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The structures of borane carbonyl compounds B_4X_6CO ($X = F$, Cl, Br and I) by gas-phase electron diffraction and *ab initio* calculations†

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Gas-phase electron diffraction is a powerful technique for structural analysis of molecules in the gas phase, where they are free from packing forces that can occur in crystals. The compound $B(BF_2)_3CO$ has been studied by gas-phase electron diffraction to compare its structure to that seen in the solid phase by low-temperature X-ray crystallography. Results show the gas-phase structure to be similar to that seen in the crystal. A model with C_3 symmetry refined to give a C–O bond length of 115.8 pm and a C–B bond distance of 150.2 pm, which compare to values of 111.7 and 152.2 pm for the solid phase. The family of borane carbonyl compounds $B(BX_2)_3CO$ (X = F, Cl, Br or I) have all been studied by *ab initio* calculations to show the effects of halogen substitution and to gauge the effects of electron correlation and basis set on each structure. Compounds X = F, Cl and Br give calculated structures with C_3 symmetry in which the boron–halogen bonds lie coplanar with the C–O bond. In the case of X = I, the BI_2 groups are twisted by approximately 35° from coplanar at the DFT level as a result of the large steric interactions between iodine atoms.

Introduction

The compound $B(BF_2)_3CO$ was first prepared in 1967.[1,2] The crystal structure, along with that of its chlorine analogue, has recently been reported by Jeffery *et al.*[3] These compounds have been studied in the past to investigate the bonding of CO to elements without accessible d electrons and for comparison with transition metal carbonyls.[4] The bonding of the CO ligand is receiving attention as a result of interest in non-classical metal carbonyls, which exhibit reduced metal-to-CO π back-bonding compared to more classical species.[4–6] The volatile nature of $B(BF_2)_3CO$ lends itself to the technique of gas-phase electron diffraction which would thus allow a comparison between the solid and gas-phase structures. The study of the series of analogous compounds with different halogens using *ab initio* calculations reveals structural trends that relate to the nature of the substituent. The four compounds studied are all of the form $B(BX_2)_3CO$, where X = F, Cl, Br and I.

Experimental

Compound synthesis

The compound $B(BF_2)_3CO$ was prepared using literature methods.[1,2]

Gas-phase electron diffraction (GED) study of $B(BF_2)_3CO$

GED data collection. Data for $B(BF_2)_3CO$ were collected at two different camera distances (128.3 and 285.6 mm) using the Edinburgh apparatus,[7] with a sample temperature of 273 K and the nozzle temperature held at 298 K. Data were recorded photographically on Kodak Electron Image films, which were converted into digital form using a PDS densitometer at the Institute of Astronomy in Cambridge with a scanning program described elsewhere.[8] The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for the two camera distances are given in Table 1, together with the electron wavelengths, which were determined from the scattering patterns of benzene vapour.[8] The data reduction and analysis were performed using standard programs,[9] employing the scattering factors of Ross *et al.*[10]

GED model. On the basis of the *ab initio* calculations described, electron diffraction refinements[11] were carried out for $B(BF_2)_3CO$ using a model with C_3 symmetry and assuming each of the $B–BF_2$ groups to be planar. The structure was refined using nine geometrical parameters as shown in Table 2. Parameters p_1 and p_2 define the C–O and C–B bond distances respectively. The B–B bonds are defined by p_3. Mean and difference values were used for B–F distances (p_4 and p_5) where the B–F bonds eclipsing B–C–O are longer than the other B–F bonds. The C–B–B angles were defined by p_6. Mean and difference B–B–F angles (p_7 and p_8) were used because the structure calculated *ab initio* indicated a significant difference. The angles involving the F atoms closest to the C–O bond were larger than those with the F atoms furthest away. The torsional angle representing C–B–B–F is defined as p_9. The structure of $B(BF_2)_3CO$ obtained in the GED refinement is shown in Fig. 1.

