

## **Supramolecular architecture of $[\text{AsPh}_2\text{Br}_2]_2[(\text{Br}_3)^-\dots(\text{Br}_2)\dots(\text{Br}_3)^-]$ obtained by bromination of $(\text{AsPh}_2)_2\text{S}$**

Luminita Silaghi-Dumitrescu,<sup>a\*</sup> Amr A.A. Attia,<sup>a</sup> Radu Silaghi-Dumitrescu,<sup>a</sup> Alexander J. Blake,<sup>b</sup> D. Bryan Sowerby<sup>b</sup>

<sup>a</sup>*Department of Chemistry, Babes-Bolyai University, 1, Kogalniceanu Str., 400084, Cluj-Napoca, Romania*

<sup>b</sup>*School of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.*

\*Corresponding author e-mail: [lusi@chem.ubbcluj.ro](mailto:lusi@chem.ubbcluj.ro);

## Abstract

Bromination of  $(\text{AsPh}_2)_2\text{S}$  leads to cleavage of the sulfide bridge to give  $\text{AsPh}_2\text{Br}$  when 1 mol of bromine is used but with 2 mols the product is the polybromide,  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$ , containing the previously unknown  $[\text{AsPh}_2\text{Br}_2]^+$  cation and a rare  $[\text{Br}_3]^- \dots [\text{Br}_2] \dots [\text{Br}_3]^-$  ensemble whose short (yet not covalent)  $\text{Br}_2 \dots \text{Br}_3$  contacts have previously supported tentative description as an octabromide  $\text{Br}_8^{2-}$  anion. X-ray crystallography shows that the compound has a three dimensional supramolecular structure based on cooperativity of weak intermolecular  $\text{C-H} \dots \pi$ ,  $\text{C-H} \dots \text{Br}$  hydrogen bonds and secondary  $\text{Br} \dots \text{Br}$  interactions in the solid state. The electronic structure and the stability of the  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  are rationalized using DFT and HF calculations and molecular orbital considerations.

Keywords: arsenic, bromine,  $\text{Br}_8$ , arsonium, crystal structure, DFT, supramolecular

## 1. Introduction

We have been interested for some years in reactions of the arsenic(III) bridged compounds,  $(\text{AsPh}_2)_2\text{E}$  where  $\text{E} = \text{O}$  or  $\text{S}$ , with both oxidising agents and transition metal compounds. Oxidation with either *t*-butyl hydroperoxide or sulfur led to the mono-oxidation products,  $\text{AsPh}_2(\text{E})\text{EAsPh}_2$ , but the corresponding di-oxidation products were hydrolytically unstable and could not be isolated.[1] Attempts to produce mono- and di-oxidation products,  $(\text{AsPh}_2\text{X}_2)\text{O}(\text{AsPh}_2)$  and  $(\text{AsPh}_2\text{X}_2)_2\text{O}$  from the reaction of  $(\text{AsPh}_2)_2\text{O}$  with halogens were also unsuccessful. Even at temperatures as low as  $-78^\circ\text{C}$ , the  $\text{As}-\text{O}-\text{As}$  linkage was always broken and only monoarsenic species were isolated. With an excess of elemental chlorine the oxidation products were diphenylarsenic(V) trichloride,  $\text{AsPh}_2\text{Cl}_3$ , and dihydroxodiphenylarsonium chloride,  $[\text{AsPh}_2(\text{OH})_2]\text{Cl}$ . [2] Oxidation of  $(\text{AsPh}_2)_2\text{O}$  with elemental chlorine or with  $\text{SO}_2\text{Cl}_2$  in a 1:1 molar ratio gave the same dihydroxodiphenylarsonium chloride accompanied by diphenylarsenic(III) chloride  $\text{AsPh}_2\text{Cl}$ . With an excess of  $\text{SO}_2\text{Cl}_2$ , diphenylarsenic(V) chloride,  $\text{AsPh}_2\text{Cl}_3$ , and dihydroxodiphenylarsonium hydrogensulfate  $[\text{AsPh}_2(\text{OH})_2] [\text{HOSO}_3]$  were the products. [2] Reactions with one mol of bromine gave dihydroxodiphenylarsonium bromide,  $[\text{AsPh}_2(\text{OH})_2]\text{Br}$ , and diphenylarsenic(III) bromide,  $\text{AsPh}_2\text{Br}$ . [3] With two mols of bromine, the course of the reaction was similar, but here both products were arsenic(V) species  $[\text{AsPh}_2(\text{OH})_2]\text{Br}$ , and diphenylarsenic tribromide,  $\text{AsPh}_2\text{Br}_3$ . [3] The  $\text{As}-\text{O}-\text{As}$  bridge was also broken in the reaction of  $(\text{AsPh}_2)_2\text{O}$  with elemental iodine, when diphenylarsenic(III) iodide,

AsPh<sub>2</sub>I,[4] and diphenylarsinic acid, AsPh<sub>2</sub> (O)OH,[5] were separated from the reaction mixture. Reactions of these bridged arsenic(III) compounds with Group 6 metal carbonyls led to products showing a variety of coordination patterns.[6] These reactions have also been investigated theoretically by our group using semiempirical, *ab initio* and DFT methods.[6-8]

In continuation of this work, we now report results of experiments in which (AsPh<sub>2</sub>)<sub>2</sub>S, is oxidised with elemental bromine.

## 2. Experimental

All experiments were carried out using standard Schlenk methods and anhydrous freshly distilled solvents (dichloromethane, toluene and acetonitrile). Experiments were carried out at both room temperature and at -78° to try to define conditions for preservation of the As-S-As bridge. The procedure described below refers to the room temperature experiments in dichloromethane; experiments using other solvents (toluene, acetonitrile) and those at -78° were similar and the products isolated were also the same. Bis(diphenylarsenic) sulfide was prepared according the literature.<sup>18</sup>

### 2.1.Reaction of AsPh<sub>2</sub>-S-AsPh<sub>2</sub> with Br<sub>2</sub> in molar ratio 1:1

The solution obtained by dissolving (AsPh<sub>2</sub>)<sub>2</sub>S (0.49 g, 1.0 mmol) in dichloromethane (10ml) was treated with bromine (0.16 g, 1.0 mmol) with stirring at room temperature. After several minutes a yellow waxy product was formed which was shown to be sulphur. The yellow solution was cannulated and the solvent evaporated slowly in an inert atmosphere to give a yellow oil, identified as AsPh<sub>2</sub>Br. (Found: C, 46.24; H, 3.16. Calc. for C<sub>12</sub>H<sub>10</sub>AsBr: C, 46.60; H, 3.23 %)

