Electron Diffraction Study of Tetraborane(8) Carbonyl in the Gas Phase: Structure Determination of an *endo*/*exo* Isomeric Mixture

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The molecular structures of the individual isomers present in a gaseous mixture of *arachno*-$B_4H_8(CO)$ have been determined by electron diffraction. The sample was known from n.m.r. experiments to consist of 62% of the *endo* isomer and 38% of the *exo* isomer and early refinements showed that the distribution in the gas phase was consistent with that found in solution. A satisfactory refinement (R_G = 0.06) was obtained with a model in which the isomers had a 'butterfly' B_4 geometry with the 'hinge' B(1) carrying either an *endo*- or *exo*-CO. The *endo* and *exo* isomers were allowed to differ only in the dihedral angles between the planes of the 'butterfly' structure [135(4) and 144(2)°, respectively] and in the angles subtended by the carbon atom at the B–B 'hinge' [125(2) and 109(2)°]. The unbridged B–B distances were 172.7(10) ('hinge') and 184.9(4) pm, and the two H-bridged B–B distances were 178.0(6) pm. The BCO angle showed no significant deviation from 180°.

The adduct tetraborane(8) carbonyl, $B_4H_8(CO)$, was the first known compound in which the reactive intermediate $\{B_4H_8\}$ was stabilized. It was reported by Burg and Spielman [1] in 1959, and has been the subject of several n.m.r. studies. The early measurements [2,3] were consistent with a structure similar to that found by *X*-ray diffraction analysis of $B_4H_8{\cdot}PF_2(NMe_2)$,[4] in which the B_4H_8 framework is structurally similar to that of B_4H_{10} but lacking two bridging hydrogens. The more recent work was interpreted in terms of the presence of two geometrical isomers in an approximate ratio of 60:40.[5,6] This raised interesting questions about the mode of formation of these isomers and about factors responsible for their relative amounts. In the context of our work on the thermal interconversions of the boranes [7] we wished to obtain definitive answers to some of these questions and have embarked upon a detailed n.m.r. study, the results of which will be reported elsewhere.[8] In the meantime to gain information about the nature of $B_4H_8(CO)$ in the gas phase, and in particular to determine accurate molecular dimensions and bond angles, we have undertaken a study of its structure by means of electron diffraction.

Experimental

Tetraborane(8) carbonyl was made from B_4H_{10} by the method of Spielman and Burg.[2] It was purified by low-temperature fractional distillation with continuous monitoring of the distillate by mass spectrometry. The vapour pressure at 0 °C was found to be 70.5 ± 0.5 mmHg (*ca.* 938 Pa) in excellent agreement with the reported value.[1,2] In solution (CD_2Cl_2) the sample was known from detailed n.m.r. work [8] to consist of 62% of the *endo* isomer and 38% of the *exo* isomer. This same ratio was observed for several different samples and did not change with temperature. Attempts to separate the isomers on the low-temperature column have so far proved unsuccessful. The boranes were handled in conventional high-vacuum systems equipped with greaseless O-ring taps and spherical joints [J. Young (Scientific Glassware) Ltd.].

Electron diffraction data were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[9] operating at *ca.* 45 kV. Samples were maintained at 250 K and the nozzle at room temperature during the exposures, three at a nozzle-to-plate distance of 128 mm and three at 285 mm. Data were obtained in digital form using a Joyce-Loebl MDM6 microdensitometer.[10] The program used to control this instrument, and those used for data reduction and least-squares refinements, have been described previously.[10,11] Scattering factors used were taken from ref. 12.

Calibration plates with benzene were also taken, to give the precise camera distances and electron wavelengths listed in Table 1, together with weighting functions used to set up the off-diagonal least-squares weight matrices.[11]

Molecular Model

The model used in the least-squares refinements allowed for the presence of both isomeric forms, and early refinements (in which no constraints were applied to the ratio of the two isomers) showed that the distribution in the gas-phase was consistent with that found in solution (see Experimental section). As the isomers could not be separated by low-temperature fractionation, the 62:38 ratio was subsequently assumed to apply to the diffraction data.

The isomers were allowed to differ only in respect of the angles between the planes B(1)B(2)B(3) and B(1)B(3)B(4), and the angles B(3)B(1)C. (The atom numbering is shown in Figure 1.) Otherwise the only assumptions imposed by the model were C_s symmetry for each isomer, the equality of the bond lengths B(1)–H(1) and B(3)–H(3) and of B(2)–$H(2)_{endo}$ and B(2)–$H(2)_{exo}$, and a constraint of these last two bonds to lie in the plane bisecting the angle B(1)B(2)B(3). The heavy-atom skeleton of each isomer was then defined by eight parameters, and a further nine parameters were needed to give co-ordinates of hydrogen atoms. These parameters and their definitions are given in Table 2.