Ab initio calculations

Geometry optimisations. All calculations were performed using the Gaussian 98 computer program.[12] Series of calculations were carried out for all compounds to determine the effects of basis set and electron correlation on the optimised

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† Electronic supplementary information (ESI) available: least-squares correlation matrix for electron diffraction structure refinement for $B(BF_2)_3CO$; tables of geometric parameters for B_4X_6CO and B_2X_4 (X = F, Cl, Br and I). See http://www.rsc.org/suppdata/dt/b2/b207192d/

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Table 1 GED data analysis parameters for $B(BF_2)_3CO$

Camera distance/mm	Δs/nm^{-1}	s_{min}/nm^{-1}	sw_1/nm^{-1}	sw_2/nm^{-1}	s_{max}/nm^{-1}	Correlation parameter	Scale factor, k[a]	Electron wavelength/pm
128.27	4	80	100	272	320	−0.2054	0.757(16)	0.06016
285.58	2	20	40	110	130	0.4415	0.739(9)	0.06015

[a] Figures in parentheses are the estimated standard deviations.

Table 2 Geometrical parameters (r_a structure) for $B(BF_2)_3CO$ (r/pm, angles in °)

Parameter		GED	MP2/6-311G*	Crystal[a]
p_1	rOC	115.8(3)	114.1	111.7
p_2	rCB	150.2(5)	150.6	152.2
p_3	rBB	169.4(3)	169.2	168.3
p_4	$r\text{BF}_m$[b]	133.0(1)	132.8	131.2
p_5	$r\text{BF}_d$[b]	1.5(1)	0.9	1.5
p_6	∠CBB	108.3(24)	110.0	109.6
p_7	$\angle\text{BBF}_m$[b]	122.2(6)	121.7	123.0
p_8	$\angle\text{BBF}_d$[b]	2.6(1)	2.0	4.1
p_9	ϕCBBF	2.02(24)	0.0	—

[a] Average crystal structure. [b] m = mean, d = difference.

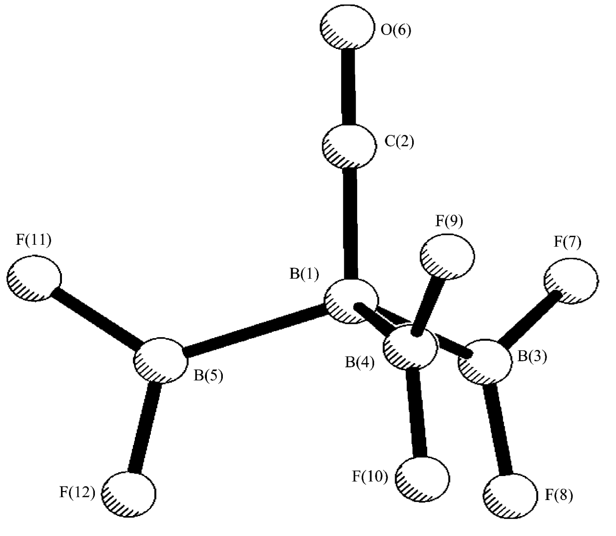

Fig. 1 Molecular framework for $B(BF_2)_3CO$.

structures. The basis set used was dependent upon the halogen substituents. Two starting geometries were used: first, conformer A, where the BX_2 groups lie coplanar with the C–O bond, and secondly conformer B, where the BX_2 groups are twisted 90° away from the coplanar arrangement. Calculations on conformer A, for X = F and Br, were performed using a Dec Alpha 1000 4/200 workstation. Calculations for X = Cl and I were carried out using resources of the UK Computational Chemistry Facility, on a DEC 8400 superscalar cluster equipped with 10 fast processors, 6 GB of memory and a 150 GB disk. Calculations were performed using HF,[13] MP2[14] and DFT[15] methods. For X = F and Cl, calculations were performed at the HF level of theory using the 3-21G*[16] and 6-31G*[17] basis sets; at the MP2 level using 6-31G* and 6-311G*[18] basis sets; and at the B3LYP[19] level using 6-31G* and 6-31+G* basis sets,[20] and a calculation using the 6-31G* basis set on the boron, oxygen and carbon atoms with the 6-31+G* basis set on the halogen atoms. For X = Br, HF calculations were carried out using the 3-21G* and 6-31G* basis sets in addition to a calculation utilising a 6-31G* basis set on the boron, oxygen and carbon atoms and CEP-4G[21] basis set on the bromine atoms. At the B3LYP level of theory, calculations were run using the 6-31G* and 6-31+G* basis sets, and with 6-31G* on the boron, oxygen and carbon atoms but with the 6-31+G* basis set on the bromine atoms. MP2 calculations were performed using 6-31G* and 6-311G* basis sets. For X = I, calculations were performed at the HF level using a 3-21G* basis set. Calculations were also carried out with 6-31G*, 6-311G* or 6-311+G* basis sets on the B, C and O atoms, coupled with a lanl2dz[22] basis set on the I atoms. MP2 calculations using 6-31G* and 6-311G* basis sets on the B, C and O atoms coupled with a lanl2dz[22] basis set on the I atoms were also performed.

