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Synthesis, Characterisation and Properties of *As*-Monohalogenated Dibenzoarsocines $S(C_6H_4S)_2AsHal$ (Hal = Cl, Br, I) – A Study of the Transannular Interaction S→As

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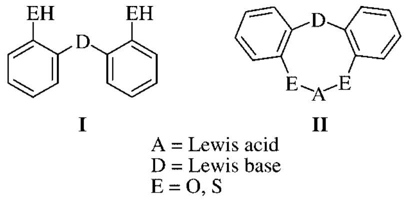
Addition of $AsCl_3$ to $S(C_6H_4SH)_2$ in benzene solution leads to the formation of the stable compound $S(C_6H_4S)_2AsCl$ (**1**). The $S(C_6H_4S)_2AsHal$ [Hal = Br (**2**), I (**3**)] compounds have been synthesised by halogen exchange from **1** and the corresponding potassium halide. X-ray structure determinations of complexes **1**–**3** reveal that the arsenic atom acts as an acceptor atom exhibiting an intramolecular transannular interaction with the thioether-like sulfur atom. The geometry of the tetracoordinate As atom in the title compounds is described as distorted pseudo-trigonal-bipyramidal with a stereochemically active lone pair and 66–63 % trigonal-bipyramidal character. The transannular interaction influences the conformation of the dibenzotrithiarsocine system, adopting the central eight-membered ring with a boat–boat conformation and C_s symmetry.

Introduction

We have been interested in the coordination chemistry of dithio ligands that can increase the coordination number around an acidic Lewis atom A, where A is a heavy p-block element. Some of these ligands, in particular $D(CH_2CH_2S)_2^{2-}$ with the donor atom D = O, S and NR, are quite flexible and led to the atom A expanding its coordination number through an *intramolecular transannular* interaction D→A. In these metallocanes, the conformational diversity is very large.[1] In addition, in these compounds the interaction is a stabilising factor in comparison with the cyclooctane ring and can be envisaged as a tool for controlling stabilities and conformations. The strength of this interaction spans over a wide range. In some cases it is very strong; for example in arsocanes the cross-ring bond has been claimed as being responsible for the stabilisation of discrete arsenium cations.[2] On the other hand, the more constrained ligands of type **I** (Scheme 1) have been explored for several groups in the coordination chemistry of transitional metals as well as light p-block elements; in these type **II** complexes the transannular interaction can also take place.[3] In particular, we have studied some *Sb*-monohalogenated dibenzometallocines and we have shown by means of X-ray crystallographic and DFT studies the acidic behaviour of the antimony atom acting as a Lewis acceptor toward sulfur in the decreasing order I > Br > Cl. These results prompt us to expand our studies to arsenic, a lighter group 15 element.



Scheme 1.

Here we report the synthesis and structural study of type **II** complexes with arsenic(III) as the acceptor atom. These compounds are good models for further understanding of the nature of the S→As interaction. After the description of the synthesis of dibenzoarsocines, IR and Raman spectra, mass spectra, NMR and X-ray crystallographic data are presented and discussed.

Results and Discussion

Synthesis of $S(C_6H_4S)_2AsHal$ (Hal = Cl, Br, I)

The ligand $S(C_6H_4SH)_2$ was prepared according to a reported method.[4] Treatment of $S(C_6H_4SH)_2$ with $AsCl_3$ in benzene yielded $S(C_6H_4S)_2AsCl$ (**1**) as colourless crystals (see Scheme 2). $S(C_6H_4S)_2AsBr$ (**2**) and $S(C_6H_4S)_2AsI$ (**3**) were obtained from a halogen-exchange reaction as reported for antimony complexes[3] between **1** and an excess of KBr/HBr or KI in hot benzene, respectively, yielding colourless crystals for **2** and pale yellow crystals for **3** (see

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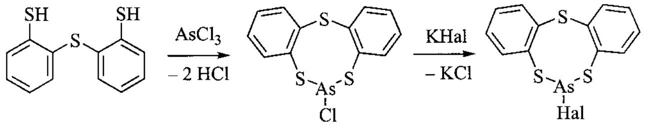
Experimental Section for details). All complexes are air-stable, soluble in benzene and chloroform, and insoluble in pentane, hexane and 2-propanol.



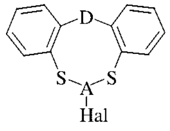
1 Hal = Br (**2**), I (**3**)

Scheme 2.

Vibrational Spectra

The Raman spectrum of each compound in the solid state was obtained for light scattered from the 1579.8 nm line of an argon ion laser. Under these conditions, compounds **1** and **2** experienced photodecomposition by the laser. The IR spectrum of each solid compound pressed on a CsI disk was collected in the 4000–200 cm^{-1} range. The Raman spectrum of the iodo complex is shown in Figure 1.