Structure Refinement

Attempts to refine the structure of $B_4H_8(CO)$ led initially to two distinct false minima. They were recognized as such by

Table 1. Camera distances, weighting functions, and other experimental data

Camera distance/mm	Δs	$s_{\text{min.}}$	sw_1	sw_2	$s_{\text{max.}}$	Correlation parameter	Scale factor	Wavelength/pm
	nm^{-1}							
285.43	2	20	40	122	144	0.310	0.596(6)	5.687
128.33	4	60	80	280	356	0.302	0.637(10)	5.686

Table 2. Geometrical parameters (distances/pm, angles/°)

P_1	r (B–B) (mean)	179.7(2)
P_2	Δr [B(1) – B(3)] minus mean of others	–8.8(11)
P_3	Δr [B(2) – B(3)] minus B(1)–B(2)	–6.9(9)
P_4	r (B–C)	151.7(4)
P_5	r (C–O)	113.7(4)
P_6	B(1)B(2)B(3)/B(1)B(3)B(4)^a	134.9(38)
P_7	B(3)B(1)C^a	124.6(23)
P_8	B(1)B(2)B(3)/B(1)B(3)B(4)^b	144.0(23)
P_9	B(3)B(1)C^b	108.5(21)
P_{10}	BCO	180.0 (fixed^c)
P_{11}	r (B–H) (terminal) (mean)	119.7(5)
P_{12}	Δr (B–H) (terminal)^d	2.0 (fixed)
P_{13}	r (B–H) (bridge) (mean)	131.9(18)
P_{14}	Δr [B(2) – H(2,3)] minus B(3)–H(2,3)	15.0 (fixed)
P_{15}	H(2)$_{exo}$B(2)H(2)$_{endo}$	114.0 (fixed)
P_{16}	BH$_2$ wag^e	2.0 (fixed)
P_{17}	B(1)B(3)H(3)	120.0 (fixed)
P_{18}	CB(1)H(1)	120.0 (fixed)
P_{19}	B(2)H(2,3)B(3)/B(1)B(2)B(3)	0.0 (fixed^c)

Errors (in parentheses) are e.s.d.s obtained in the least-squares analysis, and include an allowance for systematic errors.

[a] *endo* Isomer, 62%. [b] *exo* Isomer, 38%. [c] Refined earlier: see text. [d] [B(1)–H(1) + B(3)–H(3) – B(2)–H(2)$_{exo}$ – B(2)–H(2)$_{endo}$]/2. [e] Angle between bisectors of angles H(2)$_{exo}$B(2)H(2)$_{endo}$ and B(1)B(2)B(3): positive angle moves H atoms away from B(4).

Table 3. Interatomic distances and amplitudes of vibration/pm

			Distance	Amplitude
r_1	B(1)–B(3)		172.7(10)	6.6 (fixed*)
r_2	B(1)–B(2)		184.9(4)	7.0 (fixed*)
r_3	B(2)–B(3)		178.0(6)	6.8 (fixed*)
r_4	B(2)–H(2)		119.1(5)	
r_5	B(1)–H(1)		121.1(5)	8.2(14)
r_6	B(3)–H(2,3)		124.4(18)	
r_7	B(2)–H(2,3)		139.4(18)	
r_8	B–C		151.7(4)	6.0(7)
r_9	C–O		113.7(4)	3.7 (fixed*)
r_{10}	B(2) ··· B(4)	*endo*	294.5(33)	7.5 (fixed)
		exo	303.3(17)	
r_{11}	B(2) ··· C	*endo*	240.9(11)	8.1(11)
		exo	283.5(11)	8.4(19)
r_{12}	B(3) ··· C	*endo*	287.4(21)	
		exo	263.6(22)	8.1 (tied to u_{11} *endo*)
r_{13}	B(1) ··· O		265.4(5)	7.4(13)
r_{14}	B(3) ··· O	*endo*	390.3(26)	13.4(9)
		exo	359.7(30)	
r_{15}	B(2) ··· O	*endo*	325.7(16)	19.1 (tied to u_{14})
		exo	381.1(15)	13.4 (tied to u_{14})
r_{16}	B ··· H (two bond)		251—269	8.6(12)

Other non-bonded B ··· H, C ··· H, O ··· H, and H ··· H distances were included in the refinements, but are not listed here.

* Refined earlier: see text.