Calculations on conformer B at the HF level using 3-21G* and 6-31G* basis sets were performed for X = F, Cl and Br. The calculations for the iodide were performed at the HF level using first the 3-21G* basis set, and then using the 6-31G* basis set on the B, C and O atoms with the lanl2dz basis set on the I atoms.

Calculations were performed on the family of compounds B_2X_4 (X = F, Cl, Br, I) to determine the effects of halogen substitution and to gauge the effects of electron correlation on a simpler structure to that of the carbonyl compounds. Calculations up to HF/6-31G*, MP2/6-311G* and B3LYP/6-311+G* levels were carried out for all X. In the case of X = I, the lanl2dz basis set was used on the I atoms.

Calculations were also performed on the compounds $B(BX_2)_3$ (X = F, Cl, Br, I) to determine how the coordination of CO affects the orientation of BX_2 groups and the dimensions of the parent borane molecules. Calculations at the MP2/6-311G* level were carried out for all X. In the case of X = I, the lanl2dz basis set was used on the I atoms.

Frequency calculations. Frequency calculations allowed the nature of any stationary points to be determined, confirming the structure as either a local minimum, transition-state or saddle-point on the potential-energy surface. For $B(BF_2)_3CO$, the force field described by Cartesian force constants at the HF/6-31G* level was transformed into one described by a set of symmetry coordinates using the program ASYM40.[23]

Results and discussion

Gas-phase electron diffraction study of $B(BF_2)_3CO$

Two approaches were used during the refinement of the structure of $B(BF_2)_3CO$. First, the C–B–B–F torsion was fixed at 0° and the other parameters were allowed to refine. The torsion was then subsequently refined subject to restraint, using the SARACEN[24] method. Allowing the C–B–B–F torsion to deviate from 0° reduced the R_g factor from 0.080 to 0.077. Using a scaled harmonic *ab initio* force field to obtain approximations to vibrational amplitudes subsequently reduced the R_g factor further to give a final value of 0.047. The resultant values for the parameters determined from the least-squares refinement along with their comparison with *ab initio* values calculated at the MP2/6-311G* level and the average crystal structure are all listed in Table 2. Some parameters and amplitudes were subject to flexible restraints (Table 3). The least-squares correlation matrix for the structural refinement is listed in Table S1 (ESI). The success of the final refinement can be assessed on the basis of the molecular scattering curves (Fig. 2) and the radial distribution curve (Fig. 3). Fig. 1 shows a view of $B(BF_2)_3CO$ in the optimum refinement of the GED data.