### 2.2.Reaction of AsPh<sub>2</sub>-S-AsPh<sub>2</sub> with Br<sub>2</sub> in molar ratio 1:2

Bromine (0.48 g, 3.0 mmol) was added slowly by a syringe to a solution of (AsPh<sub>2</sub>)<sub>2</sub>S (0.735 g, 1.5 mmol) in anhydrous dichloromethane (20 ml). An orange precipitate was formed instantaneously. The supernatant solution was cannulated and the precipitate washed with small amounts of CH<sub>2</sub>Cl<sub>2</sub> (m. pt 132°C). (Found: C, 21.44; H, 1.70. Calc. for [AsPh<sub>2</sub>Br<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>]: C, 20.34; H, 1.42 %. Mass spectrum: m/z 308 [AsPh<sub>2</sub>Br]<sup>+</sup>, 229 [AsPh<sub>2</sub>]<sup>+</sup>, 227 [AsPh<sub>2</sub>- 2H]<sup>+</sup>, 154 [Ph<sub>2</sub>]<sup>+</sup>, 152 [AsPh]<sup>+</sup>). The separated solution was evaporated in a vacuum to give a yellow oil shown to be AsPh<sub>2</sub>Br. Found: C, 46.44; H, 3.06. Calc. for AsPh<sub>2</sub>Br: C, 46.60; H, 3.23 %). Crystals of the orange solid suitable X-ray diffraction were obtained by slow evaporation of a solution in dichloromethane.

### 2.3. Molecular orbital calculations

Geometry optimizations and single point calculations were carried out using the B3LYP DFT functional[9, 10] and the HF method coupled with the Dunning's correlation consistent triple- $\zeta$  basis set aug-cc-pVTZ[11] and with Grimme's dispersion correction D3.[12, 13] The nature of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies to insure that genuine minima were obtained. All calculations were performed using the ORCA 3.03 software package.[14] Molecular orbitals were visualized using the UCSF Chimera package.[15] For selected models, calculations were also performed using the BP86/6-31G\*, B3LYP/6311+G\* and B3PW91/6311+G\* DFT methodologies.[16, 17]

### 2.4. Structure determination for [AsPh<sub>2</sub>Br<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>]

Crystallographic data (cf. CCDC 1563861) are summarised in Table 1, which also includes details of the method of solution and the refinement conditions. Data were corrected for Lorentz and polarisation effects, merged and systematically absent reflections removed; an absorption correction was applied. The structure was solved by direct methods (SHELXS-86) and refined by full matrix least squares (SHELXL-93)[18]; hydrogen atoms were placed at their calculated positions and refined riding on their respective carbon atoms. A standard weighting scheme was applied and a correction was made for extinction.

**Table 1.** Crystallographic data

Empirical formula	C <sub>12</sub> H <sub>10</sub> AsBr <sub>6</sub>
Formula weight	708.59
Crystal size /mm	0.36 x 0.14 x 0.12
Space group	<i>C2/m</i>
<i>a</i> /Å	23.144(8),
<i>b</i> /Å	9.290(3),
<i>c</i> /Å	8.423(3)
$\beta$ / °	90.33(3)
<i>U</i> /Å <sup>3</sup>	1811.0 (11)
<i>Z</i>	8
<i>D<sub>c</sub></i> /Mg/m <sup>3</sup>	82.599
$\mu$ /mm <sup>-1</sup>	15.100

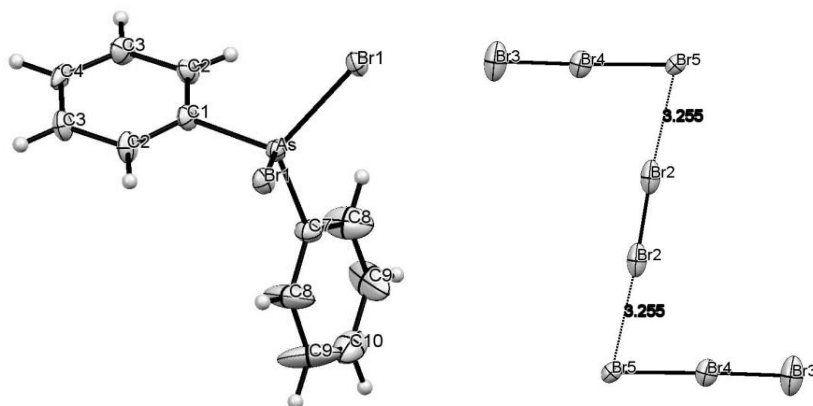
F(000)	1300
$\lambda / \text{\AA}$	0.71073
T/K	150(2)
Reflections collected	2863
$\theta$ range / $^\circ$	2.98 - 25.01 $^\circ$
Index ranges	-27 $\leq h \leq$ 27, 0 $\leq k \leq$ 11, -4 $\leq l \leq$ 10
Independent reflections	1689 [R(int) = 0.041]
Observed reflections	1394 [I $>$ 2 $\sigma$ (I)]
Absorption correction	Numerical (T <sub>min</sub> = 0.094, T <sub>max</sub> = 0.278)
Structure solution	Direct and difference Fourier methods
Data / restraints / parameters	1689/26/101 (least-squares on F <sup>2</sup> )
Final R indices [I $>$ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0725, wR <sub>2</sub> = 0.1871
Final R indices (all data)	R <sub>1</sub> = 0.0879, wR <sub>2</sub> = 0.2067
Goodness-of-fit on F <sup>2</sup>	1.077
Weighting scheme	w=1/[ $\sigma^2(F_o^2) + (0.106P)^2 + 115.90P$ ] where P=(F <sub>o</sub> <sup>2</sup> + F <sub>c</sub> <sup>2</sup> )/3
Final difference map / $\text{\AA}^{-3}$	+2.93 and -2.98

### 3. Results and Discussion

Treatment of (AsPh<sub>2</sub>)<sub>2</sub>S with one mol of bromine gave a single product diphenylarsenic(III) bromide, AsPh<sub>2</sub>Br, but when two mols were added, a yellow precipitate was formed in good yield almost immediately. Elemental analysis pointed to a Br:As:C:H ratio of 6:1:12:10 and the product contained neither sulfur from the starting sulfide nor oxygen from hydrolysis. The reaction was reproducible and the product was stable showing no bromine loss after 6 months. The final formula was established by single crystal X-ray diffraction as [AsPh<sub>2</sub>Br<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>] if, as previously done in references [19-22], the short [Br<sub>3</sub>]<sup>-</sup>...[Br<sub>2</sub>]<sup>-</sup>...[Br<sub>3</sub>]<sup>-</sup> contacts (below the sum of van der Waals radii) are taken as evidence for a single octabromide species. No compound with this composition nor any compound containing the dibromodiphenylarsonium cation has been reported previously. There are only few previously described examples of putative Br<sub>8</sub><sup>2-</sup> anions: the diquinclidinium octabromide,[19] the benzyltriphenylphosphonium octabromide [(Bz)(Ph)<sub>3</sub>P]<sub>2</sub>[Br<sub>8</sub>],[20] [Cu(dafone)<sub>3</sub>]<sup>-</sup>(Br<sub>5</sub>)(Br<sub>8</sub>)<sub>0.5</sub>·CH<sub>3</sub>CN, (dafone = 4,5-Diazafluoren-9-one),[21] [BrC(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>].[22]

#### 3.1. Structure of [Ph<sub>2</sub>AsBr<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>]

The solid-state three-dimensional supramolecular structure of  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  features dibromodiphenylarsonium cations and  $[(\text{Br}_3)_2(\text{Br}_2)]^{2-}$  octabromide dianions as building blocks. Bond lengths and angles are listed in Table 2 and a diagram showing the geometry and atom numbering scheme is given in Figure 1.



