b and B–H_t distances, that at *ca.* 180 pm in the B(1)–B(2) and B(1)–B(3) distances, and that at *ca.* 270 pm in the B(2) $\cdots$ B(4) and six non-bonded B $\cdots$ H distances. The weak features at distances in excess of 300 pm result from long B $\cdots$ H and H $\cdots$ H distances.

In the analysis of the electron-diffraction data, strong correlations were found, particularly between parameters defining the various B–H (bonded) distances and between B–B–H angles, and it became clear that the limited information available from the data was insufficient to define the structure fully. Analysis of the microwave spectrum of tetraborane(10) by Simmons *et al.*[9] gives an r_s structure for the B_4 skeleton of the molecule in close agreement with our r_a structure. However, these authors have made no attempt to fit the overall rotational constants and it seemed profitable therefore for us to use the rotational constants for $^{11}B_4{}^1H_{10}$ as additional data in our refinements.

Each extra observation was given a weight inversely proportional to the square of the estimated uncertainty of the observation and scaled to the standard deviation of the electron-diffraction observations. As no force field was available, it was not possible to correct observed rotational constants B_0 to B_z, nor could $r_\alpha{}^0$ parameters be derived from the diffraction data. However, the combined analysis was not being used to give extreme precision in the refined parameters but to resolve parameters that would otherwise be unacceptably strongly correlated, and so no vibrational corrections were applied. The close agreement of the microwave r_s and electron-diffraction r_a structures for the B_4 skeleton suggests that no major errors are introduced by this technique. The procedure provided a dramatic resolution of some of the problems posed by correlation of molecular parameters.

In our least-squares analysis of the electron scattering with the additional constraints imposed by the rotational constants, we have been able to refine simultaneously all ten of the geometrical parameters used to specify the tetraborane(10) molecule, as well as six amplitudes of vibration. The vibrational parameters relate to the atom pairs B(1)–B(2), B(1)–B(3), B(2) · · · B(4) and three groups of distances each refined as a single parameter comprising (*i*) the bonds involving the bridging hydrogen atoms B(1)–H_b and B(2)–H_b, (*ii*) the bonds to the terminal hydrogen atoms B(1)–H_t and B(2)–H_t, and (*iii*) six non-bonded B · · · H atom pairs with separations in the neighbourhood of 260 pm. The convergence of the structural refinement was relatively well defined and inspection of the final least-squares correlation matrix (given in Table 2) shows strong correlation between the angles α (the dihedral angle), β [defining displacement of the bridging hydrogen atoms with respect to the plane B(1)B(2)B(3)], H_t–B(2)–H_t', and H_t–B(1)–B(3), and the distances B(1)–B(2), B(1)–B(3), and B–H (average).

The closeness of the fit may be gauged by the difference (*i*) between the experimental radial-distribution curve and that derived from the optimum refinement (Figure 2) and (*ii*) between the experimental and calculated intensities of molecular scattering (the results appropriate to both nozzle-to-plate distances being combined to yield a single intensity curve in Figure 3). Table 3 lists the values of the geometric and vibrational parameters associated with the optimum refinement (for which $R_G = 0.098$ and $R_D = 0.079$), together with the estimated standard deviations. It includes (*i*) the magnitudes of the rotational constants calculated on the basis of the $^{11}B_4H_{10}$ molecule (to be compared with the corresponding parameters deduced from the microwave spectrum) and (*ii*) co-ordinates of the non-equivalent components B(1), B(2) and the four different species of hydrogen atom which make up the B_4H_{10} molecule.

TABLE 2

Least-squares correlation matrix (× 100) * for the molecule tetraborane(10)

Distances						Angles				Vibrational amplitudes						Scale factors			
P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	u_1	u_2	u_3	u_5	u_7	u_9	k_1	k_2	k_3	
100	**72**	**77**	−24	47	−48	**95**	**92**	**−96**	**75**	13	24	**70**	8	**−71**	**−79**	−2	−2	8	P_1
	100	57	7	18	−47	68	**83**	**−73**	59	−37	−11	48	5	−52	−68	−3	−3	7	P_2
		100	−20	**74**	−33	**92**	**88**	**−88**	**74**	9	30	60	−14	−54	**−78**	28	26	23	P_3
			100	−54	35	−26	−4	10	−8	−30	5	−33	−25	38	24	48	45	38	P_4
				100	−22	63	46	−54	46	9	14	21	−33	−51	−60	0	0	−3	P_5
					100	−49	−46	46	−32	3	0	−22	−48	50	34	12	12	5	P_6
						100	**95**	**−98**	**78**	14	29	**70**	2	−68	**−83**	11	10	15	P_7
							100	**−97**	**78**	−1	22	68	1	−62	**−81**	17	15	21	P_8
								100	**−79**	−8	−30	−64	1	66	**81**	−15	−14	−20	P_9
									100	−6	5	51	−13	−63	−63	0	−1	0	P_{10}
										100	**72**	40	34	11	13	28	27	28	u_1
											100	31	24	15	5	**70**	68	62	u_2
												100	37	−38	−51	6	6	13	u_3
													100	4	21	7	7	12	u_5
														100	66	36	35	36	u_7
															100	15	16	11	u_9
																100	**86**	**72**	k_1
																	100	**70**	k_2
																		100	k_3

* Numbers in bold type indicate marked correlation.

