Molecular structures of the 1,6-disubstituted triptycenes $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ using gas-phase electron diffraction and *ab initio* and DFT calculations†

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The structures of the D_{3h} -symmetric molecules dodecafluoro-1,6-distibatriptycene and dodecafluoro-1,6-dibismatriptycene [$\text{Z}_2(\text{C}_6\text{F}_4)_3$ ($\text{Z} = \text{Sb}, \text{Bi}$)] have been determined in the gas phase by electron diffraction, using the SARACEN method, with restraints obtained from quantum chemical calculations. Several methods of *ab initio* and density functional theory geometry calculations have been performed and recommendations made as to their relative suitabilities for determining the structures of such species. Calculations using the MP2 method with a small-core pseudopotential (aug-cc-pVQZ-PP) on the Sb and Bi atoms and the 6-311G* basis set on the light atoms were found to give the closest correlation with the experimental results for both molecules. Differences in structure were found depending on whether a large-core or small-core pseudopotential was used on the heavy atoms.

Introduction

In stark contrast to the organic cage molecule adamantane, where chemists have succeeded in substituting carbon atoms for a wide variety of non-transition-metal elements, the three-dimensional triptycene molecule had until the 1970s proved far more difficult to substitute. Theoretically, it should be feasible for any element that is capable of approximately tetrahedral coordination geometry to be substituted for the bridgehead carbon atoms. In practice, however, although 1,6-diazatriptycene was first synthesised in 1875, it remained the only known heteroatomic analogue of triptycene for almost 100 years.¹ This owes much to the fact that the nitrogen-substituted molecule is the only substituted triptycene that can be built in a stepwise manner from stable intermediates.² Only with the advent of specialist direct synthesis techniques did it become possible to extend the series of analogues to other elements in Group 15.

Fluorinated 1,6-disubstituted triptycenes have many potential applications. $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ is used in the preparation of non-cluster type bismuth compounds utilised as contrast agents in a variety of medical imaging techniques and is also reported as having uses in the treatment of gastrointestinal disorders, such as ulcers.³ $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ has very recently been trialled as a dopant for a perfluorinated graded index polymer fibre (PFGI-POF).⁴ In this application the triptycene acts to raise the refractive index of the optical fibre. Although some other perfluorinated molecules proved to be more effective in that role than $\text{Sb}_2(\text{C}_6\text{F}_4)_3$, it demonstrates the industrial demand for novel fluorinated compounds.

Previous diffraction studies on Group 15 1,6-disubstituted fluorinated triptycenes are limited to an X-ray crystallographic study⁵ of $\text{As}_2(\text{C}_6\text{F}_4)_3$. This work showed the absence of high symmetry, with the substance crystallising in the monoclinic Cc space group. Although the aromatic rings are essentially planar, the dihedral angles between the ring planes were found to be $111(2)^\circ$, $125(2)^\circ$ and $125(2)^\circ$. Similar deviations from 120° were previously noted in some hydrogen-substituted triptycenes, where the lack of high symmetry was attributed to crystal forces.⁶ It has also been noted that although triptycenes are depicted as totally rigid systems, it may be the case that they behave as rigid aromatic rings that are connected flexibly *via* the bridgehead atoms.⁷

These studies concerning the structures of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$, as determined by gas-phase electron diffraction and theoretical methods should add to the structural understanding of the Group 15 1,6-disubstituted triptycenes.

Experimental

Preparation of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$

Samples of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ were prepared by direct synthesis in heated, sealed tubes where, in each case, the appropriate Group 15 element was reacted with $1,2\text{-C}_6\text{F}_4\text{I}_2$.⁸

Ab initio and DFT studies

All calculations reported in this work were performed using the Gaussian 03 suite of programs,⁹ with the resources of the EPSRC National Service for Computational Chemistry Software.¹⁰

Starting coordinates for geometry optimisation calculations for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ were created using the GaussView 3.0 package, which allowed the symmetry to be constrained to D_{3h} .