Besides the expected benzene group bands, there are several bands below 400 cm^{-1}. In the 400–300 cm^{-1} region we found two very intense bands assignable to the asymmetric and symmetric stretching vibration modes of the S–As–S group. In order to confirm the assignment of these bands, we compared these data with those exhibited by the antimony analogue complexes previously reported (see Scheme 3). The data are listed in Table 1. In the case of the arsenic complexes, the $\nu_{\text{asym}} - \nu_{\text{sym}}$ difference (Δ) is 59 ± 3 cm^{-1}, whereas in antimony complexes with sulfur as the donor atom, Δ is 46 ± 4 cm^{-1}.



A = As, Sb

Scheme 3.

In the IR spectra of complexes **1** and **2** we assigned the 392 and 280 cm^{-1} bands to the As–Cl and As–Br stretching bands, respectively.[5] In order to establish the presence of the As–I group frequency band, we used the Varshni ap-

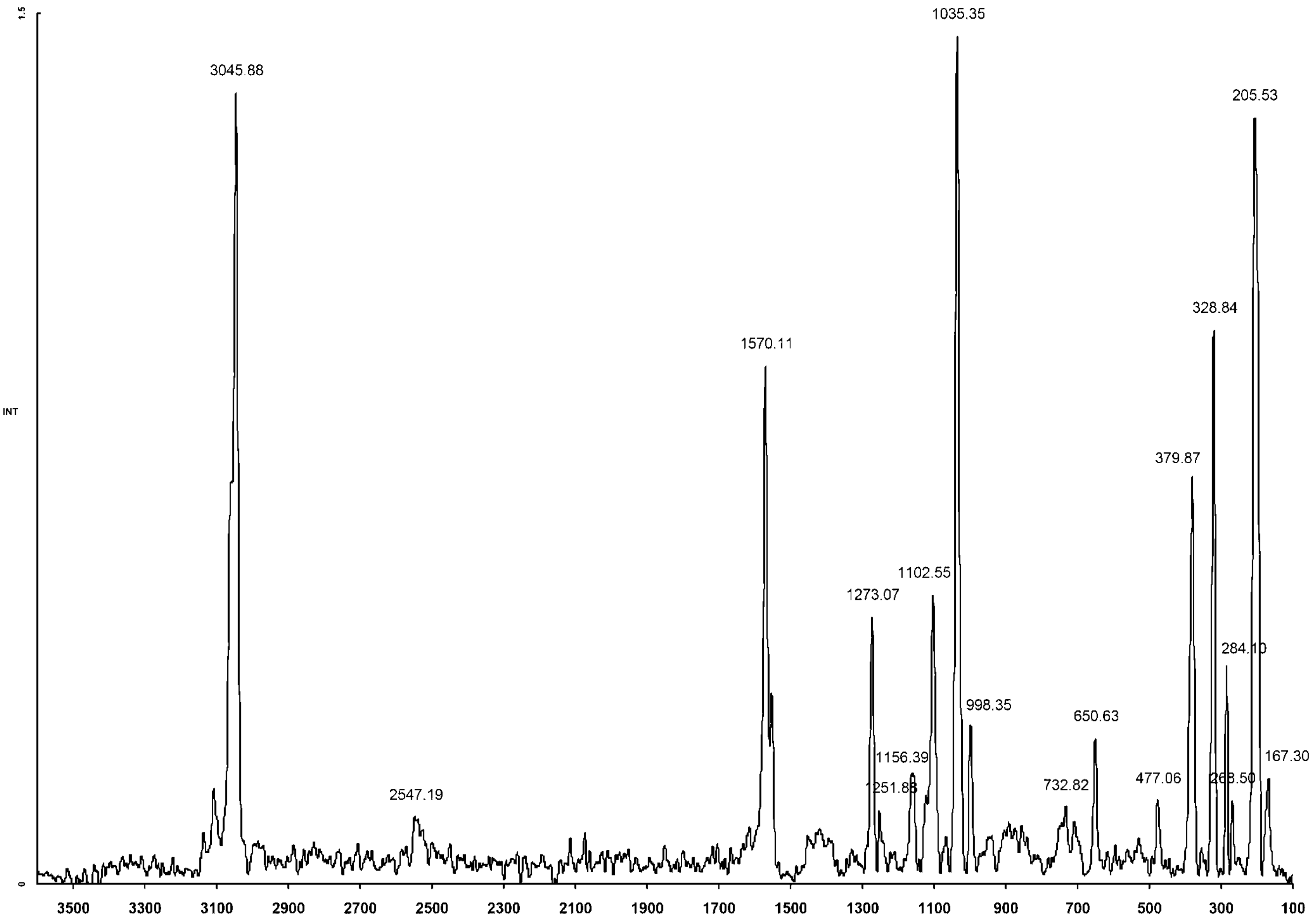


Figure 1. Raman spectra of $S(C_6H_4S)_2AsI$ (**3**).