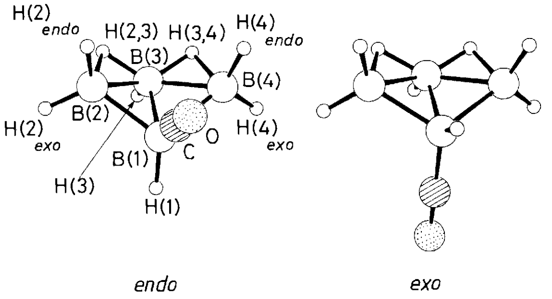

Figure 1. Perspective view of the structures of $B_4H_8(CO)$ isomers

physically unreasonable parameters, notably very wide dihedral angles between the two BBB planes, small B(3)B(1)C angles, and marked deviation from linearity in the BCO fragment. However, after taking great care in the choice of starting parameters, making particular use of data for crystalline $B_4H_8{\cdot}PF_2(NMe_2)$,[4] a structure was found which had reasonable geometrical and vibrational parameters, while giving an R factor substantially lower than those obtained earlier.

The B–B bond lengths all refined without difficulty, although B(1)–B(2) was *shorter* than B(2)–B(3) in the false minima, whereas it was longer in the final structure. The amplitudes of vibration for the B–B bonds were refined as a single parameter, with an estimated standard deviation (e.s.d.) of 0.8 pm, but were fixed in the final stages of the work. The B–C and C–O distances and B–C amplitude of vibration all refined satisfactorily, but the C–O amplitude dropped to the rather small value of 3.2(3) pm when freed, and so was reset to the more reasonable 3.7 pm.

While the bond lengths were assumed to be identical for the two isomers, the angles describing the heavy-atom structures were allowed to differ. Starting values for the dihedral angles between the planes B(1)B(2)B(3) and B(1)B(3)B(4) and the angles B(3)B(1)C were those found in the analogous compound $B_4H_8{\cdot}PF_2(NMe_2)$,[4] 137 and 135° respectively. This phosphine complex exists entirely in the *endo* form, so these values are a more reliable guide to likely angles in the *endo* isomer of $B_4H_8(CO)$ than to those in the *exo* isomer. Three of the four parameters refined without any difficulty giving 135(4) and 125(2)° for the dihedral and BBC angles in the *endo* form, and 144(2)° for the *exo* dihedral angle. The BBC angle in the *exo* isomer wandered in the range 108—114° as refinements progressed, ultimately settling at 109(2)°. The quoted error in this case should clearly be regarded as an underestimate. Finally, the BCO angle was allowed to vary, and values in the range 173—185° were obtained, with e.s.d.s of *ca.* 4°. There was thus no significant deviation from linearity, and so this was assumed in the remaining refinements, for both isomers.

Parameters relating to hydrogen-atom positions are not well determined, and in the final refinement only the mean terminal and mean bridge distances were included, with amplitudes of vibration for bonded B–H atom pairs, and for a group of two-bond B ··· H pairs, where the interatomic distance was between 250 and 270 pm. Several other hydrogen-atom parameters were varied stepwise, with negligible effects on R or other parameters. The values chosen for these parameters are mainly derived from those observed for B_4H_{10}.[13]

Geometrical parameters, interatomic distances, and amplitudes of vibration obtained in the final refinement, for which R_G

Table 4. Least-squares correlation matrix (× 100)*

	P_2	P_3	P_6	P_7	P_9	P_{13}	u_4	u_{12}	u_{13}	u_{14}
P_1	57	−52			−60					
P_2		−74						61		
P_3								−59		
P_5						−54	87			
P_6				−62			53	−65	−51	
P_8			−70	73						
P_9				57						
P_{11}						−52				
P_{13}			−61				−78			
u_{11}										55
u_{13}								68		−55

* Only elements with absolute values > 50 are included.

Table 5. A comparison of some molecular parameters for *endo*- and *exo*-$B_4H_8(CO)$ with those for B_4H_{10} and $B_4H_8{\cdot}PF_2(NMe_2)$

Parameter	*endo*-$B_4H_8(CO)$	*exo*-$B_4H_8(CO)$	B_4H_{10}	*endo*-$B_4H_8{\cdot}PF_2(NMe_2)$
Dihedral angle at B(1)B(3)/°	135(4)	144(2)	117	137
B(1)–B(2)/pm	184.9(4)	184.9(4)	185.6(0.4)	184.4(11)
B(1)–B(4)/pm	184.9(4)	184.9(4)	185.6(0.4)	182.6(11)
B(1)–B(3)/pm	172.7(10)	172.7(10)	170.5(1.2)	168.7(12)
B(2)–B(3)/pm	178.0(6)	178.0(6)	185.6(0.4)	175.9(13)
B(3)–B(4)/pm	178.0(6)	178.0(6)	185.6(0.4)	175.3(14)