For $\text{Sb}_2(\text{C}_6\text{F}_4)_3$, initial low-level calculations were undertaken at the Hartree–Fock level of theory using Pople's 3-21G* basis set¹¹ (RHF/3-21G*). A geometry optimisation was carried out

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as well as a frequency calculation to ensure that the calculated structure represented a minimum on the potential energy surface. These calculations were repeated using the 6-31G* basis set¹² on the light atoms (C and F) and, as 6-31G* has not been coded for Sb, the LanL2DZ basis set¹³ on the heavy atoms. In the case of $\text{Bi}_2(\text{C}_6\text{F}_4)_3$, not even the 3-21G* basis set is optimised for Bi and therefore the LanL2DZ basis set was used from the outset with, once again, the 3-21G* and then the 6-31G* basis set on the light atoms. In later calculations the size of the basis set on the light atoms was increased to 6-311G* and further to include a diffuse function on each C and F atom.¹⁴

The choice of basis set for use on the heavy atoms is based on their ability to offer a pseudopotential (PP) or effective core potential (ECP), which reduces the number of electrons that are considered explicitly and speeds up the calculations. By doing this, however, there is a concern that the number of electrons considered to be valence electrons is too few to describe the molecular structure accurately. To this end another basis set was tested on these systems. New correlation-consistent basis sets have been developed specifically for the post-d block Group 13–15 elements. The basis set used (aug-cc-pVQZ-PP) is of quadruple- ζ quality, augmented by diffuse and polarisation functions.¹⁵ It employs a small-core pseudopotential,¹⁶ which for Sb includes 28 core electrons ([Ar] + 4d) while the LanL2DZ large core includes 46 electrons in the core ([Kr] + 5d). For Bi, the aug-cc-pVQZ-PP ECP includes 60 electrons in the core ([Kr] + 4d3f) and the LanL2DZ ECP includes 78 electrons ([Xe] + 5d4f).

Density functional theory (DFT) calculations are known to be very good for predicting the geometries of transition-metal compounds. In a previous GED and theoretical study on the complex $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}'_2)_3]$ it was reported that DFT methods can also produce reliable results for molecules containing a heavy p-block element (Sn).¹⁷ During the course of this work several DFT methods have again been tested to compare their results with those obtained experimentally.

Becke's three-parameter hybrid functional¹⁸ was used with the non-local PW91 correlation functional¹⁹ (B3PW91), which performed well for the Sn compound. It was also paired with the LYP functional²⁰ (B3LYP) and that in turn was used in conjunction with Becke's 1988 exchange functional²¹ (BLYP). Calculations were also performed at the MP2 level of theory;²² all MP2 calculations were frozen core.

Analytical force fields were calculated for both $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ (RHF/aug-cc-pVQZ-PP/6-31G*). These were used by the SHRINK program²³ to calculate accurate estimates of the amplitudes of vibration (u_{h1}), some of which were subsequently refined during the electron diffraction refinement, and also to calculate curvilinear corrections (k_{h1}), which are used to counteract the effects of shrinkage that are associated with the GED experiment.²⁴

Gas-phase electron diffraction (GED)

Data were collected for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ using the Edinburgh gas-phase electron diffraction apparatus.²⁵ An electron wavelength of approximately 6.0 pm was achieved using an accelerating voltage of around 40 kV. Scattering patterns were recorded on Kodak Electron Image films at three nozzle-to-film distances for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ (94.55, 199.49 and 257.01 mm) and two

for $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ (199.49 and 256.88 mm). For $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ it proved impossible to collect data at a shorter distance, at which a higher vapour pressure is generally required. In the case of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$, scattering intensity data were recorded with sample and nozzle temperatures held at 490 and 520 K, respectively, for the shortest distance, 494 and 507 K for the intermediate distance and 483 and 494 K for the longest distance. The variation in nozzle temperature of 26 K, whilst larger than would normally be expected, will have no significant implications for the final results. For $\text{Bi}_2(\text{C}_6\text{F}_4)_3$, the sample and nozzle temperatures were 499 and 516 K, respectively, for the shorter distance and 481 and 514 K for the longer distance.

The GED experiment made use of a new reservoir developed in Edinburgh. The reservoir works on a reverse condenser design, with warm air heating the ampoule rather than a heating tape. This design ensures even heating of the sample and eliminates the possibility of hot or cold spots.