Table 3 Flexible restraints for $B(BF_2)_3CO$

Restraint	Value/pm or °	Uncertainty/pm or °
p_8	2.60	0.25
p_9	2.02	0.20
u_2	4.1	0.4
u_4	33.5	2.9
u_5	29.6	2.3
u_7	31.3	2.6
u_9	21.2	3.1
u_{14}	11.7	0.8

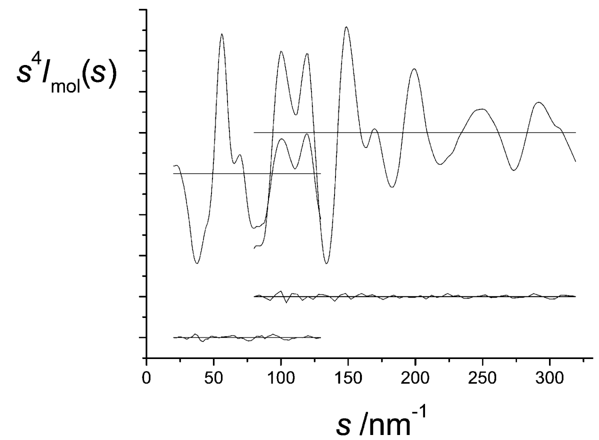

Fig. 2 Experimental and final weighted difference (experimental − theoretical) molecular scattering intensities for $B(BF_2)_3CO$.

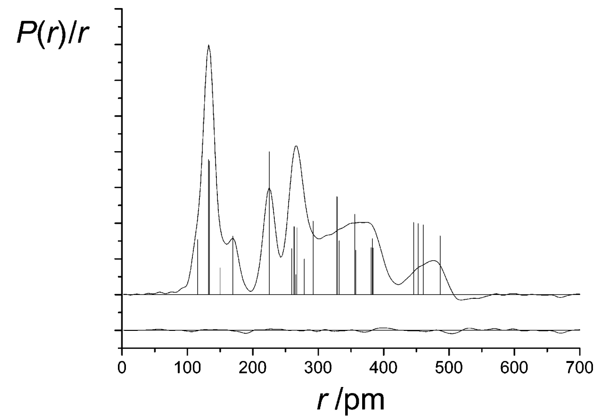

Fig. 3 Experimental and difference (experimental − theoretical) radial distribution curves, $P(r)/r$ for $B(BF_2)_3CO$. Before Fourier inversion the data were multiplied by $s\cdot\exp(-0.00002s^2)/(Z_B - f_B)/(Z_F - f_F)$.

Of the nine geometrical parameters, seven refined without the application of restraints. Parameters p_8 (∠BBF$_d$) and p_9 (ϕCBBF) were restrained using the SARACEN[24] method, where each restraint has a value and an uncertainty derived from *ab initio* calculations, and so the refined parameters are the best fit to all available information, both experimental and theoretical. Direct amplitude restraints for u_2[F(8)–B(3)], u_4[F(10) ··· F(8)], u_5[F(7) ··· O(6)], u_7[F(9) ··· F(8)], u_9[F(9) ··· F(7)] and u_{14}[F(8) ··· C(2)] were found to be necessary to avoid obtaining unrealistic values in the least-squares refinement. Final bond distances and amplitudes of vibration are listed in Table 4.

Ab initio calculations

For all cases of X, conformer B returns imaginary frequencies, indicating that these structures represent saddle points or maxima, and that the calculations have failed to reach energy minima on the potential energy surfaces. For conformer A, energy minima were found for all levels of calculation performed for X = F and Cl [see Tables 5, S2 and S3 (ESI)]. For X = Br [Tables 5 and S4 (ESI)], one imaginary frequency was returned at HF/3-21G*, indicating a transition state. However, when the level of calculation was increased to HF/6-31G*, no imaginary frequency was found, indicating a real structure and confirming C_{3v} symmetry. The results of the calculations performed when X = I [Tables 5 and S5 (ESI)] differ in that three imaginary frequencies were found for conformer A. When the size of the basis set was increased a transition state was reached, in which one BI_2 group lay as in conformer B and the other two BI_2 groups lay as in conformer A. The mode corresponding to one imaginary frequency was in the torsional motion of the perpendicularly positioned BI_2 group, so further calculations were performed in which the C–B–B–I angle torsion was allowed to deviate from 0°. The C–B–B–I starting torsion was changed from 0 to 30° whilst maintaining C_3 symmetry to allow a greater distance between iodine atoms and calculations at the HF level were performed. The structure optimised to give a minimum when the twist had a value of approximately 35°. The basis sets used were 3-21G* and 6-31G*, 6-311G* or 6-311+G* on the B, C and O atoms with lanl2dz on the I atoms. Calculations at the B3LYP level using a 6-31G*, 6-311G* or 6-311+G* basis set on the B, C and O were performed with the lanl2dz basis set on the I atoms.