Table 1. Stretching vibration frequencies of the S–A–S group [cm^{-1}] of $D(C_6H_4S)_2AHal$.

D	A–Hal[a]	Spectroscopy	ν_{asym}	ν_{sym}	Δ ($\nu_{asym} - \nu_{sym}$)
S	As–Cl	IR	380	326	54
		Raman	[b]	[b]	–
S	Sb–Cl	IR	371	330	41
		Raman	370	328	42
S	As–Br	IR	387	325	62
		Raman	[b]	[b]	–
S	Sb–Br	IR	371	327	44
		Raman	373	322	51
S	As–I	IR	380	320	60
		Raman	380	321	59
S	Sb–I	IR	372	325	47
		Raman	372	323	49
O	Sb–Cl	IR	369	316	53
		Raman	370	311	59

[a] For the data of antimony complexes see ref.[3] [b] Not measured.

proach reported for a series of metallocanes containing As, Sb and Bi linked to halide ligands, in conjunction with the As–I bond length found in complex **3**.[6] By using this treatment, we calculated the stretching frequency at 172 cm^{-1}. However, we did not observe any significant band at this frequency. Therefore the intense band at 205 cm^{-1} has been assigned to the As–I stretching frequency.[5] In this sense, Draeger et al. stated that the most intense bands in their series studied belong to the iodo complexes.[6] The vibrational data analysis has shown the usual tendency that the higher the mass of the halogen ligand, the lesser the frequency of the stretching As–Hal group band.

Mass Spectra

The EI mass spectra were obtained at 70 eV. In **1** and **2** the molecular ion was observed as a low-intensity peak with the appropriate isotopic ratio; for **3** the molecular ion was not observed. In all cases the intense ion fragment in *m*/*z* = 323 is assigned to the loss of the halogen atom in the compounds, yielding an $S(C_6H_4S)_2As$ tricyclic moiety, confirming the binding of arsenic to sulfur atoms and the stability of the dibenzotrithiarsocine system. In all the spectra there are peaks corresponding to the $S(C_6H_4S)_2$, $S(C_6H_4)S$ and $S(C_6H_4)_2$ fragments. No more peaks could be assigned.

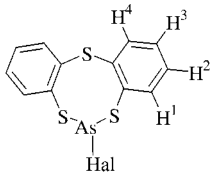
NMR Spectroscopy

The NMR spectra of the three complexes were recorded in $CDCl_3$ solution at room temperature and the chemical shifts are relative to TMS. The assignments of these complexes were made by two-dimensional heteronuclear and homonuclear correlation experiments (coloc and hetcor).

^{1}H NMR spectra of complexes **1**–**3** each displayed four signals in an ABCD pattern (see Table 2, Scheme 4). In these spectra the disappearance of the signal of the SH proton at δ = 4.10 ppm indicated that the arsenic complexes were formed. In solution the two $S(C_6H_4SAs)$ halves are equivalent. In all complexes the signals of the protons 2-H, 3-H and 4-H are shifted towards high frequencies with respect to those of the free neutral ligand.[4]

Table 2. ^{1}H NMR chemical shift (δ values [ppm]) for **1**–**3**.

	Hal	1-H	2-H	3-H	4-H
1	Cl	7.53	7.29	7.21	7.56
2	Br	7.53	7.29	7.21	7.54
3	I	7.48	7.28	7.21	7.52

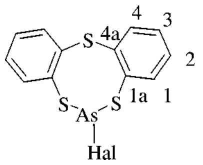


Scheme 4.

The ^{13}C NMR spectra of complexes **1**–**3** in $CDCl_3$ each show an important paramagnetic effect from the arsenic atom to the *ipso* carbon atom C-1a, causing chemical shift variations in the order of 8.6, 7.9 and 7.3 ppm at higher frequencies with respect to the free neutral ligand.[4] Similar shifts have been reported in dibenzostibocine analogues.[3] Another interesting feature was the observation of a small deshielding of the C-1a atom due to the increment of the electronegativity of the halogen ligand (see Table 3, Scheme 5).

Table 3. ^{13}C NMR chemical shift (δ values [ppm]) for **1**–**3**.

	Hal	C-1	C-1a	C-2	C-3	C-4	C-4a
1	Cl	134.7	143.6	130.0	127.7	130.9	131.7
2	Br	134.9	142.9	130.0	127.6	130.7	131.6
3	I	135.3	141.6	129.9	127.7	130.7	131.9



Scheme 5.

X-ray Structures of Compounds 1–3

The structures in the crystalline solid state of all complexes were definitely determined by single-crystal X-ray diffraction analyses. The molecular structure drawings are depicted in Figure 2 and selected bond lengths, angles and torsion angles are given in Table 4. Compounds **1** and **3** crystallise with mirror symmetry in space groups *Pmn*2$_1$ and *Pnma*, respectively; the two $S(C_6H_4SAs)$ halves are related by a mirror plane containing the S2–As–Hal plane.