The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for all camera distances for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ are given in ESI Table S1†. Also included are the exact electron wavelengths as determined from the scattering patterns for benzene, which were recorded immediately after the patterns for the sample compounds. The scattering intensities were measured using an Epson Expression 1600 Pro flatbed scanner and converted to mean optical densities as a function of the scattering variable, s , using an established program.²⁶ The data-reduction and the least-squares refinement processes were carried out using the ed@ed program²⁷ employing the scattering factors of Ross *et al.*²⁸

Results and discussion

GED study

On the basis of the calculations described previously, a D_{3h} -symmetric model was written to describe the coordinates of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ for use in the GED refinement. An identical model (except that Bi was substituted for Sb) was used in the refinement of the data collected for $\text{Bi}_2(\text{C}_6\text{F}_4)_3$.

In total 11 independent parameters were required to describe the geometry of $\text{Z}_2(\text{C}_6\text{F}_4)_3$ (Z = Sb, Bi). The molecule has four distinct C–C distances [$r\text{C}(6)\text{--C}(1)$, $r\text{C}(1)\text{--C}(2)$, $r\text{C}(2)\text{--C}(3)$ and $r\text{C}(3)\text{--C}(4)$]; see Table 1 and Fig. 1 for atom numbering] and these

Fig. 1 Gas-phase structure of $\text{Z}_2(\text{C}_6\text{F}_4)_3$ (Z = Sb, Bi) with atom numbering. One ring is numbered explicitly and symmetry-related atoms on the other two rings are denoted C(1)' and C(1)'' *etc.*

Table 1 Experimental (r_{hl}) and calculated (r_{c}) geometric parameters for $\text{Z}_2(\text{C}_6\text{F}_4)_3$ ($\text{Z} = \text{Sb, Bi}$)^{a, b}

Independent	Parameter	$\text{Sb}_2(\text{C}_6\text{F}_4)_3$		Restraint	$\text{Bi}_2(\text{C}_6\text{F}_4)_3$		Restraint
		r_{hl}	r_{c}		r_{hl}	r_{c}	
p_1	$r\text{C}-\text{C}$ average	139.2(1)	139.8	—	139.3(2)	139.7	—
p_2	$r\text{C}-\text{C}$ difference 1	2.3(4)	1.3	1.3(5)	0.8(5)	0.8	0.8(5)
p_3	$r\text{C}-\text{C}$ difference 2	−0.4(2)	−0.5	−0.5(2)	−0.9(3)	−0.4	−0.4(3)
p_4	$r\text{C}-\text{C}$ difference 3	0.4(2)	0.1	0.1(2)	0.2(2)	0.0	0.0(2)
p_5	$r\text{C}-\text{F}$ average	133.8(2)	133.8	—	133.0(3)	134.0	—
p_6	$r\text{C}-\text{F}$ difference	2.1(4)	1.4	1.4(5)	1.8(5)	1.5	1.5(5)
p_7	$r\text{Z}-\text{C}$	214.4(1)	213.4	—	222.9(3)	222.9	—
p_8	$\angle\text{C}(2)-\text{C}(3)-\text{F}$	120.5(4)	120.9	—	120.5(5)	121.0	—
p_9	$\angle\text{C}(1)-\text{C}(2)-\text{F}$	121.8(3)	120.6	—	121.9(4)	120.7	—
p_{10}	$\angle\text{C}(6)-\text{C}(1)-\text{C}(2)$	118.7(1)	119.1	—	120.0(2)	119.2	—
p_{11}	$\angle\text{C}(6)-\text{C}(1)-\text{Z}$	124.0(1)	124.1	—	124.8(1)	125.0	—
<i>Dependent</i>							
p_{12}	$r\text{C}(6)-\text{C}(1)$	140.9(4)	140.8	—	139.9(5)	140.3	—
p_{13}	$r\text{C}(1)-\text{C}(2)$	138.3(2)	139.2	—	138.5(3)	139.2	—
p_{14}	$r\text{C}(2)-\text{C}(3)$	138.9(2)	139.7	—	139.5(2)	139.6	—
p_{15}	$r\text{C}(3)-\text{C}(4)$	138.5(2)	138.6	—	139.3(3)	139.6	—
p_{16}	$r\text{C}(3)-\text{F}$	132.8(3)	133.1	—	132.1(4)	133.2	—
p_{17}	$r\text{C}(2)-\text{F}$	134.9(2)	134.5	—	133.9(4)	134.7	—
p_{18}	$\angle\text{C}(1)-\text{C}(2)-\text{C}(3)$	122.1(3)	121.5	—	120.1(4)	121.5	—
p_{19}	$\angle\text{C}(2)-\text{C}(3)-\text{C}(4)$	119.2(1)	119.3	—	119.9(3)	119.3	—
p_{20}	$\angle\text{C}(1)-\text{Z}-\text{C}(1)$	91.8(1)	91.6	—	90.6(1)	90.4	—