Geometry changes for $B(BF_2)_3CO$ were found as a result of the inclusion of electron correlation and from increasing the size of the basis set. Increasing the size of the basis set from 3-21G* to 6-31G* at the HF level; from 6-31G* to 6-311G* at the MP2 level, and from 6-31G* to 6-31+G* at the B3LYP level resulted in decreased C–O bond lengths (by 1.5, 1.1 and 0.2 pm at the HF, MP2 and DFT levels respectively). Increased C–B bond distances resulted from the same increase in basis set (by 2.6 pm at HF, 0.4 pm at MP2 and 1.1 pm at the DFT level). These differences are more sensitive to increased levels of theory, which include electron correlation effects. Of particular interest are the increased differences found for the three B–F bonds lying closest to the C–O bond compared to the three furthest away. This occurs when the basis set size is increased.

Table 4 Bond distances (r_a/pm) and amplitudes of vibration (u/pm) obtained in the GED refinement of $B(BF_2)_3CO$[a]

u	Atom pair	r_a	Amplitude
1	F(8) ··· F(7)	225.1(2)	6.5(2)
2	F(8)–B(3)	132.3(6)	4.1(2)
3	F(7)–B(3)	133.7(7)	4.5 (tied to u_2)
4	F(10) ··· F(8)	328.7(14)	33.5(12)
5	F(7) ··· O(6)	355.9(7)	29.6(16)
6	F(7) ··· C(2)	292.1(5)	17.0(13)
7	F(9) ··· F(8)	445.9(10)	31.3(15)
8	F(10) ··· F(7)	452.9(10)	28.1 (tied to u_7)
9	F(9) ··· F(7)	460.7(10)	21.2 (19)
10	F(8) ··· B(1)	263.1(5)	8.2(3)
11	F(7) ··· B(1)	267.6(7)	7.6 (tied to u_{10})
12	F(8) ··· O(6)	486.7(8)	14.4(9)
13	B(3)–B(1)	169.4(3)	6.5(3)
14	F(8) ··· C(2)	382.8(7)	11.7(3)
15	O(6)–C(2)	115.8(3)	4.2(4)
16	F(8) ··· B(4)	328.5(8)	18.8 (tied to u_4)
17	F(8) ··· B(5)	331.9(8)	18.8 (tied to u_4)
18	F(7) ··· B(5)	381.0(8)	19.6 (tied to u_{14})
19	F(7) ··· B(4)	383.8(8)	19.6 (tied to u_{14})
20	B(3) ··· C(2)	259.3(4)	9.8 (tied to u_{10})
21	O(6) ··· B(3)	357.4(5)	12.7 (tied to u_5)
22	B(4) ··· B(3)	278.6(6)	11.9(18)
23	C(2)–B(1)	150.2(5)	1.1(22)
24	O(6) ··· B(1)	266.0(5)	6.2 (tied to u_{10})

[a] Estimated standard deviations, derived from the least-squares refinement, are given in parentheses.

Table 5 Geometric parameters for $B(BX_2)_3CO$ (X = F, Cl, Br, I) (r_e/pm, angles in °), calculated at the MP2/6-311G* level

Geometric parameter	X = F	X = Cl	X = Br	X = I[a]
rOC	114.1	114.0	114.0	114.5
rCB	150.6	151.6	152.4	150.3
rBB	169.2	169.9	170.5	171.1
rBX$_m$[b]	132.8	175.1	191.6	210.3
rBX$_d$[b]	0.9	2.1	2.7	1.5
∠CBB	110.0	107.6	106.9	107.6
∠BBX$_m$	121.7	121.2	121.5	120.8
∠BBX$_d$[b]	2.0	0.6	2.3	1.5
∠XBX	116.6	117.5	116.9	118.2
ϕCBBX	0.0	0.0	0.1	38.1
Energy[c]	−810.5703	−2970.8036	−15647.3655	−279.5947

[a] 6-311G* on B, C, O atoms and lanl2dz on I atoms. [b] m = mean, d = difference. [c] Absolute energy in Hartrees.

