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Thioacylsulfanylarsines $(RCS_2)_xAsPh_{3-x}$, $x = 1$–3: synthesis, structures, natural bond order analyses and reactions with piperidine †

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A series of thioacylsulfanylarsines ($(RCS_2)AsPh_2$, $(RCS_2)_2AsPh$, $(RCS_2)_3As$) were synthesized by treating piperidinium dithiocarboxylates with Ph_2AsCl, $PhAsCl_2$ or $AsCl_3$, respectively and characterized. Their molecular structures were determined by X-ray crystallography and compared with those of the corresponding acylsulfanyl derivatives ($(RCOS)AsPh_2$, $(RCOS)_2AsPh$, $(RCOS)_3As$). They exist as monomers, and the environment around the arsenic atoms is distorted tetrahedral with one lone pair at the apex. The structure of the mono(dithiocarboxylate) is different from that of the corresponding thiocarboxylic acid derivative, while the bis and tris derivatives showed similar structure to the corresponding thiocarboxylic acid derivatives ($(RCOS)_2AsPh$, $(RCOS)_3As$), respectively. The new compounds showed intramolecular interactions between the thiocarbonyl sulfur and the central arsenic atom. NBO (Natural Bond Orbital) analyses performed on the model compounds $(CH_3CS_2)As(CH_3)_2$ and $(CH_3CS^1{}_2)$-$(CH_3CS^2{}_2)AsCH_3$ at the RHF/LANL2DZ level of theory showed the presence of interactions between the non-bonding orbitals on the thiocarbonyl sulfur (n_S) and the σ^*_{MS} orbitals together with that between the n_S and the σ^*_{MC} orbitals for the former compound; for the latter the presence of both orbital interactions between n_S and σ^*_{MS1} and between n_s and σ^*_{MS2} are present. The reaction of the mono(dithiocarboxylate) derivative (R = 4-CH_3-C_6H_4) with piperidine in ethanol gave piperidinium diphenyldithioarsinate along with the corresponding *N*-thioacyl- or *N*-acyl-piperidine. A similar reaction of the bis(dithiocarboxylate) derivative (R = 4-$CH_3C_6H_4$) gave the novel di(piperidinium) phenyltrithioarsonate in which two anion charges are delocalized on the AsS_3 moiety and a cyclic phenylarsine sulfide tetramer $(PhAsS)_4$. The diphenyldithioarsinate and phenyltrithioarsonate salts exist as a dimer and a polymer, respectively, in which 12-membered rings are formed by intermolecular N–H $\cdots$ S hydrogen bonds.

Introduction

The chemistry of arsenic compounds with dithio-carbamato and -carbonato ligands has been investigated in great detail.[1] In contrast, the preparation of arsenic compounds with thio- and dithio-carboxylato ligands was limited to only seven thiocarboxylic[2] and two dithiocarboxylic acid arsenic derivatives[3] when our study began in 1974. Their spectral data and crystal structure analyses have not been described. The reason for this seemed to be the difficulty of purification and of the preparation of the starting compounds such as dithiocarboxylic acids and their alkali metal and ammonium salts. The arsenic compounds with dithio- and thio-carboxylato ligands are considered to be effective precursors for the synthesis of organoarsenic thiolate anion species such as R_2AsS^-,[4] which can be used easily to introduce the arsenic–sulfur framework into a molecule. It is possible that the reactions of alkali metal diorganoarsenides with elemental sulfur may be used for the synthesis of organoarsenic thiolates. In our research the preparation of $R_2As^-M^+$ (M = alkali metal) appeared to be impractical. We previously developed convenient syntheses of ammonium and alkali metal chalcogenocarboxylates,[5] and synthesized a variety of their main group element derivatives.[6] In addition, diphenyl(selenocarboxylato)arsines[7] have been found to be effective precursors for the synthesis of diphenylseleno-arsenic(III) ammonium salts.[8] Recently the structure of tris-(benzoylsulfanyl)arsine was reported by Nöth and co-workers.[9] This prompted us to reveal our results concerning Group 15 element derivatives of thio- and dithio-carboxylic acids. We describe here in detail the synthesis and structural analyses of a series of dithiocarboxyarsines $[(RCS_2)_xAsPh_{3-x}, x = 1–3]$ along with a structural comparison with the corresponding thiocarboxyarsines $[(RCOS)_xAsPh_{3-x}, x = 1–3]$ and in addition reactions with amines, leading to the first isolation of the organotrithioarsonate dianion $RAsS_3^{2-}$.