**Figure 1.** Diagram showing the structure and atom numbering schemes for (a) the  $[\text{AsPh}_2\text{Br}_2]^+$  cation and (b) the  $[(\text{Br}_3)_2(\text{Br}_2)]^{2-} / [\text{Br}_8]^{2-}$  anion

**Table 2.** Selected bond lengths (Å) and angles (°) in  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$ . Primed and double primed atoms are related by the symmetry operations:  $-x+1, -y+2, -z+1$ , and  $x, -y+1, z$ , respectively

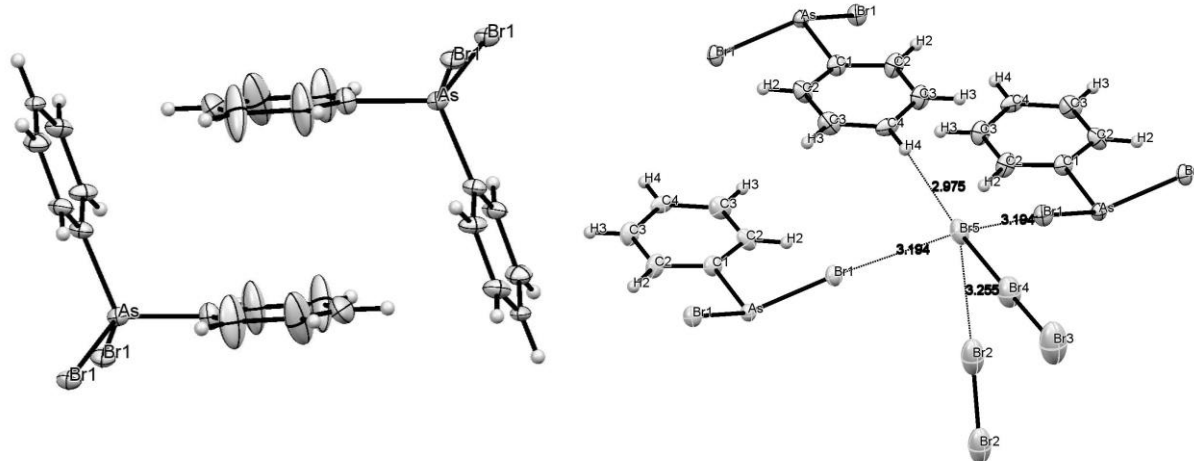
As-Br(1)	2.268(2)
As-C(1)	1.924(16)
As-C(7)	1.911(17)
Br(2)-Br(2')	2.369(6)
Br(3)-Br(4)	2.389(4)
Br(4)-Br(5)	2.672(3)
Br(2)...Br(5')	3.255(4)
Br(1)-As-C(1)	108.9(3)
Br(1)-As-C(7)	107.9(3)
C(1)-As-C(7)	111.9(8)
Br(1)-As-Br(1'')	111.4(1)
Br(3)-Br(4)-Br(5)	178.2(2)
Br(4)-Br(5)...Br(2')	76.8(1)

The dibromodiphenylarsonium cation is tetrahedral and lies on a mirror plane with bond angles in the range 107.9 (3)–111.9(8)°. The unique As-Br separation, 2.268(2) Å, is marginally shorter than the equatorial distance in AsPh<sub>2</sub>Br<sub>3</sub> [2.286(2) Å] and, as expected, substantially shorter than the corresponding axial distance [2.518(2) Å]. [2] Axial distances for AsPh<sub>3</sub>Br<sub>2</sub>[23] and As(neo-pentyl)<sub>3</sub>Br<sub>2</sub>[24] are 2.551 and 2.564 Å, respectively. As-Br separations in the isoelectronic As(III) anion [Ph<sub>2</sub>AsBr<sub>2</sub>]<sup>-</sup>, as expected, are even longer 2.674(1) Å. [25] As-C bond lengths are normal.

The [(Br<sub>3</sub>)<sub>2</sub>(Br<sub>2</sub>)]<sup>2-</sup> octabromide dianion, also lying on a mirror plane, is Z-shaped as shown in Figure 1, and can probably best be described as formed from two effectively linear Br<sub>3</sub><sup>-</sup> anions interconnected by a Br<sub>2</sub> molecule. Within the anion there are five short Br–Br contacts, i.e. a Br(2)-Br(2') contact of 2.369(6) Å, two Br(3)-Br(4) separations of 2.389(4) Å, and two Br(4)-Br(5) contacts of 2.672(2) Å; in addition there are two longer Br(2)-Br(5) contacts of 3.255(4) Å. These Br-Br contacts are, in fact, very similar to those in the related quinuclidine compound but the Br(4)-Br(5)-Br(2) angles differ widely – 76.8(1)° in the present compound compared with 106.79(4)° in the quinuclidine analogue - probably as a consequence of different crystal packing forces (see later).

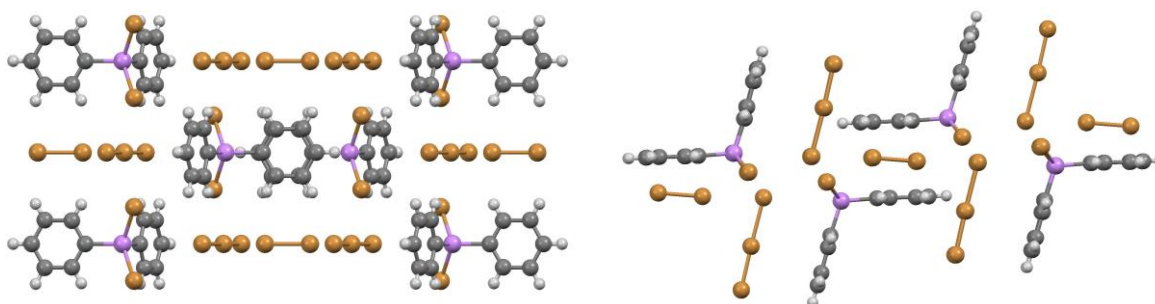
There are further weak solid state interactions which link cations and anions in [AsPh<sub>2</sub>Br<sub>2</sub>]<sub>2</sub>[Br<sub>8</sub>] to generate a three dimensional supramolecular structure. These can best be understood initially by considering two motifs: firstly dimer formation between two dibromodiphenylarsonium cations and secondly sheet formation from Br<sub>8</sub><sup>2-</sup> anions.