^a Refers to [MP2/aug-cc-pVQZ-PP/6-311G*] calculation for both $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$. ^b Distances (r) are in pm and angles ($\angle$) in degrees. See text for parameter definitions and Fig. 1 for atom numbering. The figures in parentheses are the estimated standard deviations, as derived from the least-squares refinement, of the last digits.

were described using a simple average of the four (p_1) and three difference parameters (p_{2-4}), which were defined as follows:

$$p_2 = [r\text{C}(6)-\text{C}(1)] - (\{[r\text{C}(1)-\text{C}(2)] + [r\text{C}(2)-\text{C}(3)] + [r\text{C}(3)-\text{C}(4)]\} / 3),$$

$$p_3 = [r\text{C}(1)-\text{C}(2)] - (\{[r\text{C}(2)-\text{C}(3)] + [r\text{C}(3)-\text{C}(4)]\} / 2),$$

and

$$p_4 = \{[r\text{C}(2)-\text{C}(3)] - [r\text{C}(3)-\text{C}(4)]\} / 2.$$

The two different C–F bond lengths were described using a simple average and the difference between the two ($p_{5,6}$). The final distance parameter that was employed in the model was $r\text{Z}-\text{C}$ (p_7), where Z is the appropriate Group 15 heteroatom. The four angle parameters that were required to complete the model were $\angle\text{C}(2)-\text{C}(3)-\text{F}$ (p_8), $\angle\text{C}(1)-\text{C}(2)-\text{F}$ (p_9), $\angle\text{C}(6)-\text{C}(1)-\text{C}(2)$ (p_{10}) and $\angle\text{C}(6)-\text{C}(1)-\text{Z}$ (p_{11}).

Starting parameters were taken from the MP2/aug-cc-pVQZ-PP/6-311G* calculations and all 11 independent geometric parameters for both compounds were refined using a least-squares refinement method. Restraints were applied, as described in the SARACEN method,²⁹ only to the four difference parameters used in each model. Additionally, 15 amplitudes of vibration were refined for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ (two were restrained) and 14 were refined for $\text{Bi}_2(\text{C}_6\text{F}_4)_3$, with four requiring to be restrained. See Table S2† for lists of amplitudes of vibration for both molecules.

Each refinement has an associated goodness of fit that is expressed as an R factor. For $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ $R_{\text{G}} = 0.055$ ($R_{\text{D}} = 0.034$) and for $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ $R_{\text{G}} = 0.061$ ($R_{\text{D}} = 0.037$). The success of a refinement can also be gauged from the fit of the radial-distribution and experimental – theoretical difference curves shown in Figs. 2

Fig. 2 Experimental radial-distribution curve and theoretical – experimental difference curve for the refinement of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2) / (Z_{\text{Sb}} - f_{\text{Sb}})(Z_{\text{C}} - f_{\text{C}})$; $r\text{Sb}-\text{C}$, sitting at the saddle point of a partially obscured double peak, is marked (*) for clarity.

and 3. The least-squares correlation matrices are given in Tables S3 and S4† and contain some relatively large correlation factors, which are expected this type of molecule. The molecular-scattering intensity curves are shown in Fig. S1 and S2 and coordinates from the final GED refinements are given in Tables S5 and S6†.