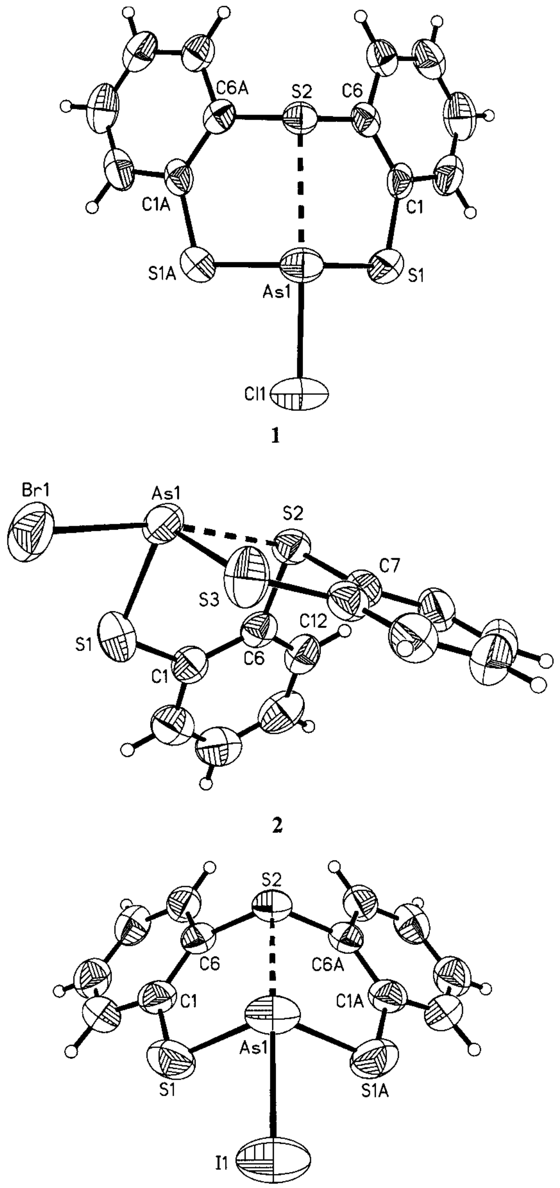


Figure 2. ORTEP diagrams of $S(C_6H_4S)_2AsCl$ (**1**), $S(C_6H_4S)_2AsBr$ (**2**) and $S(C_6H_4S)_2AsI$ (**3**) (50% probability ellipsoids).

Table 4. Selected bond lengths [Å], angles and torsion angles [°] of $S(C_6H_4S)_2AsHal$.

	1	**2**	**3**
Hal	Cl	Br	I
S2→As	2.705(3)	2.698(2)	2.740(1)
As–S1	2.268(2)	2.291(2)	2.283(1)
As–S3	–	2.268(3)	–
As–Hal	2.296(2)	2.482(1)	2.692(1)
S2–C6	1.789(6)	1.801(8)	1.786(4)
S2–C7	–	1.794(7)	–
S2→As–Hal	166.4(1)	168.36(6)	166.96(3)
S1–As–Hal	87.00(8)	87.30(6)	87.70(3)
S3–As–Hal	–	88.12(6)	–
S1–As–S2	84.55(6)	84.84(7)	84.31(3)
S1–As–S1A	102.8(1)	–	104.30(7)
S1–As–S3	–	103.22(9)	–
C6–S2–C6a	102.7(4)	–	103.0(2)
C6–S2–C7	–	101.8(3)	–
C1–C6–S2–C6A	–104.3(5)	–	–104.7(3)
C1–S1–As–S1A	85.8(2)	–	–84.7(1)
C1–C6–S2–C7	–	100.1(6)	–
C12–C7–S2–C6	–	–102.9(7)	–
C1–S1–As–S3	–	–83.9(3)	–
C12–S3–As–S1	–	83.4(3)	–

In all complexes **1**, **2** and **3** the As–S distances are in good agreement with the covalent radii sum [$\Sigma r_{cov}(As,S)$ = 2.22 Å][7] and with those reported in other heterocycles with arsenic–sulfur bonds.[8–19] The As–Hal distances (Hal = Cl, Br, I) are 5–7% longer than the corresponding covalent radii sum [($\Sigma r_{cov}(As,Cl)$ = 2.19 Å; $\Sigma r_{cov}(As,Br)$ = 2.34 Å; $\Sigma r_{cov}(As,I)$ = 2.53 Å][5] and are similar to other distances in several heterocycles containing As–Hal bonds.[1,2,8,9,11,16,20,21] The angles around the arsenic atom can be divided in two sets. The larger angles are the endocyclic S–As–S ones, the largest found in the iodo complex [102.84(11), 103.22(9) and 104.30(7)° in **1**, **2** and **3**, respectively]. On the other hand, the angles involving the halogen atom are on average substantially smaller [87.00(8), 87.71(6) and 87.70(3)° in **1**, **2** and **3**, respectively]. At first glance, the local geometry of the tricoordinate arsenic atom could be described as pyramidal.