As shown in Figure 2a, the cations form dimers via short (C)H...π interactions (2.764 Å), which are then further interlinked in pairs (see Figure 2(b)) by two Br(1)...Br(5)...H(C) bridges. Separations here are 3.194 Å [Br(1)...Br(5)] and 2.975 Å [Br(5)-H(C)].









**Figure 4.** Supramolecular structure, (a) viewed along the c axis, (b) viewed along the b axis.

### 3.2. Calculated molecular structure of $[(\text{Br}_3)_2(\text{Br}_2)]^{2-} / \text{Br}_8^{2-}$

Table 3 contains a summary of DFT-calculated Br-Br distances in a  $\text{Br}_8^{2-}$  anion and, for comparison purposes, there are also experimental values for a number of other (previously assigned/reported) polybromide species. Quinulidine tribromide ( $\text{QBr}_3$ ) was chosen as a  $\text{Br}_3^-$  example as it contains the same cation as one of the known octabromides. The  $\text{Br}_8^{2-}$  geometries listed in Table 3 feature a planar *anti* conformation. A *syn* conformation (not shown) was also identified as a local minimum (0.1-0.9 kcal/mol higher in energy compared to *anti*, depending on the density functional employed).

The main structural features of the  $\text{Br}_8^{2-}$  anion in solid state are retained in isolated ions: i.e. a central  $\text{Br}_2$  unit loosely connected to two terminal  $\text{Br}_3^-$  anions. The more opened gas phase (DFT) structure where the  $\text{Br}(2)\text{-Br}(3)\text{-Br}(4)$  angle is  $100^\circ$  is likely due to relaxation on removing the ion from the crystal. The sensitivity of this angle to the nature of the counterion is supported by the values found in solid state for  $\text{QBr}_8$   $106^\circ$ <sup>9</sup> and  $76.8^\circ$  in this work. Elongation of the two  $\text{Br}(2)\text{-Br}(5)$  contacts to  $3.7 \text{ \AA}$  (i.e., at the limit of the sum of van der Waals radii), was found to cost 4.6 kcal/mol (B3LYP/ aug-cc-pVTZ) – implying that the strength of a  $\text{Br}_2\text{-Br}_3^-$  interaction is  $\sim 2.3$  kcal/mol. By the same methodology, the  $\text{Br}(2)\text{-Br}(3)$  contact discussed above cf. Figure 3 (also between a  $\text{Br}_2$  and a  $\text{Br}_3^-$  moiety) was found to be 0.4 kcal/mol.

**Table 3.** Experimental and calculated Br-Br contacts in  $\text{Br}_8^{2-}$  and related polybromide species.

Compound	Bonds in $\text{Br}_3^-$ fragments ( $\text{\AA}$ )		Bonds in $\text{Br}_2$ units	Secondary bonds	Br(4)- Br(5)-Br(2) angles
$[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$	2.389(4)	2.672(3)	2.369(6)	3.225	76.80(10)
$2\text{QBr}_8$ [19]	2.432(1)	2.663(1)	2.354(3)	3.172(1)	106.79(4)

$[(\text{Bz})(\text{Ph})_3\text{P}]_2[\text{Br}_8]$	251.8	249.8	230.8	310.1	88.0
$[\text{Cu}(\text{dafone})_3]-(\text{Br}_5)(\text{Br}_8)_{0.5}\cdot\text{CH}_3\text{CN}$	2.5213(9)	2.5731(9)	2.3588(12)	3.0374(10)	82.75(3)
$[\text{BrC}(\text{NMe}_2)_2]_2[\text{Br}_8]$	2.415	2.717		3.018	145.2
$\text{Br}_8^{2-}$ , B3LYP/aug-cc-pVTZ	2.560/2.569	2.643/2.647	2.414	3.125	100.5
$\text{Br}_3^-$ , B3LYP/aug-cc-pVTZ	2.622	2.622			
$\text{Br}_2$ , B3LYP/aug-cc-pVTZ			2.280		
$\text{QBr}_3$ [19]	2.457(2)	2.652(2)			
$\text{Br}_{10}^{2-}$ [26]	2.91	2.94	2.74	3.47 3.50	
2D Network[27]			2.411(3) 2.357(2)	3.041(3) 3.108(3) 3.197(3)	
$\text{Br}_2$ [28]			2.301(1)		

Based on the Br-Br distances, the  $\text{Br}_8^{2-}$  moiety may be described as a combination of a central  $\text{Br}_2$  with two symmetrically placed  $\text{Br}_3^-$  moieties. For  $\text{Br}_2$ , it is straightforward to anticipate that the two occupied  $\pi^*$  orbitals and the empty  $\sigma^*$  would participate in bonding with  $\text{Br}_3^-$ . On the other hand, the  $\text{Br}_3^-$  frontier orbitals are more complex – and any discussion thereof may benefit from comparison with other triatomics of interest such as  $\text{I}_3^-$ ,  $\text{N}_3^-$ ,  $\text{O}_3$  and others. Figure 5 shows the general molecular orbital diagram for a triatomic moiety, drawn as a combination between a central main group element and a pair of two identical atoms; for this latter pair, the contributing orbitals are simple linear combinations (in-phase and out-of-phase) of the respective s and p orbitals. Bonding, antibonding and non-bonding components may be identified in this diagram. For  $\text{Br}_3^-$ , with a total of 22 electrons, all orbitals except  $\sigma^*$  are occupied. The non-bonding molecular orbitals offer a charge asymmetry, as the central atom is formally not involved in them; this is in line with the partial atomic charges computed for  $\text{Br}_3^-$  – where the terminal atoms harbor ~0.50 units of charge and the central atom is almost electrically neutral. Similar charge imbalances are computed for other triatomics –  $\text{F}_3^-$ ,  $\text{Cl}_3^-$ ,  $\text{I}_3^-$ ,  $\text{O}_3$  and its

congeners  $S_3$  and  $Se_3$ ,  $N_3^-$  and its congeners  $P_3^-$  and  $As_3^-$ .