Table 6 Geometric parameters for B_2X_4 (X = F, Cl, Br, I) (r_e/pm, angles in °) at the MP2/6-311G* level

Geometric parameter	X = F	X = Cl	X = Br	X = I[a]
rBB	172.0	169.1	168.1	166.4
rBF	132.2	174.2	190.4	210.9
∠XBX	117.613	119.963	121.120	122.848
∠XBB	121.194	120.018	119.440	118.576
ϕXBBX	0	90	90	90
Energy[b]	−448.4525	−1888.2806	−10338.9937	−94.4762

[a] 6-311G* on B, C, O atoms and lanl2dz on I atoms. [b] Absolute energy in Hartrees.

For example at the HF level, the difference in the B–F bond distance between the substituent closest to the C–O bond and the substituent furthest away (rBF$_d$) increased from 0.8 pm (3-21G* basis set) to 1.1 pm when the 6-31G* basis set was used. This led to the conclusion that this effect should be modelled in the gas-phase electron diffraction refinement.

The C–B–B angle lies close to the classic sp^3 hybrid angle of 109.5°, but the F–B–F angle deviates significantly from 120° (116.6°) as the fluorine atoms closest to the C–O bond position themselves as far away as possible from this region of high electron density. This also results in large differences between B–B–F angles of up to 3°.

For X = Cl, increasing the level of theory from HF to MP2 and DFT resulted in a dramatic decrease in the length of the C–B bond, by around 9 pm in both cases. Increasing the size of the basis set used had little effect on this distance, so the change can be attributed to electron correlation effects. The C–O bond increased in length by approximately 5 pm as the level of theory increased from HF/6-31G* to MP2/6-31G*, but increasing the basis set to 6-311G* resulted in a decreased bond length compared to that found at MP2/6-31G* (115.1 pm compared to 114.0 pm). The crystal structure for $B(BCl_2)_3CO$ has been reported,[3] and shows a very similar structural motif to that determined by these *ab initio* calculations. However, several differences occur in the parameter values. For example, the C–O bond in the solid phase (109.1 pm)[3] is much shorter than that determined by *ab initio* calculations at the MP2/6-311G* level (114.0 pm). This is in part due to the underestimation of the inter-nuclear distance in the crystal by X-ray diffraction, which yields distances between centres of electron density. In contrast the C–B bond has a greater value in the crystal structure[3] (154.4 pm compared to 151.6 pm at MP2/6-311G*). In the solid phase[3] there was no difference between B–Cl bond lengths, but at MP2/6-311G* the difference was 2.1 pm.

For X = Br, DFT calculations produced structures with longer C–O bond distances and shorter C–B bond distances compared to calculations at the HF level. The size of the basis set had little effect on these parameters. $B(BBr_2)_3CO$ has parameter values that more closely match those for $B(BCl_2)_3CO$ than the values found for $B(BF_2)_3CO$.

For X = I, minima were found with all computational methods when BI_2 groups were twisted approximately 35° away from the positions in which they were coplanar with the C–O bond. This allows the iodine atoms to achieve a greater separation from each other. For the optimised structure of conformer A, the distance of separation between atoms I(9) ··· I(12) equals 421.7 pm (HF/6-311G*). When the BI_2 groups are twisted by 34.8°, as at B3LYP/6-311+G*, the separation distance increases to 444.5 pm, thus reducing the amount of steric hindrance between substituent iodines. At the HF level the value of the C–B–B–I torsion angle increased as the size of basis set on the B, C and O atoms was increased from 3-21G* and 6-31G* to 6-311G* (32.0, 33.8 and 34.3° respectively). The same level of theory saw the C–O bond length decrease from 112.2 pm using a 3-21G* basis set to 109.8 pm using a 6-311+G* basis set. The inclusion of electron correlation led to an increase in the length of the C–O bond, from 107.8 pm at HF/6-311+G* to 113.2 pm at B3LYP/6-311+G*. The C–B bond length decreased by approximately 9 pm when the level of theory was increased from HF (159.5 pm) to DFT (150.9 pm) using the 6-311+G* basis set on the B, C and O atoms and the lanl2dz basis set on the I atoms. Increasing the size of the basis set at the DFT level mirrored the effect found at the HF level, where the C–B–B–I torsion increased when the basis set was increased from 6-31G* to 6-311G* (33.6° increasing to 34.6°). Values for the other parameters were not significantly affected by increasing the basis set from 6-31G* to 6-311G* and 6-311+G*.