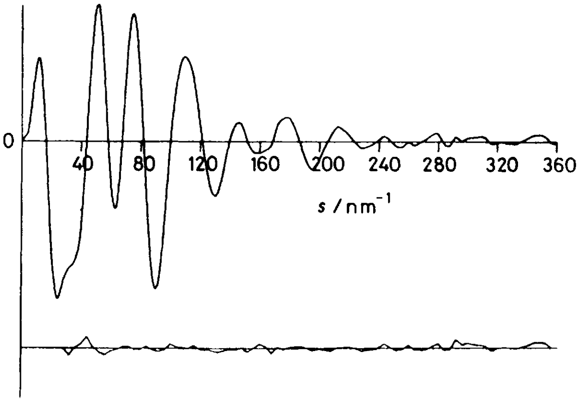

FIGURE 3 Experimental and final difference molecular-scattering intensities (combined) for tetraborane(10)

DISCUSSION

The results of our structural analysis of the gaseous tetraborane(10) molecule, based on its electron-diffraction pattern, are not radically different from those deduced for the molecule in the crystalline solid at low temperature by *X*-ray diffraction;[4,5] the principal innovation is the more realistic location of the hydrogen atoms. Table 4 affords a detailed comparison of the dimensions of B_4H_{10} as determined not only by different physical methods[3,4,9] but also on the basis of FSGO (floating spherical Gaussian orbital) calculations.[20] The table also includes the dimensions of the molecule $Be(B_3H_8)_2$ whose structure, as determined by crystallographic methods,[18] is likely to be closely related to that of B_4H_{10}.

TABLE 3

Molecular parameters [a] for tetraborane(10)

(*a*) Independent geometrical parameters

P_1	r[B(1)–B(3)]/pm	170.5(1.2)
P_2	r[B(1)–B(2)]/pm	185.6(0.4)
P_3	r(B–H) (average)/pm	129.2(0.8)
P_4	Δ_1/pm, $r(\mathrm{B{-}H_b})$ (average) − $r(\mathrm{B{-}H_t})$ (average)	18.7(1.0)
P_5	Δ_2/pm, $r[\mathrm{B(1){-}H_t''}]$ − $r[\mathrm{B(2){-}H_t}]$	2.8(1.9)
P_6	Δ_3/pm, $r[\mathrm{B(1){-}H_b}]$ − $r[\mathrm{B(2){-}H_b}]$	−16.9(0.9)
P_7	Dihedral angle, α/°	117.1(0.7)
P_8	Angle $\mathrm{H_t{-}B(2){-}H_t'}$/°	122.7(3.5)
P_9	Angle $\mathrm{B(3){-}B(1){-}H_t''}$/°	111.2(3.5)
P_{10}	Dip angle, β/° [b]	3.1(0.6)

(*b*) Final distances and vibrational amplitudes

	Distance/pm	Amplitude/pm
d_1[B(1)–B(3)]	170.5(1.2)	7.6(0.9)
d_2[B(1)–B(2)]	185.6(0.4)	8.4(0.3)
$d_3[\mathrm{B(1){-}H_b}]$	131.5(0.9)	8.0(1.3)
$d_4[\mathrm{B(2){-}H_b}]$	148.4(0.9)	8.0 (tied to u_3)
$d_5[\mathrm{B(1){-}H_t''}]$	122.1(1.4)	8.1(0.6)
$d_6[\mathrm{B(2){-}H_t}]$	119.4(0.7)	8.1 (tied to u_5)
d_7[B(2) ··· B(4)]	281.3(1.0)	24.5(6.0)
$d_8[\mathrm{B(3) \cdots H_t''}]$	242.9(2.9)	11.2 (tied to u_9)
$d_9[\mathrm{B(2) \cdots H_t''}]$	276.6(1.1)	11.2(1.2)
$d_{10}[\mathrm{B(2) \cdots H_b''}]$	278.3(1.9)	11.2 (tied to u_9)
$d_{11}[\mathrm{B(1) \cdots H_t'}]$	267.6(2.4)	11.2 (tied to u_9)
$d_{12}[\mathrm{B(4) \cdots H_t'}]$	394.0(1.3)	39.2 (fixed)
$d_{13}[\mathrm{B(4) \cdots H_t}]$	286.2(1.5)	49.8 (fixed)
$d_{14}[\mathrm{B(1) \cdots H_b'}]$	255.7(1.7)	11.2 (tied to u_9)
$d_{15}[\mathrm{B(1) \cdots H_t}]$	251.4(1.5)	11.2 (tied to u_9)