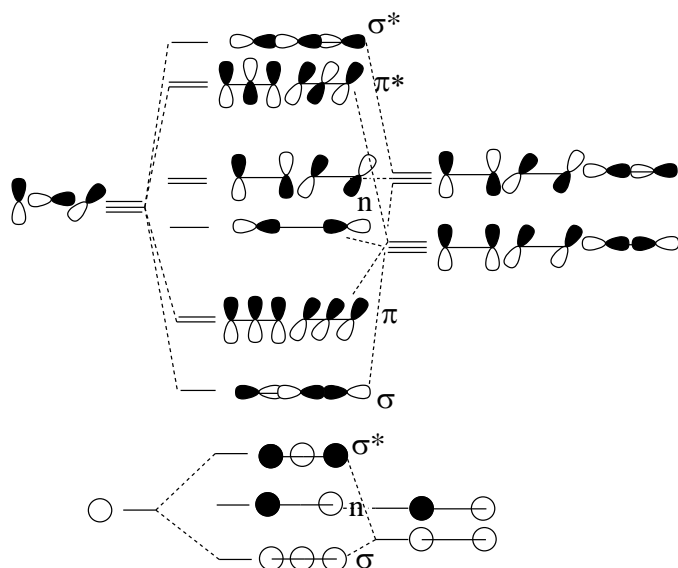


Figure 5. General molecular orbital diagram for a homo-triatomic moiety.

The diagram in Figure 5 would fail to predict the observed linear geometry of  $N_3^-$  since the respective 16 electron-configuration would lead to a situation where only one of the two degenerate  $n(\pi)$  orbitals would be occupied – prompting a Jahn-Teller distortion which can only occur via loss of linearity. The diagram would also fail to predict the experimentally-known bent geometry for  $O_3$ , since the 18-electron configuration would not lead to a degenerate state and hence would not justify loss of linearity. However, the computed molecular orbitals for  $N_3^-$  and  $O_3$  reveal an inversion of relative energies for some of the frontier orbitals: the single  $n(\sigma)$  orbital gains in energy and is now higher than the two  $\pi^*$  orbitals; this leaves the  $O_3$  in a degenerate state with respect to the  $\pi^*$  orbitals (explaining its non-linearity as a consequence of Jahn-Teller distortion) whereas the  $N_3^-$  avoids this situation since its two degenerate HOMO orbitals are both occupied. This inversion of orbital energies seen in  $O_3$  and  $N_3^-$  is also observed in  $S_3$ ,  $P_3^-$  and  $As_3^-$  but not in  $Se_3$  or in the trihalide anions. Furthermore, the energy separation between the two sets of orbitals may be seen to vary with the covalent radius of the element for group 5 and group 6 elements but not for group 7 elements, as seen in Figure 6. For the group 5 and group 6 triatomics, the holes in the antibonding  $\pi$  orbitals lead to shorter bond lengths so much so that the s orbital of the central atom finds itself in close enough contact with the formally  $n(\sigma)$  molecular orbital to mix and thus raise the energy of the latter. Supporting Information Figure S1 shows graphical representations of the degrees of mixing for several of these species. An extreme illustration of this trend may be seen in the case of  $Se_3$ , where the interatomic distance is apparently so large that

mixing of the s orbital becomes sufficiently small to reverse the order of orbitals and to avoid the degeneracy problem – so that  $\text{Se}_3$  is, unlike  $\text{O}_3$  or  $\text{S}_3$ , linear; nevertheless, the energy gap remains very low so that one may anticipate that external factors may cause  $\text{Se}_3$  to become non-linear. Similar considerations can be made on group 14 triatomic units – where if one equates the C-H bonds with lone pairs then one obtains the allene as isoelectronic with azide with 16 electrons (hence its linearity) while the allyl radical, with one more electron, has partial occupation in the degenerate  $\pi^*$  pair of orbitals and is hence bent as a result of a Jahn-Teller distortion. For the halide trianions, there is no net  $\pi$  bonding and all relevant frontier orbitals are occupied, so that there is no possibility of Jahn-Teller distortions. Hence,  $\text{Br}_3^-$  and its halogen congeners are all linear.

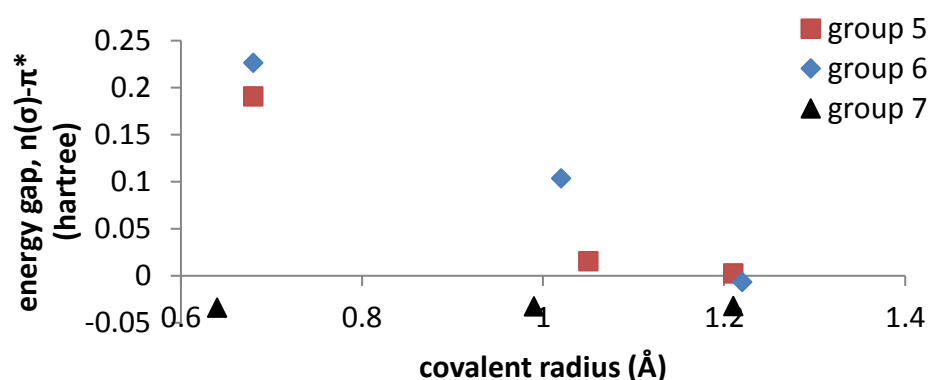
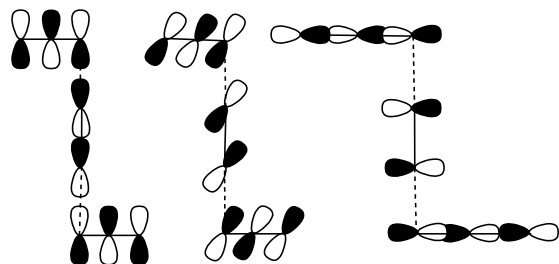


Figure 6. Energy difference between the  $n(\sigma)$  and  $\pi^*$  orbitals in  $\text{F}_3^-$ ,  $\text{Cl}_3^-$ ,  $\text{I}_3^-$ ,  $\text{O}_3$ ,  $\text{S}_3$ ,  $\text{Se}_3$ ,  $\text{N}_3^-$ ,  $\text{P}_3^-$  and  $\text{As}_3^-$ .