The molecules with general formula B_2X_4 (X = F, Cl, Br and I) all optimised with staggered conformations, except for B_2F_4, at levels from HF/6-311G* upwards. The conformations obtained in high level *ab initio* calculations are in agreement with those determined in gas-phase electron diffraction studies of B_2F_4,[25] B_2Cl_4[26] and B_2Br_4.[27] The calculated geometric parameters are listed in Tables 6 and S6–S9 (ESI). In the case of X = F, Cl and Br, the calculated values are also in close agreement with the experimentally determined parameters.[25–27] The calculated distances and angles are within 1 pm and 1° respectively of the experimental gas-phase parameters[25–27] at the MP2/6-311G* level. Halogens have a negative inductive effect since they pull the bonding pair of electrons away from the respective boron atoms.[28] The B–B bond distances in B_2X_4 decrease as X is changed from F to I. The B–B bond in the

Table 7 Geometric parameters for $B(BX_2)_3$ (X = F, Cl, Br, I) (r_e/pm, angles in °) at the MP2/6-311G* level

Geometric parameter	X = F	X = Cl	X = Br	X = I[a]
*r*BB	168.7	166.1	165.6	164.5
*r*BX	132.6	174.3	190.5	210.8
∠BBB	120	120	120	120
∠XBX	117.677	121.154	122.359	123.853
∠BBX	121.161	119.423	118.820	118.073
*ϕ*BBBX	90	90	90	90
Energy[b]	−697.4262	−2857.1829	−15534.2435	−166.4841

[a] 6-311G* on B, C, O atoms and lanl2dz on I atoms. [b] Absolute energy in Hartrees.

fluoro compound is 5.2 pm longer than the iodo compound at the MP2/6-311G* level.

The compounds $B(BX_2)_3$ (X = F, Cl, Br and I) all optimised with D_{3h} symmetry, with the X atoms lying above and below the plane of the BB_3 group. This includes the iodo compound, for which the CO adduct differed in conformation from its analogues with different halogens. Addition of CO to $B(BI_2)_3$ results in twisting of the BI_2 groups by 38.1°. The calculated geometric parameters are listed in Table 7. The $B(BX_2)_3$ compounds contain planar B_4 skeletons, in contrast to the carbonyl compounds.

Jeffery *et al.*[3] have reported *ν*(CO) frequencies of 2176 and 2162 cm^{-1} in the IR spectra of $B(BF_2)_3CO$ and $B(BCl_2)_3CO$ respectively. These experimental values compare to calculated values of 2210.5 cm^{-1} [for $B(BF_2)_3CO$ at B3LYP/6-31+G*] and 2217.7 cm^{-1} [for $B(BCl_2)_3CO$ at B3LYP/6-31G*]. *Ab initio* calculations at the MP2/6-311G* level show these compounds to have C–O bond distances differing by only 1 pm, and the observed and calculated CO stretching frequencies support the view that there is little difference between the natures of the ligands in the two molecules.