It is worth noting that, as is routine nowadays, the scattering factors used were complex (*i.e.* they contain both a real and an imaginary factor).²⁸ This is particularly important for the

Fig. 3 Experimental radial-distribution curve and theoretical – experimental difference curve for the refinement of $\text{Bi}_2(\text{C}_6\text{F}_4)_3$. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_{\text{Bi}} - f_{\text{Bi}})(Z_{\text{C}} - f_{\text{C}})$.

refinement of data collected for molecules such as the ones described here. The presence in a molecule of very heavy atoms (Sb and Bi) with relatively light atoms (C, F) gives rise to a relativistic phase effect. This manifests itself as a double peak in the radial-distribution curve. By using complex scattering factors, the theoretical model can account for the double peak, rather than a single peak, which would lead to huge errors in the structure determination. On close inspection of, for example, Fig. 2 it can be seen that the broad peak at about 200–260 pm appears to have a shoulder but that no distances (represented by sticks) are under the shoulder to account for its existence. However, the stick representing the Sb–C distance (214 pm; marked (*) in Fig. 2) is positioned in the saddle point of a double peak. The right-hand side of the double peak is overlapped by a stronger peak representing various distances at about 250 pm. A similar phenomenon is observed for the Bi–C distance in Fig. 3, and, in fact, occurs for every distance between Sb or Bi and a lighter atom.

The D_{3h} models that were written for both compounds fit the experimental data excellently. That this high symmetry is observed in the gas phase, contrary to the findings of a crystallographic study of $\text{As}_2(\text{C}_6\text{F}_4)_3$,⁵ adds weight to the theory that the distortions observed in 1,6-diarsatriptycene were attributable to packing forces.

Ab initio and DFT studies

During this project a considerable amount of work has been directed towards calculating accurately the structures of 1,6-disubstituted triptycenes $[\text{Z}_2(\text{C}_6\text{F}_4)_3]$ ($\text{Z} = \text{Sb}, \text{Bi}$). Relatively little work exists where methods of calculation and types of basis set have been tested for all p-block elements, hence the need to perform such a comprehensive search for a suitable calculation.

As described in the Experimental, various levels of theory and pseudopotential basis sets were tested (see Table 2). The validity of these calculations will be assessed using the experimental (GED) structures determined above.

The coordinates for the calculated geometries of $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ using each of MP2, B3PW91, B3LYP and BLYP with both the LanL2DZ and aug-cc-pVQZ-PP ECPs are given in Tables S7–S14†.

All of the methods were reasonably good at calculating the values of the ring parameters and also the C–Sb–C angle, but the calculated Sb–C and Sb...Sb distances were longer than the experimentally determined values in almost every case. For some methods this discrepancy was almost 7 pm for the bonded distance and 9 pm for the non-bonded distance, with the BLYP method performing poorly with both of the pseudopotentials that were tested. The best results were obtained using the MP2/aug-cc-pVQZ-PP/6-311G* combination, giving $r_{\text{Sb–C}}$ to within 1 pm and $r_{\text{Sb...Sb}}$ to within approximately 1 pm. A calculation was also performed including a diffuse function on the C and F atoms (6-311+G*) but this was found to have little effect (maximum 0.1 pm, 0.1°) on any parameter. Increasing the size of the basis set on Sb to quintuple- ζ (aug-cc-pV5Z-PP) had a similarly negligible effect on the structure.

Table 2 Selected GED parameters (r_{h}) and calculated parameters (r_{c}) for $\text{Sb}_2(\text{C}_6\text{F}_4)_3$ and $\text{Bi}_2(\text{C}_6\text{F}_4)_3$ at different levels of theory with the 6-311G* basis set on C and F and comparing the large-core (LC) LanL2DZ and small-core (SC) aug-cc-pVQZ-PP pseudopotential basis sets on the heavy atoms^a