In addition to the covalent bonds of the arsenic atom, a transannular interaction S2→As1 within the eight-membered rings was observed (see Figure 2). The S2→As1 bond lengths in **1**, **2** and **3** are 2.705(3), 2.698(2) and 2.740(1) Å, respectively, which are 22, 21 and 24% longer than the covalent radii sum of As and S but significantly shorter than the van der Waals radii sum [$\Sigma r_{vdW}(As,S)$ = 3.65 Å],[7] prompting us to propose the existence of a secondary bonding.[22] These S2→As1 distances in **1**, **2** and **3** are significantly longer than those reported for the two crystallographic different cations in $[S(CH_2CH_2S)_2As][GaCl_4]$[2] [2.347(10) and 2.391(9) Å] and are similar to those reported for $S(CH_2CH_2S)_2AsCl$[9] [2.719(3) Å], $S(CH_2CH_2S)_2AsBr$[1] [2.70 Å], $S(CH_2CH_2S)_2AsI$[1] [2.77 Å], $[AsCl_3(9)aneS_3]$[20] [2.715(3) Å], $[AsBr_3\{MeS(CH_2)_2SMe\}]$[20] [2.725(3) Å] and $[AsI_3\{MeS(CH_2)_2SMe\}]$[20] [2.697(2) Å] for neutral tetra- and hexacoordinate arsenic complexes, but significantly shorter than those reported for $[AsCl_3(14)aneS_4]$[20] [2.8709(9) and 2.9655(9) Å] $[AsBr_3\{MeS(CH_2)_2SMe\}]$[20] [2.876(3) Å], $[AsI_3\{MeS(CH_2)_2SMe\}]$[20] [2.792(2) Å], $[S(CH_2CH_2S)_2AsS_2CN(CH_2CH)_2]$[1] [3.170(2) and 3.113(2) Å], $S(CH_2CH_2S)_2AsS_2CNEt_2$[12] [3.172(2) Å], $S(CH_2CH_2S)_2AsS_2PPh_2$[10] [2.881(4) Å], $S(CH_2CH_2S)_2AsS_2P(OMe)_2$[11] [2.911(1) Å] and $S(CH_2CH_2S)_2AsS_2P[OCH(Me)]_2CH_2$[1] [2.942(11) Å]. In the title compounds it can be clearly seen that the transannular interaction (S2→As1) decreases in the order Br > Cl > I with the shortest distance in the bromo compound. A similar phenomenon has been observed in the arsocanes.[1]

If the transannular interaction S→As is taken into account, the geometry of the coordination sphere of the arsenic atom can be described as pseudo-trigonal-bipyramidal, where the halogen and thioether-like sulfur atoms are in

Table 5. Comparison of S→As–Hal geometrical bond parameters, bond lengths [Å], bond angles [°], and % TBP and BO in **1**–**3** complexes.

	Hal	S→As	S→As–Hal	% TBP	Δd[a]	BO[b] S→As
1	Cl	2.705(3)	166.4(1)	66.1	0.485	0.207
2	Br	2.698(2)	168.36(6)	66.6	0.478	0.212
3	I	2.740(1)	166.96(3)	63.7	0.520	0.185

[a] Bond widening, $\Delta d = (d_{\mathrm{exp}} - \Sigma r_{\mathrm{cov}})$ according to standard bond lengths $d(\mathrm{As,S}) = 2.22$ Å.[7] [b] Mode of calculation $\mathrm{BO} = 10^{-(1.41\cdot\Delta d)}$.[26–28]