Comparison of the B–B bonds in the four carbonyl molecules shows that there is a small increase in the length of these bonds as the halogen becomes heavier. The effect of electronegative substituents is to make the atom to which they are attached more positive.[28] In X_2BBX_2 the B atoms are positive, and so repel one another, to the greatest extent when X = F. A comparison of the gas-phase structures of B_2F_4,[25] B_2Cl_4[26] and B_2Br_4[27] shows that the B–B bond length in the fluoro compound is 1.8 and 3.1 pm longer than in the chloro and bromo analogues respectively. In $B(BX_2)_3CO$, the central B will not be made positive in this way, so there will be a somewhat greater *attractive* force for X = F. In $B(BX_2)_3CO$, the B–B bonds for X = Cl are 0.6 pm longer than for X = F at MP2/6-311G* and 1.3 pm longer at the B3LYP/6-31+G* level. The distance in the bromo compound is about the same as in the chloro compound, and there is a further slight lengthening in the iodo compound. For $B(BX_2)_3$, as X is changed from F to I, the B–B bond distances decrease steadily, from 168.7 pm when X = F to 164.5 pm when X = I. This is opposite to the trend found in the carbonyl compounds. The difference between B–B bond distances in $B(BX_2)_3$ and $B(BX_2)_3CO$ equals 0.5, 3.8, 4.9 and 6.6 pm for X = F, Cl, Br and I respectively, at MP2/6-311G* level.

The calculated C–B–B angle is greatest in the fluoro compound, at 110.0° (MP2/6-311G* level), whereas the angles are smaller, but similar, in the other compounds (107.6, 108.2 and 107.6° for X = Cl, Br and I, respectively). This results in the central boron atom of the fluoro molecule being more regularly tetrahedral than those in the chloro, bromo and iodo analogues.

The starting parameters for the r_a refinement were taken from the theoretical geometry optimised at the MP2/6-31G* level. The r_α structure was not refined because the rectilinear vibrational corrections (*i.e.* parallel and perpendicular correction terms) are known to be unreliable for molecules with many low-lying vibrational modes. The gas-phase structure exhibits pronounced lengthening of the B–F bonds closest to the B–C–O fragment compared to those furthest away. This effect is also seen by *ab initio* calculations and in the crystal structure.[3] The C–O bond in the gas phase is more than 4 pm longer than when the compound is in the solid phase.[3] This could be because X-ray crystallography measures centres of electron density whereas gas-phase electron diffraction measures inter-nuclear distances. The C–O bond is shorter in the calculated structure (114.1 pm) than found experimentally in the gas phase (115.8 pm). The experimental value is an r_a distance and the r_e distance, equivalent to the computed parameter, would be almost exactly the same. The computed distance is 2.4 pm longer than the value found in the solid phase.[3] The C–B bond length in the gas-phase structure is similar to that found by calculation but is 2.1 pm shorter than that determined for the solid-phase structure.[3]

The C–B–B angles found by X-ray crystallography, gas-phase electron diffraction and *ab initio* calculations are close to the classic sp^3 hybrid angle (109.6, 108.7 and 110.0° respectively). The need for fluorines F(7), F(9) and F(11) to distance themselves from the region of high electron density (B–C–O) is more pronounced in the solid-phase structure. This is shown by the value of p_8 that measures the difference between angles B(1)–B(3)–F(7) and B(1)–B(3)–F(8), and the corresponding angles for B(4) and B(5). The difference in the solid state is 4.1° compared to 2.6° in the gas phase and 2.0° in the calculated structure.

Conclusion

The gas-phase structure of the borane carbonyl adduct $B(BF_2)_3CO$ has been determined in conjunction with high-level *ab initio* calculations and is found to have C_3 symmetry. The result is a structure similar to that seen in the solid phase as determined by low-temperature X-ray crystallography.[3]

Using *ab initio* calculations has allowed comparison of the analogous compounds $B(BX_2)_3CO$, where X = F, Cl, Br and I. The halogen substituents do not alter the overall symmetry of the molecule, except in the case of X = I, but they do have important effects on the bond lengths and angles in the molecules. When X = I, the BI_2 groups are twisted by approximately 35° from being coplanar with the B–C–O fragment, as a result of the strong steric interactions between the large iodine atoms. The B–B distance decreases slightly as fluorine is replaced by heavier halogens, whereas in the compounds B_2X_4 and $B(BX_2)_3$ there is a substantial shortening of the B–B bonds.

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