(*c*) Dependent angles/°

Angle between planes $\mathrm{B(1)B(3)H_bH_b'}$ and $\mathrm{B(2)H_bH_b'}$, γ	170.3(1.6)
$\mathrm{B(3)B(1)H_b}$	115.1(1.8)
$\mathrm{B(1)H_bB(2)}$	82.8(0.7)
$\mathrm{H_bB(2)H_b'}$	143.7(3.5)
$\mathrm{H_bB(1)H_t''}$	108.7(3.3)
$\mathrm{H_bB(1)H_b''}$	97.0(1.9)
B(1)B(2)B(3)	54.7(0.6)
B(2)B(1)B(3)	62.7(0.6)

(*d*) Co-ordinates/pm [c]

Atom	x	y	z
B(1)	0.0	−85.2	0.0
B(2)	140.6	0.0	86.1
$\mathrm{H_b}$	98.5	−141.0	66.9
$\mathrm{H_t}$	120.3	0.0	203.7
$\mathrm{H_t'}$	250.6	0.0	39.6
$\mathrm{H_t''}$	0.0	−129.3	−113.9

(*e*) Rotational constants/MHz

Constant	Observed value [d]	Calculated value	Difference
B_z	5 592.817(21)	5 594.171	−1.354
B_y	6 198.643(23)	6 200.627	−1.984
B_x	11 013.388(19)	11 015.213	−1.825

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] The dip angle, β, represents the movement of $\mathrm{H_b}$ out of the plane B(1)B(2)B(3) and around the axis B(1)–B(2), a positive sign indicating movement towards the concave side of the molecule. [c] The origin is at the mid-point of B(1)–B(3). [d] Ref. 9.

The gaseous B_4H_{10} molecule can be described in terms of a skeleton comprising a folded diamond of boron atoms with a dihedral angle of 117° between the two planes B(1)B(2)B(3) and B(1)B(3)B(4) with bridging hydrogen atoms spanning the edges of the diamond. These hydrogen atoms do not coincide with the planes B(1)B(2)B(3) and B(1)B(3)B(4) but are located 5.6(5.0) pm above them so as to fall within the fold of the tetraboron skeleton; this compares with a displacement of 16 pm found for the B_4H_{10} molecule in crystalline tetraborane(10).[4]

The unsymmetrical nature of the B–H–B bridges is also evident in that the bridging hydrogen atom forms a bond to the apical BH_2 group which is 17 pm longer than that to the middle BH group. Again this is in keeping not only with the molecular structure established by *X*-ray diffraction in which the two bonds differ in length by 16 pm,[4] but also with the ^{11}B–^{1}H coupling constants in the n.m.r. spectra of tetraborane(10) in the liquid phase.[21] The rather different result found by Simmons *et al.*[9] may arise from the fact that in determining the r_s structure no allowance has been made for the probable change in B–H distances on replacement of hydrogen by deuterium. Such unsymmetrical B–H–B bridges appear to be a feature of the higher boranes as witnessed for example by the structures of the molecules B_3H_7CO,[22] $B_6H_{10}(PPh_3)_2$,[23] and $B_{10}H_{14}$.[24,25] For the purposes of our calculations, we have assumed that the hydrogen atoms surrounding the apical boron atoms B(2) and B(4) conform locally to C_{2v} symmetry. On this basis, the puckering of the two five-membered rings B(1)(μ-H)B(2)(μ-H)B(3) and B(1)(μ-H)B(4)(μ-H)B(3) can be interpreted as relieving the potential non-bonded $\mathrm{H_t \cdots H_t}$ contact between the two opposing BH_2 fragments. The assumption that the B_4H_{10} molecule as a whole belongs to the C_{2v} symmetry group does not require that the immediate environments of the B(2) and B(4) atoms belong to the same symmetry group and it would be possible in principle to explore the capacity of the electron-diffraction pattern to accommodate departures from this local symmetry. In practice, however, the problems of correlation mentioned in the preceding section limit the definition of the parameters associated with the BH_2 groups which are subject as a result to comparatively large standard deviations. These circumstances make it unrealistic to seek a more precise definition of the apical $H_2B(\mu\text{-}H)_2$ fragments but we estimate that any changes in the parameters occasioned by relaxation of the local C_{2v} symmetry are within the limits of the standard deviations quoted in Table 3.