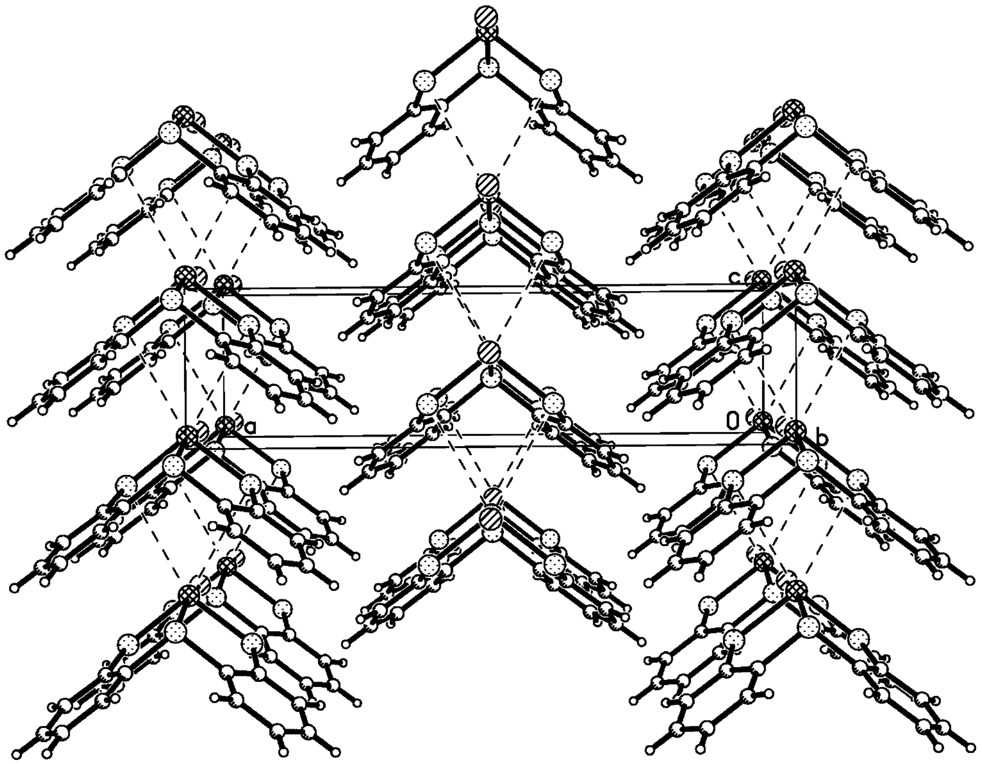


Figure 3. View of the As···S intermolecular interactions in the crystal structure of **1**.

axial positions; meanwhile the equatorial positions are occupied by the two thiolate-like sulfur atoms and the stereochemically active lone pair of the arsenic(III) atom.

The influence of the S→As interaction on the local geometry of the arsenic atom from pyramidal to trigonal-bipyramidal (TBP) can be evaluated. In this regard, we used the method of Holmes based upon donor–acceptor atom bond length.[23–25] Likewise, in order to establish the magnitude of the interaction, we calculated the Pauling-type bond order (BO) for all compounds.[26–28] The results are presented in Table 5. The displacement at geometry and bond order are related to bond lengths.

The percentages of TBP in the title compounds are slightly smaller than those reported for the antimony analogues, in spite of the smaller angles S→As–Hal to the ideal linear *trans* angle in comparison with the same S→Sb–Hal data. With regard to the BO, these values are relatively smaller than those observed for the trithiarsocanes $S(CH_2CH_2S)_2AsHal$ (Hal = Cl, Br, I) despite the apparent rigidity of the dibenzoarsocine system, and are also smaller than those calculated for the $S(C_6H_4S)_2SbHal$ analogues (0.308, 0.287 and 0.274 for Hal = I, Br and Cl, respectively).

The transannular interaction also influences the eight-membered ring conformation, which can be described as boat–boat (C_s symmetry).[29] This conformation was also found in the iodo–antimony analogue with the shortest transannular interaction for that series and the arsenium cation $[S(CH_2CH_2S)_2As]^+$, which displays the largest BO in the series of arsocanes.

In the crystal the packing is mainly due to As···S intermolecular weak interactions, as is shown in Figure 3 for the chloro compound. These As···S distances are 3.602(2), 3.595(3)–3.662(3) and 3.711(2) Å for **1**, **2** and **3**, respectively; the increase in these distances can be ascribed to the increasing halogen atom sizes.

Conclusions

In order to gain a better insight into the nature of the D→A interactions and their relation to the geometrical features in the dibenzometallocine systems containing heavier p-block elements, $S(C_6H_4S)_2AsHal$ compounds **1**–**3** have been synthesised and structurally fully characterised. All compounds exhibit a pseudo-bipyramidal-trigonal local geometry of the arsenic atom with intramolecular weak As···S interactions in the crystal structure.

The title compounds exhibit a relatively strong S→As transannular interaction, where the distances are 21–23% longer than the covalent radii sum. All compounds have shown relatively high TBP displacement values, with Pauling-type bond orders similar to the more flexible arsocane systems. However, these BO values are smaller than those calculated for the antimony analogues, suggesting a much poorer Lewis acidity of As^{III} in comparison to the heavier antimony atom.

Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out under argon at room temperature with use of standard Schlenk techniques. Solvents were dried and distilled before use. Melting points were determined with a Melt-Temp II instrument and are uncorrected. Spectra were recorded with the following instruments. Mass spectra: EI, 70 eV, Hewlett Packard MS-598 mass spectrometer. Elemental analysis: Perkin–Elmer Series II CHNS/O Analyzer. IR spectra: 4000–400 cm^{-1} range, Perkin–Elmer System 2000 FTIR spectrometer, as KBr pellets and 400–200 cm^{-1} range, Bruker Tensor 27 spectrometer, as CsI pellets. Raman spectra: In the solid state, 4000–100 cm^{-1} range, Perkin–Elmer Spectrum GX NIR FT-RAMAN spectrometer with 10–280 mW laser power and 4 cm^{-1} resolution. NMR: Jeol Eclipse 400 spectrometer, residual protio-solvent signal used as reference for ^{1}H NMR spectra; ^{13}C{^{1}H} NMR spectra referenced through the solvent peaks; chemical shifts quoted on the δ scale (downfield shifts positive) relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}); spectra recorded at 25 °C; ^{1}H, 399.78 MHz; ^{13}C{^{1}H}, 100.53 MHz. $AsCl_3$, KBr, HBr and KI were obtained commercially and used as received. $S(C_6H_4SH)_2$ was prepared as reported.[4]

$S(C_6H_4S)_2AsCl$ (1): $AsCl_3$ (1.38 g, 7.55 mmol) was added to a solution containing $S(C_6H_6SH)_2$ (1.76 g, 7.59 mmol) in benzene (25 mL). The yellow solution was stirred for 30 min, during which the colour changed to green, and then was refluxed for 24 h. The solution was cooled to room temperature and dried by means of a column of Celite and Na_2SO_4. Slow concentration of the benzene solution afforded colourless crystals of **1**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 2.18 g (80%). M.p. 124–126 °C. MS (EI): *m/z* (%) = 358 (30) [$M^{\cdot+}$], 323 (70) [$M^{\cdot+}$ – Cl], 248 (10) [$S(C_6H_4S)_2^{\cdot+}$], 216 (100, base peak) [$S(C_6H_4S)^{\cdot+}$]. $C_{12}H_8AsClS_3$ (358.76): calcd. C 40.17, H 2.25; found C 40.29, H 2.28. ^{1}H NMR ($CDCl_3$): δ = 7.21 (ddd, $^{3}J_{3\text{-H},2\text{-H}} = {}^{3}J_{3\text{-H},4\text{-H}}$ = 7.68 Hz, $^{4}J_{3\text{-H},1\text{-H}}$ = 1.48 Hz, 2 H, 3-H), 7.29 (ddd, $^{3}J_{2\text{-H},1\text{-H}} = {}^{3}J_{2\text{-H},3\text{-H}}$ = 7.68 Hz, $^{4}J_{2\text{-H},4\text{-H}}$ = 1.48 Hz, 2 H, 2-H), 7.53 (dd, $^{3}J_{1\text{-H},2\text{-H}}$ = 7.68 Hz, $^{4}J_{1\text{-H},3\text{-H}}$ = 1.48 Hz, 2 H, 1-H), 7.56 (dd, $^{3}J_{4\text{-H},3\text{-H}}$ = 7.68 Hz, $^{4}J_{4\text{-H},2\text{-H}}$ = 1.48 Hz, 2 H, 4-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 127.7, 130.0, 130.9, 131.7, 134.7, 143.6 ppm. IR (KBr): $\tilde{\nu}$ = 3049, 1567, 1447, 1417, 1255, 1032, 732 cm^{-1}.

$S(C_6H_4S)_2AsBr$ (2): $S(C_6H_4S)_2AsCl$ (**1**, 200 mg, 0.56 mmol), KBr (400 mg, 3.32 mmol) and HBr (48%, 4 mL) were suspended in benzene (25 mL) and the mixture was refluxed for 24 h. The water was removed from the resulting colourless solution by means of a Dean–Stark trap. The yellow solution obtained was dried by means of a column of Celite and Na_2SO_4. Slow concentration of the benzene solution afforded colourless crystals of **2**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 160 mg (71%). M.p. 138–140 °C. MS (EI): *m/z* (%) = 402 (7) [$M^{\cdot+}$], 323 (100, base peak) [$M^{\cdot+}$ – Br], 248 (20) [$S(C_6H_4S)_2^{\cdot+}$], 215 (30) [$S(C_6H_4S)^{\cdot+}$ – 1], 184. $C_{12}H_8AsBrS_3$ (403.22): calcd. C 35.74, H 2.00; found C 36.14, H 2.06. ^{1}H NMR ($CDCl_3$): δ = 7.21 (ddd, $^{3}J_{3\text{-H},2\text{-H}} = {}^{3}J_{3\text{-H},4\text{-H}}$ = 7.50 Hz, $^{4}J_{3\text{-H},1\text{-H}}$ = 1.48 Hz, 2 H, 3-H), 7.29 (ddd, $^{3}J_{2\text{-H},1\text{-H}} = {}^{3}J_{2\text{-H},3\text{-H}}$ = 7.50 Hz, $^{4}J_{2\text{-H},4\text{-H}}$ = 1.48 Hz, 2 H, 2-H), 7.53 (dd, $^{3}J_{1\text{-H},2\text{-H}}$ = 7.50 Hz, $^{4}J_{1\text{-H},3\text{-H}}$ = 1.48 Hz, 2 H, 1-H), 7.54 (dd, $^{3}J_{4\text{-H},3\text{-H}}$ = 7.50 Hz, $^{4}J_{4\text{-H},2\text{-H}}$ = 1.48 Hz, 2 H, 4-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 127.6, 130.0, 130.7, 131.6, 134.9, 142.9 ppm. IR (KBr): $\tilde{\nu}$ = 3042, 1551, 1444, 1415, 1252, 1033, 741 cm^{-1}.