The frontier molecular orbitals of the  $[(\text{Br}_3)_2(\text{Br}_2)]^{2-} / \text{Br}_8^-$  moiety, illustrated in Figure 7, reveal simple expected interactions between the set of frontier orbitals of the central  $\text{Br}_2$  moiety and the  $\pi^*$  and  $\sigma^*$  orbitals of the two  $\text{Br}_3^-$  units. As illustrated in Scheme 1, optimal overlap between these the  $\text{Br}_3^-$  and the  $\text{Br}_2$  orbitals can either occur at  $90^\circ$  or at  $180^\circ$ . Of the  $\text{Br}_3^-$  and  $\text{Br}_2$  frontier orbitals, only the  $\text{Br}_2 \sigma^*$  and the  $\text{Br}_3^- \sigma^*$  are empty – and hence only these two orbitals may contribute to net bonding. Indeed, HOMO and HOMO-3 in Figure 7 feature distinguishable  $\text{Br}_2 \sigma^*$  contributions. This charge donation into  $\text{Br}_2 \sigma^*$  is reflected in the elongation of the central Br-Br bond relative to an isolated  $\text{Br}_2$  molecule by  $\sim 0.13 \text{ \AA}$  (from 2.41 to 2.28  $\text{ \AA}$ ). However, as LUMO and LUMO+3 feature even stronger  $\text{Br}_2 \sigma^*$  contributions than HOMO and HOMO-3, one may conclude that the  $\text{Br}_2 \sigma^*$  remains largely unoccupied (or else, indeed, the Br-Br bond would formally cease to exist). Conversely, as the  $\text{Br}_3^- \pi^*$  orbitals are transferring part of their electron density to  $\text{Br}_2$  via these HOMO and HOMO-3 interactions, one expects that the internal bonds of the  $\text{Br}_3^-$  moiety would be stronger than in an isolated  $\text{Br}_3^-$  moiety; however,

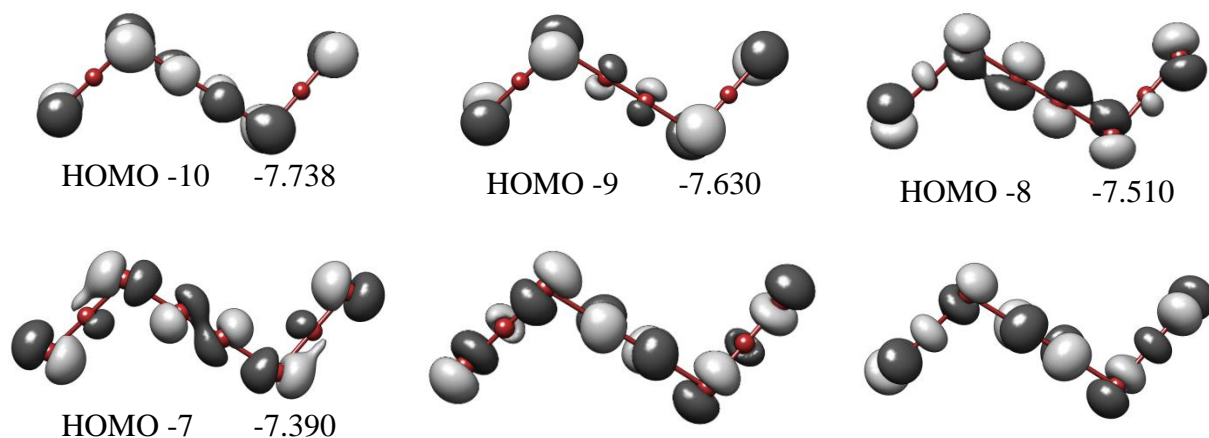
here the effects are much smaller than on the  $\text{Br}_2$  moiety: indeed: from 2.62 Å in  $\text{Br}_3^-$ , the Br-Br bonds are shortened on average by 0.3 Å in  $\text{Br}_8^{2-}$  (to 2.56/2.57 Å for the terminal bonds, 2.64/2.65 for the other ones).



Scheme 1

The partial atomic charges in Table 4 reveal that the  $\text{Br}_3^-$  and  $\text{Br}_2$  moieties are essentially unaffected by complexation to each other: only a total of  $\sim 0.1$  charge units are transferred to the from the two  $\text{Br}_3^-$  to  $\text{Br}_2$ ; this is in line with the fact that in  $\text{Br}_8^{2-}$  the  $\text{Br}_2$   $\sigma^*$  orbital (the only one available to receive charge donated by the tribromide anions) has stronger contributions to the LUMO set of orbitals than to the HOMO set of orbitals. Within the  $\text{Br}_3^-$  moiety, complexation to  $\text{Br}_2$  causes a negligible degree of asymmetry/polarization, affecting the partial atomic charges by less than 0.05 units.

While the internal  $100^\circ$  bond angles within  $\text{Br}_8^{2-}$  are nearly optimal for orbital overlap cf. Scheme 1, distortions of these angles to a range of values seen in the crystal structures appears to only marginally affect the electronic structure. Thus, Table 4 shows that contraction of the angle to  $75^\circ$  or expansion to  $140^\circ$  lead to changes of at most 0.01-0.03 units in the individual partial atomic charges; the energy difference between the computed global minimum and the two hypothetical distorted structures is 2.8 kcal/mol for  $75^\circ$  and 1.5 kcal/mol for  $140^\circ$ . On the other hand, compression of the angle below  $75^\circ$  would entail the central atom of the  $\text{Br}_3$  moieties breaching the van der Waals radius of the nearest  $\text{Br}_2$  bromine.