	Experimental	Theoretical							
		MP2		B3PW91		B3LYP		BLYP	
	GED	LC	SC	LC	SC	LC	SC	LC	SC
$\text{Sb}_2(\text{C}_6\text{F}_4)_3$									
$r_{\text{Sb–C}}$	214.4(1)	217.1	213.4	218.7	216.7	219.2	218.4	221.2	221.1
$r_{\text{Sb...Sb}}$	380.6(2)	385.4	380.1	384.4	381.9	385.6	384.9	389.0	389.8
$\angle \text{C–Sb–C}$	91.8(1)	91.4	91.6	91.8	91.9	91.8	91.7	91.7	91.5
$r_{\text{C(1)–C(6)}}$	140.9(4)	140.9	140.8	140.0	140.2	140.4	140.3	141.3	141.2
$r_{\text{C(2)–F}}$	134.9(2)	134.6	134.5	134.2	134.4	135.0	135.2	136.8	137.1
$\text{Bi}_2(\text{C}_6\text{F}_4)_3$									
$r_{\text{Bi–C}}$	222.9(3)	224.4	222.9	225.7	226.6	226.4	225.6	228.3	231.6
$r_{\text{Bi...Bi}}$	394.4(4)	398.2	395.9	396.1	397.6	397.1	396.2	400.2	404.8
$\angle \text{C–Bi–C}$	90.6(1)	90.3	90.4	90.9	90.8	91.0	90.9	90.9	90.7
$r_{\text{C(1)–C(6)}}$	139.9(5)	140.6	140.3	139.8	139.6	140.1	139.8	141.0	140.7
$r_{\text{C(2)–F}}$	133.9(4)	135.0	134.7	134.7	134.7	135.3	134.6	137.2	137.4

^a Distances are in pm, angles in degrees. See Fig. 1 for atom numbering.

It should be emphasised that the distances obtained from GED (r_{hl}) and from quantum chemical calculations (r_{c}) are not identical. A more accurate comparison can be made by subtracting a term for the GED distance to account for the anharmonicity of the motion of two atoms relative to one another. This anharmonic term is given in eqn (1), where u is the amplitude of vibration and a is an anharmonicity constant.

$$\text{anharmonic term} = \frac{3au^2}{2} \quad (1)$$

The value of a is given in the SHRINK program²³ output file where the values are those calculated by Sipachev.³⁰ For $r\text{Sb}-\text{C}$ $a = 0.017 \text{ pm}^{-1}$ and, using eqn (1), the anharmonic term for $r\text{Sb}-\text{C}$ is approximately 0.4 pm. Applying this to the GED distance gives a value of 214.0 pm, even closer to the value calculated using the MP2 and small-core pseudopotential combination. For non-bonded distances a is approximately zero and so any anharmonic correction to the $\text{Sb} \cdots \text{Sb}$ distance is negligible.

The same set of test calculations was performed to determine the most suitable method for calculating the structure of $\text{Bi}_2(\text{C}_6\text{F}_4)_3$. In this instance, Table 2 shows that the MP2 calculation using the small-core pseudopotential (aug-cc-pVQZ-PP) and the 6-311G* basis set gave a result (224.4 pm) that matched very accurately the GED value for $r\text{Bi}-\text{C}$ [222.9(3) pm] and a $\text{Bi} \cdots \text{Bi}$ distance that was calculated to be 1.5 pm longer than the GED value, which one method had overestimated by 10 pm. Applying an anharmonic correction term, as defined in eqn (1), shortens $r\text{Bi}-\text{C}$ to 222.0 pm. This value is still closer to the MP2 calculated values than those obtained from any of the DFT methods. (Coordinates for all methods tested are in Tables S15–S22†.) The B3PW91/aug-cc-pVQZ/6-311G* calculation, which performed relatively well for Sb, predicts $r\text{Bi}-\text{C}$ better than most methods but models $r\text{Bi} \cdots \text{Bi}$ relatively poorly (3 pm longer than the GED value).

Conclusions

The availability of experimental GED data has allowed conclusions to be drawn as to the suitability of different methods of calculating geometries and has allowed comparison of the use of different basis sets. In this case MP2 calculations proved best, albeit with the footnote that they were very time-consuming and computationally demanding. However, the most significant finding during this work was the improved performance of the aug-cc-pVQZ-PP ECP over the larger core basis set LanL2DZ. It must be concluded that large-core pseudopotentials should be used with caution as the inclusion of so few electrons in the valence shell can have a sizable effect on the quality of calculated geometries.

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