$S(C_6H_4S)_2AsI$ (3): $S(C_6H_4S)_2AsCl$ (**1**, 200 mg, 0.56 mmol) and KI (550 mg, 3.32 mmol) were suspended in benzene (25 mL) and the mixture was refluxed for 24 h. The yellow solution obtained was dried by means of a column of Celite and Na_2SO_4. Slow concentration of the benzene solution afforded pale yellow crystals of **3**,

Table 6. Crystallographic data for compounds **1**–**3**.

Compound	1	2	3
Empirical formula	$C_{12}H_8AsClS_3$	$C_{12}H_8AsBrS_3$	$C_{12}H_8AsIS_3$
M_r [g/mol]	358.73	403.19	450.18
Crystal size [mm]	0.60 × 0.09 × 0.09	0.50 × 0.05 × 0.04	0.17 × 0.13 × 0.07
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$Pmn2_1$	$P2_1/c$	$Pnma$
$\rho_{\text{calcd.}}$ [Mg/m^3]	1.778	1.987	2.135
Z	2	4	4
a [Å]	17.306(5)	4.5694(10)	19.062(2)
b [Å]	8.533(2)	17.148(4)	15.8609(17)
c [Å]	4.5381(12)	17.218(4)	4.6332(5)
β [°]	90	92.167(6)	90
V [Å^3]	670.1(3)	1348.1(5)	1400.8(3)
μ [mm^{-1}]	3.175	5.922	5.051
F(000)	356	784	856
Gof	0.891	0.879	1.041
Absorption correction	SADABS	SADABS	SADABS
Reflections collected	4346	8046	16873
Unique reflections, R_{int}	1310, 0.0752	2362, 0.0642	1570, 0.0509
R_1, wR_2 [$I > 2\sigma(I)$]	0.0470, 0.0854	0.0382, 0.0863	0.0347, 0.0868
R_1, wR_2 (all data)	0.0734, 0.0914	0.0875, 0.1236	0.0518, 0.0929
Large residuals [e/Å^3]	0.696/–0.345	0.538/–0.527	0.466/–0.598

which were washed with hexanes (40 mL) and filtered by suction. Yield: 250 mg (80%). M.p. 153–156 °C. MS (EI) *m*/*z* (%) = 323 (100, base peak) [$M^{\cdot+}$ – I], 248 (33) [$S(C_6H_4S)_2^{\cdot+}$], 215 (40) [$S(C_6H_4S)^{\cdot+}$ – 1]. $C_{12}H_8AsIS_3$ (450.22): calcd. C 32.01, H 1.79; found C 31.29, H 1.86. ^1H NMR ($CDCl_3$): δ = 7.21 (ddd, $^3J_{3\text{-H},2\text{-H}} = {}^3J_{3\text{-H},4\text{-H}}$ = 7.48 Hz, $^4J_{3\text{-H},1\text{-H}}$ = 1.46 Hz, 2 H, 3-H), 7.28 (ddd, $^3J_{2\text{-H},1\text{-H}} = {}^3J_{2\text{-H},3\text{-H}}$ = 7.48 Hz, $^4J_{2\text{-H},4\text{-H}}$ = 1.46 Hz, 2 H, 2-H), 7.48 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 7.48 Hz, $^4J_{1\text{-H},3\text{-H}}$ = 1.46 Hz, 2 H, 1-H), 7.52 (dd, $^3J_{4\text{-H},3\text{-H}}$ = 7.48 Hz, $^4J_{4\text{-H},2\text{-H}}$ = 1.46 Hz, 2 H, 4-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 127.7, 129.9, 130.7, 131.9, 135.3, 141.6 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 1550, 1445, 1414, 1251, 1032, 751 cm^{-1}.

X-ray Crystallography: Suitable single crystals of all complexes were grown by slow concentration of benzene solutions. X-ray diffraction data on **1**–**3** were collected at room temperature with a CCD Smart 6000 diffractometer through the use of Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). The data were integrated, scaled, sorted and averaged using the SMART software package. The structures were solved by direct methods, using SHELXTL NT Version 5.10 and refined by full-matrix least squares against F^2.[30] An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS.[31] The displacement parameters of non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter. Selected crystallographic data are given in Table 6. CCDC-600909 (**1**), -600910 (**2**) and -600911 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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