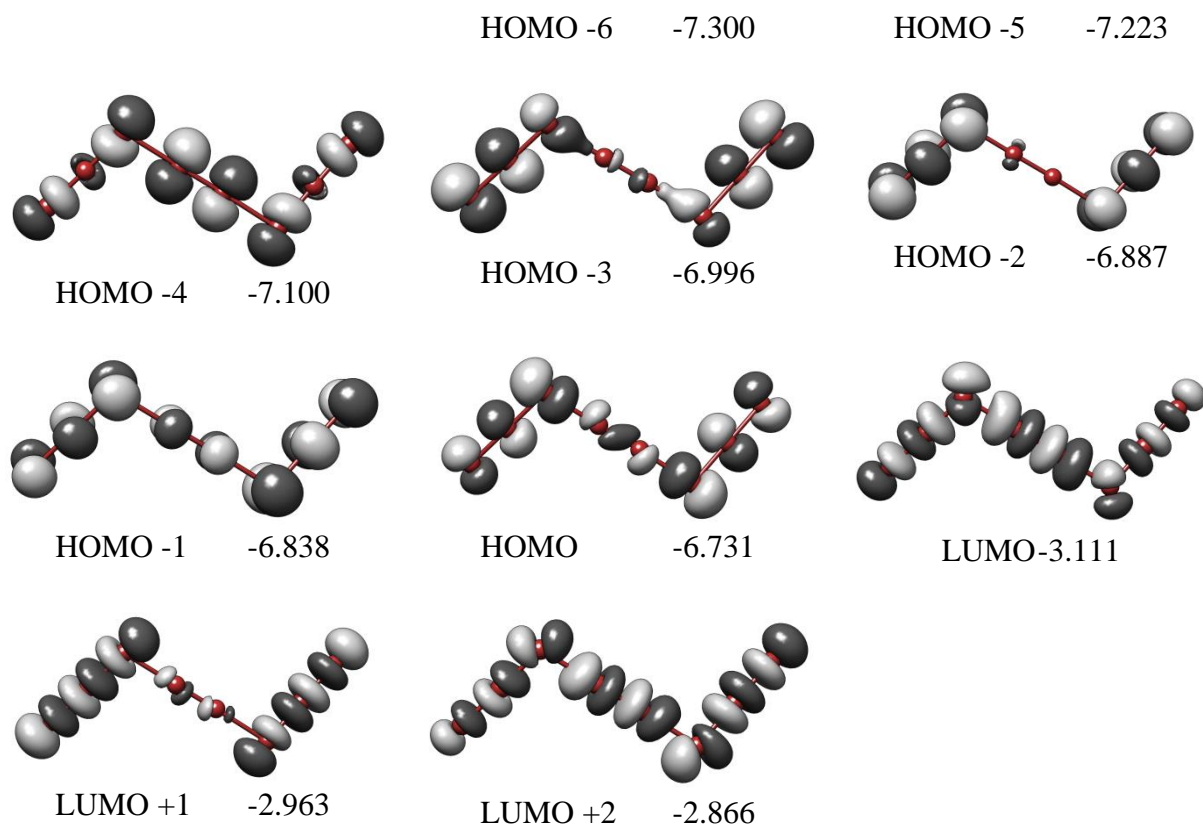


Figure 7. Frontier molecular orbitals for  $\text{Br}_8^{2-}$  as computed by B3LYP/aug-cc-pVTZ.

Each terminal atom of a  $\text{Br}_3^-$  moiety in the crystal structure is at less than 4 Å from three surrounding  $[\text{AsPh}_2\text{Br}_2]^+$  units: two identical 3.94-Å distances to a single  $[\text{AsPh}_2\text{Br}_2]^+$  and two single contacts at 3.19 Å with the other two arsonium ions. These latter two distances are  $\sim 0.05$  Å below the van der Waals radii; however, since Table 4 expectedly shows that the two bromine atoms in this interaction are both negatively charged (e.g., in model  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3^-][\text{Br}_2]$ ), one may conclude that the 3.19-Å contact is due to electrostatic attraction between the arsonium and the  $\text{Br}_8^{2-}$ , rather than to a discrete  $\text{Br}\cdots\text{Br}$  attractive interaction. The influence of this attractive electrostatic interaction on the  $\text{Br}_3^-$  is distinctly stronger than the influence of complexation to  $\text{Br}_2$ , according to the partial atomic charges in Table 4. This is despite the fact that the  $\text{Br}_3^-$ - $\text{Br}_2$  distance is essentially identical to the  $\text{Br}_3^-$ - $\text{Br}$ (arsonium) one. Conversely, the arsenic-bound bromine atoms are also measurably affected by the vicinity of the  $\text{Br}_3^-$  (e.g., in the asymmetric  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3^-][\text{Br}_2]$  model the difference in charge between Br and  $\text{Br}^*$  is  $\sim 0.1$  units).

**Table 4.** Mulliken atomic charges (HF/aug-cc- pVTZ) for various models: isolated optimized  $[\text{Br}_8]^{2-}$  and two of its distorted versions (Br-Br-Br angles modified to  $75^\circ$  and  $140^\circ$ , respectively), isolated  $[\text{Br}_3]^-$ ,  $[\text{AsPh}_2\text{Br}_2]^+$ ,  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]$  and  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]_4$ . For the octabromide, the Br atoms are marked in different shades of grey/black based on which of the three formal components they belong to. For the As-containing models, the atomic coordinates are taken from the crystal structure – with single-point energy calculation.

Atom	$\text{Br}_8^{2-}$	$\text{Br}_8^{2-} / 140^\circ$	$\text{Br}_8^{2-} / 75^\circ$	$\text{Br}_3^-$	$[\text{AsPh}_2\text{Br}_2]^+$	$[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]$	$[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]_4$
Br1	-0.54	-0.52	-0.57				
Br2	-0.04	-0.05	-0.03			-0.14	-0.12
Br3	-0.04	-0.05	-0.04			0.09	0.07
Br4	0.10	0.09	0.11				
Br5	-0.51	-0.52	-0.51				
Br6	-0.54	-0.52	-0.57	-0.54		-0.29	-0.27
Br7	0.10	0.09	0.11	0.08		0.08	0.07
Br8	-0.51	-0.52	-0.51	-0.54		-0.64	-0.62
As					0.88	0.85	1.05
Br(As)1*					-0.10	-0.03	-0.01
Br(As)2					-0.10	-0.15	-0.08
Ph*					0.16	0.11	0.12
Ph					0.17	0.11	0.12

\*differentiated as the As-bound bromine/phenyl closer to the  $\text{Br}_8$ , in the asymmetric models

Examination of the asymmetric  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]$  model also allows one to estimate the effect of the  $\text{Br}_8$ ---phenyl contacts - since in this model only one of the two phenyl moieties is involved in such interactions. However, the total charge per phenyl moiety is essentially unaffected (differences are seen only on the third decimal of partial atomic charges). The larger model,  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]_4$ , features partial atomic charges very similar to those of the smaller  $[\text{AsPh}_2\text{Br}_2]^+[\text{Br}_3]^-[\text{Br}_2]$ .

If one describes the potential energy between two dipoles as  $-(2\mu_1\mu_2)/(4\pi\epsilon r^3)$ , where  $\mu$  are the respective dipole moments,  $r$  is the distance and  $\epsilon$  is the dielectric constant, a set of two identical dipoles of  $\mu=2$ , placed at  $\sim 7 \text{ \AA}$  from each other (as is the case for  $[\text{AsPh}_2\text{Br}_2]^+$  in the currently-discussed crystal structure, if one measures the As-As distances), would have an interaction energy of 0.15 kcal/mol. This would then be the stabilization energy added by the dipole-dipole interaction for the antiparallel stacked packing of the As-Ph units in the crystal structure. For each As center, there are also two other distances to take into account, towards two other As at 7.8  $\text{ \AA}$  - which accounts for an additional 0.25 kcal/mol stabilization energy. None of

the short contacts between  $[\text{AsPh}_2\text{Br}_2]^+$  and its neighboring units fall below the limit of van der Waals radii, with the noted exception of a Br-Br contact discussed above as being at most repulsive, and the CH $\cdots\pi$  interaction also discussed above and for which a value of 1.1 kcal/mol would constitute an upper limit given that in this case the interaction is at the limit of the sum of van der Waals radii[29]). Then, one may interpret that the electrostatic attraction between the counterions, alongside with the dipole-dipole interactions and the CH $\cdots\pi$  interactions are the driving force for the  $[\text{AsPh}_2\text{Br}_2]^+$  arrangement in the crystal structure.