There is one notable difference between the dimensions deduced for the B_4H_{10} molecule in the gas phase and the crystalline solid. This concerns the length of what is commonly termed the 'direct' B–B bond between the atoms B(1) and B(3). The tetrahedral covalent radius of 88 pm assigned to boron[26] implies a B(1)–B(3) distance close to that reported for the B_4H_{10} molecule in crystalline tetraborane(10), namely 175 pm.[4] On the basis of both the microwave and electron diffraction measurements, the B(1)–B(3) distance in the gaseous molecule is about 171 pm, close to the distance between

TABLE 4

A comparison of the molecular parameters of tetraborane(10) as determined by various methods with those determined for beryllium bis(octahydridotriborate) [a]

	B_4H_{10}					
Parameter	Electron diffraction [b]	*X*-ray [c]	Microwave [d]	Electron diffraction [e]	FSGO calculation [f]	$Be(B_3H_8)_2$ *X*-ray [g]
(*a*) Distances/pm						
B(1)–B(3)	176	175.0	171.8(0.2)	170.5(1.2)	231	176.6(0.3)
B(1)–B(2)	185	184.5	185.4(0.2)	185.6(0.4)	193	183.4(0.4)
B(2) · · · B(4)	288	278.6	280.6(0.1)	281.3(1.0)	245	
B(1)–H_b	143	121	142.8(2.0)	131.5(0.9)	134	106—119(2)
B(2)–H_b	133	137	142.5(2.0)	148.4(0.9)	178	131—138(2)
B(2)–H_t	119	111		119.4(0.7)	124, 130	105—110(2)
B(1)–H_t''	119	111		122.1(1.4)	127	106—114(2)
(*b*) Angles between pairs of planes/°						
B(1)B(3)B(2) and B(1)B(3)B(4)	124.5	118.1	117.4(0.3)	117.1(0.7)	104.4	115.0
B(1)B(3)H_bH_b' and B(2)H_bH_b'		154		170.3(1.6)		
B(1)B(3)B(2) and B(1)H_bB(2)		170		176.9(0.6)		
(*c*) Displacement of H_b from the B(1)B(2)B(3) plane/pm		16		5.6(5.0)	23.6	0—6
(*d*) Angles/°						
H_tB(2)H_t'	125.8	126		122.7(3.5)		122.2 (1.6)
B(3)B(1)H_t''	118.3	118		111.2(3.5)		$\left.\begin{matrix}114.5\\115.3\end{matrix}\right\}(1.1)$
B(3)B(1)H_b				115.1(1.8)		$\left.\begin{matrix}109.3\\106.5\end{matrix}\right\}(1.2)$
B(1)H_bB(2)		91.8		82.8(0.7)		$\left.\begin{matrix}94.5\\96.9\end{matrix}\right\}(1.4)$
H_bB(2)H_b'		134.7		143.7(3.5)		$\left.\begin{matrix}133.7\\131.5\end{matrix}\right\}(1.3)$
H_bB(1)H_t''		95.6		108.7(3.3)		$\left.\begin{matrix}109.2\\113.5\end{matrix}\right\}(1.5)$
H_bB(1)H_b''		95.6		97.0(1.9)		$\left.\begin{matrix}98.1\\100.6\end{matrix}\right\}(1.4)$
B(1)B(2)B(3)		56.6		54.7(0.6)	73.5	57.5 (0.1)
B(2)B(1)B(3)		61.7		62.7(0.6)	53.2	61.2 (0.1)

[a] Estimated standard deviations are given in parentheses where values are available. [b] Ref. 3. [c] Ref. 4. [d] Ref. 9. [e] This work. [f] Ref. 20. [g] Ref. 18.

the apical and basal boron atoms in the gaseous B_5H_9 molecule [27] and some related compounds.[28]

It may be remarked that the eclipsing of the terminal B–H bonds of the adjacent B–H and BH_2 units in the tetraborane(10) molecule can be relaxed by a combination of the vibrational fundamentals ν_{17} and ν_{18} (see ref. 12). It is possible therefore for the molecule to assume C_2 rather than C_{2v} symmetry in its equilibrium conformation without any marked distortion of the B(1)B(2)B(3)B(4) skeleton. With a more complete characterization of the vibrational properties of the B_4H_{10} molecule, it is possible that the vibrational amplitudes calculated on the basis of a suitable force field will improve upon the analysis of the electron-diffraction results. Hence it may be possible to assess the effects of shrinkage and of the assumption by the molecule of an equilibrium configuration with less than C_{2v} symmetry. There is no reason to suppose, however, on the evidence of the analysis reported here, that the molecular model we have adopted is in need of significant improvement.

In conclusion, therefore, we feel that our analysis affords the most realistic determination of the molecular structure of tetraborane(10) to be achieved to date, with all the atoms relatively well located.

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