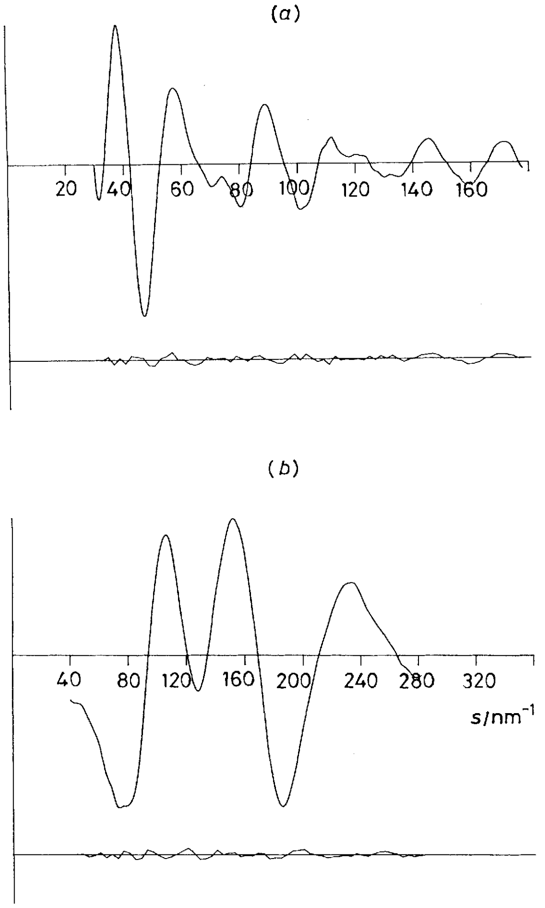

Figure 2. Observed and final weighted difference molecular scattering intensities for $B_4H_8(CO)$ at camera distances of (*a*) 285 and (*b*) 128 mm

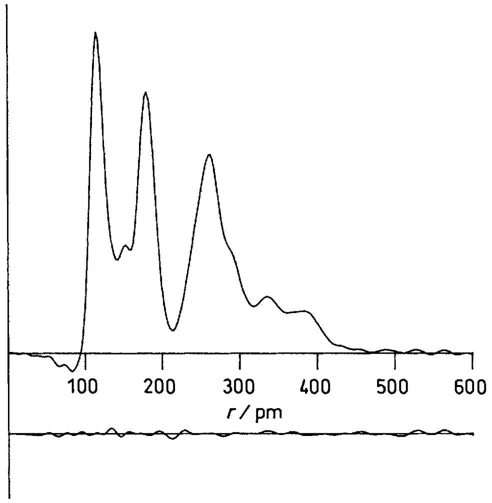

Figure 3. Observed and final weighted difference radial distribution curves, $P(r)/r$, for $B_4H_8(CO)$. Before Fourier inversion the data were multiplied by $s{\cdot}\exp(-0.000\,02\,s^2)/(Z_B - f_B)(Z_C - f_C)$

was 0.06, are listed in Tables 2 and 3, and Table 4 contains the most significant elements of the least-squares correlation matrix. Molecular scattering intensities are shown in Figure 2, the radial distribution curve in Figure 3, and perspective views of the molecules in Figure 1.

Discussion

The structural analysis of gaseous $B_4H_8(CO)$ confirms the earlier conclusions from n.m.r. data that the cluster framework geometry (see Figure 1) is closely related to that of crystalline $B_4H_8{\cdot}PF_2(NMe_2)$.[4] It is also apparent that there is very close agreement between all the main interatomic distances in the phosphine derivative and the corresponding ones in the carbonyl species, and that the dihedral ('butterfly') angles at B(1)B(3) in the two *endo* molecules are essentially identical. This latter observation in particular gives confidence in the details of the present analysis.

It is perhaps surprising that the dihedral angle for *exo*-$B_4H_8(CO)$ is significantly larger (at the 90% significance level) than that for the *endo* isomer [144(2) compared with 135(4)°]. On steric grounds one might at first sight have expected the opposite to be the case. Whilst it is possible that interaction between C and H(2) might increase this angle in the *exo* form, it seems more likely that the explanation lies in the details of the bonding. In this respect it is interesting that La Prade and Nordman[4] have suggested that the gross differences in the geometry of the B_4H_8 group in $B_4H_8{\cdot}PF_2(NMe_2)$ and B_4H_{10} indicated in Table 5, namely those involving the dihedral angle at B(1)B(3) and the H-bridged interatomic distances B(2)–B(3) and B(3)–B(4), might be accounted for in terms of the non-bonded repulsion of the fluorine atom on the concave side of the molecule. However, in view of the fact that these differences persist when the bulky phosphine ligand is replaced by CO, it now seems unlikely that this can be the case, and one is forced to conclude that factors other than purely steric ones are involved in this aspect also.

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