To conclude, the crystal structure of the polybromide,  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  was reported here, containing the previously unknown  $[\text{AsPh}_2\text{Br}_2]^+$  cation and a rare  $[(\text{Br}_3)_2(\text{Br}_2)]^{2-}$  ensemble of a type previously assigned as an octabromide  $\text{Br}_8^{2-}$ . The crystalline supramolecular structure of  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  is based on a complex of weak intermolecular C-H $\cdots\pi$ , C-H $\cdots\text{Br}$  and secondary Br $\cdots\text{Br}$  interactions. The electronic structure and the stability of the  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  are analysed using DFT and HF calculations, with emphasis on the  $[(\text{Br}_3)_2(\text{Br}_2)]^{2-} / \text{Br}_8$  dianion and on the weak  $\text{Br}_3^- \cdots \text{Br}_2$  interactions – the nature of which is rationalized both in terms of energies of interactions and in terms of molecular orbitals.

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**Supporting Information available:** cif data for the crystal structure of  $[\text{AsPh}_2\text{Br}_2]_2[\text{Br}_8]$  (as deposited in the Cambridge Crystallographic Data Centre, CCDC 1563861), and plots of frontier molecular orbitals for selected models.

### References

- [1] L. Silaghi-Dumitrescu, M.N. Gibbons, I. Silaghi-Dumitrescu, J. Zukerman-Schpector, I. Haiduc, D.B. Sowerby, *J. Organomet. Chem.*, 517 (1996) 101-106.
- [2] L. Silaghi-Dumitrescu, R. Silaghi-Dumitrescu, A.J. Blake, P.A. Cooke, D.B. Sowerby, Chlorination of  $(\text{AsPh}_2)_2\text{O}$ : Supramolecular structure of dihydroxodiphenylarsonium hydrogensulfate  $[\text{AsPh}_2(\text{OH})_2][\text{HOSO}_3]$ , *Revue Roumaine De Chimie*, 47 (2002) 1063-1068.
- [3] L. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, R. Silaghi-Dumitrescu, I. Haiduc, A.J. Blake, D.B. Sowerby, Bromination of  $(\text{AsPh}_2)_2\text{O}$ : the structure of tribromo-diphenylarsonic(V). *Rev. Soc. Quim. Mexico*, 44 (2000) 134-138.



- [4] L. Silaghi-Dumitrescu, I. Haiduc, M.N. Gibbons, D.B. Sowerby, *Studia Univ. Babeş-Bolyai, Ser. Chem.*, 41 (1996) 43-49.
- [5] M. J. Begley, D. B. Sowerby, C. L. Silaghi-Dumitrescu, , *Acta Crystallogr., Sect. C*, 51 (1995) 1632-1634.
- [6] L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, *Rev. Roum. Chim.*, 42 (1997) 747-752.
- [7] L. Silaghi-Dumitrescu, R. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, *Studia Univ. Babeş-Bolyai, Ser. Chem.*, 42 (1997) 101-110.
- [8] L.H. Doerrer, J.C. Green, M.L.H. Green, I. Haiduc, C.n.N. Jardine, S.I. Pascu, L. Silaghi-Dumitrescu, D.J. Watkin, *J. Chem. Soc. Dalton Trans.*, DOI (2000) 3347-3355.
- [9] A.D. Becke, *J. Chem. Phys.* , 98 (1993) 5648-5652.
- [10] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, 37 (1988) 785-789.
- [11] A.K. Wilson, D.E. Woon, K.A. Peterson, T.H. Dunning, *J. Chem. Phys.*, 110 (1999) 7667-7676.
- [12] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 132 (2010) 154104.
- [13] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, 32 (2011) 1456-1465.
- [14] F. Neese, *The ORCA program system.*, Wiley Interdisciplinary Reviews - Computational Molecular Science 2(2012) 73–78.
- [15] E.G. Pettersen, T.D. Goddard, C.C. Huang, G.S. Couch, D.M. Greenblatt, E.C. Meng, T.E. Ferrin, UCSF Chimera - A Visualization System for Exploratory Research and Analysis, *J Comput Chem*, 25 (2004) 1605-1612.
- [16] S. Spartan, Spartan 5.0, Wavefunction, Inc., 18401 Von Karman Avenue Suite 370, Irvine, CA 92612 U.S.A., Spartan 5.0, Wavefunction, Inc., 18401 Von Karman Avenue Suite 370, Irvine, CA 92612 U.S.A., DOI.
- [17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. Montgomery, J. A., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, ; Gaussian, Inc., Wallingford CT, 2004, Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.;

- Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004, DOI (2003).
- [18] G.M. Sheldrick, SHELXL-93, Institut für Anorganische Chemie der Universität Göttingen, Germany, 1993.
- [19] K.N. Robertson, P.K. Bakshi, T.S. Cameron, O. Knop, *Z. Anorg. Allgem. Chem.*, 623 (1997) 104-114.
- [20] M. Wolff, A. Okrut, C. Feldmann, *Inorg. Chem.*, 50 (2011) 11683-11694.
- [21] R. Babu, G. Bhargavi, M.V. Rajasekharan, *Eur. J. Inorg. Chem.*, DOI (2015) 4689-4698.
- [22] K. Sonnenberg, P. Pröhm, S. Steinhauer, A. Wiesner, C. Müller, S. Riedel, *Z. Anorg. Allg. Chem.*, 643 (2017) 101-105.
- [23] N. Bricklebank, S.M. Godfrey, C.A. McAuliffe, R.J. Pritchard, J.-M. Moreno, *J. Chem. Soc., Dalton Trans.*, DOI (1995) 3873-3879.
- [24] J.C. Pazik, C. George, *Organometallics*, 8 (1989) 482-487.
- [25] S. Grewe, T. Haeusler, M. Mannel, B. Rossenbeck, W.S. Sheldrick, *Z. Anorg. Allg. Chem.*, 624 (1998) 613-619.
- [26] C.W. Cunningham, G.R. Burns, V. McKee, *Inorg. Chim. Acta*, 167 (1990) 135-137.
- [27] M.C. Aragoni, M. Arca, F.A. Devillanova, F. Isaia, V. Lippolis, A. Mancini, L. Pala, A.M.Z. Slawin, J.D. Woollins, *Chem. Commun.*, DOI (2003) 2226-2227.
- [28] B.M. Powell, K.M. Heal, B.H. Torrie, *Molecular Physics*, 53 (1984) 929-939.
- [29] K. Shibasaki, A. Fujii, N. Mikami, S. Tsuzuki, Magnitude of the CH/ $\pi$  interaction in the gas phase: experimental and theoretical determination of the accurate interaction energy in benzene-methane, *J. Phys. Chem. A*, 110 (2006) 4397-4404.