Results and discussion

Synthesis of complexes

Initially, the synthesis of diphenyl(dithiocarboxy)arsines **3**, phenylbis(dithiocarboxy)arsines **4** and tris(dithiocarboxy)-arsines **5** was examined using piperidinium 4-methylbenzene-carbodithioate. Under the conditions as shown in Scheme 1 these compounds were obtained in 70–90% yields.[10a] Although small amounts of alkanedithioic acid derivatives are lost during purification, the main reactions (to give **3**, **4** and **5**) proceed quantitatively. In order to compare structure and spectral data, a series of diphenyl(thiocarboxy)arsines **6**, phenylbis(thiocarboxy)arsines **7** and tris(thiocarboxy)arsines **8** were synthesized in similar yields by treating potassium thiocarboxylates **2** instead of piperidinium dithiocarboxylates **1**[10b] (Scheme 1). The resulting dithio- and thio-carboxylic acid arsenic derivatives (especially aromatic derivatives) are stable both thermally and toward oxygen and water. Upon exposure

† Electronic supplementary information (ESI) available: characterisation data for compounds **3**–**8**, selected bond lengths and angles for **3g**, **4e**, **5e**, **6h**, **7g**, **8e**, **9** and **15**. See http://www.rsc.org/suppdata/dt/b0/b008702p/

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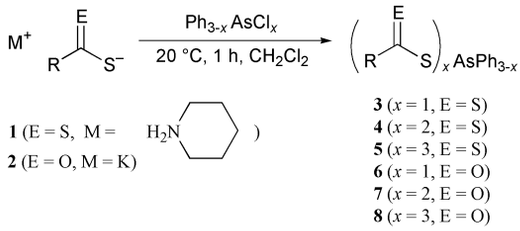


1 (E = S, M =)
2 (E = O, M = K)

3 (*x* = 1, E = S)
4 (*x* = 2, E = S)
5 (*x* = 3, E = S)
6 (*x* = 1, E = O)
7 (*x* = 2, E = O)
8 (*x* = 3, E = O)

No.	R	No.	R
3, **4**, **5a**	CH_3	**6**, **7**, **8a**	CH_3
b	C_2H_5	**b**	t-C_4H_9
c	i-C_3H_7	**c**	C_6H_5
d	C_6H_5	**d**	2-$CH_3C_6H_4$
e	4-$CH_3C_6H_4$	**e**	4-$CH_3C_6H_4$
f	2-$CH_3OC_6H_4$	**f**	2-$CH_3OC_6H_4$
g	4-$CH_3OC_6H_4$	**g**	4-$CH_3OC_6H_4$
h	4-ClC_6H_4	**h**	4-ClC_6H_4
i	1-$C_{10}H_7$	**i**	4-$NO_2C_6H_4$

Scheme 1

to air they do not show any appreciable change for three months.

Crystal structures

The structures of (4-methoxythiobenzoylsulfanyl)diphenyl- **3g**, bis(4-methylthiobenzoylsulfanyl)phenyl- **4e** and tris(4-methylthiobenzoylsulfanyl)arsine **5e** are shown in Fig. 1. The dithiocarboxylato ligand and the phenyl ring containing C(21) in **3g** are twisted (S(11)–As(1)–C(21)–C(22) 60.0(2)°) (Fig. 1a). In **4e** the two dithiocarboxyl ligands exist in the same plane with the same orientation, where two thiocarbonyl sulfurs are located in the same direction (Fig. 1b). In **5e** the three dithiocarboxylato ligands exist in C_3 symmetry and no two ligands of the three exist in the same plane (Fig. 1c). The distances between the central As atom and the thiocarbonyl sulfur (As(1)···S 2.96–3.15 Å) are within the sum of the van der Waals radii of both atoms (3.65 Å),[11] indicating interactions between the unshared electron pair on the thiocarbonyl sulfur and the σ* orbitals of the As–S and/or As–C_{ipso} bonds (S(11)–As(1)–C(31) 155.54(8)°). It is noted that the two As···S distances in **4e** (As(1)···S(11) 2.958(4), As(1)···S(21) 2.956(4) Å) are shorter than those in the mono **3g** (3.1470(8) Å) and tris derivatives **5e** (2.969(4) Å). This may facilitate interaction because the two dithiocarboxylato ligands of **4e** exist in the same plane. These complexes can be described as having a distorted tetrahedral structure and the bonds around the As atoms can be considered to exhibit a p^3-type bond.[1b,g]

For comparison, the structure analyses of the corresponding thiocarboxylato complexes were carried out. The ORTEP[12] drawings of (4-chlorobenzoylsulfanyl)diphenyl- **6h**, bis(4-methoxybenzoylsulfanyl)phenyl- **7g** and tris(4-methylbenzoylsulfanyl)arsine **8e** are shown in Fig. 2. Unlike the dithiocarboxylato complex **3g**, the thiocarboxylato ligand of **6h** exists nearly in the same plane as the phenyl ring containing C(21). Although the crystal system and space group of **7g** are different from those of **4e**, the structures of both compounds resemble one another (Fig. 2b). The structure of **8e** is comparable to both that in **5e** and the recently reported tris(benzoylsulfanyl)-arsine[9] (Fig. 2c). Similarly to dithiocarboxylato complexes, the distances between the central As atom and the carbonyl oxygens (As···O 2.71–2.94 Å) are elongated in the order bis **7g**, tris **8e**, mono **6h**.

Packing

The molecular arrangement of compounds **3g** and **6h** is shown in Fig. 3. It is noteworthy that in **3g** two molecules form a pair

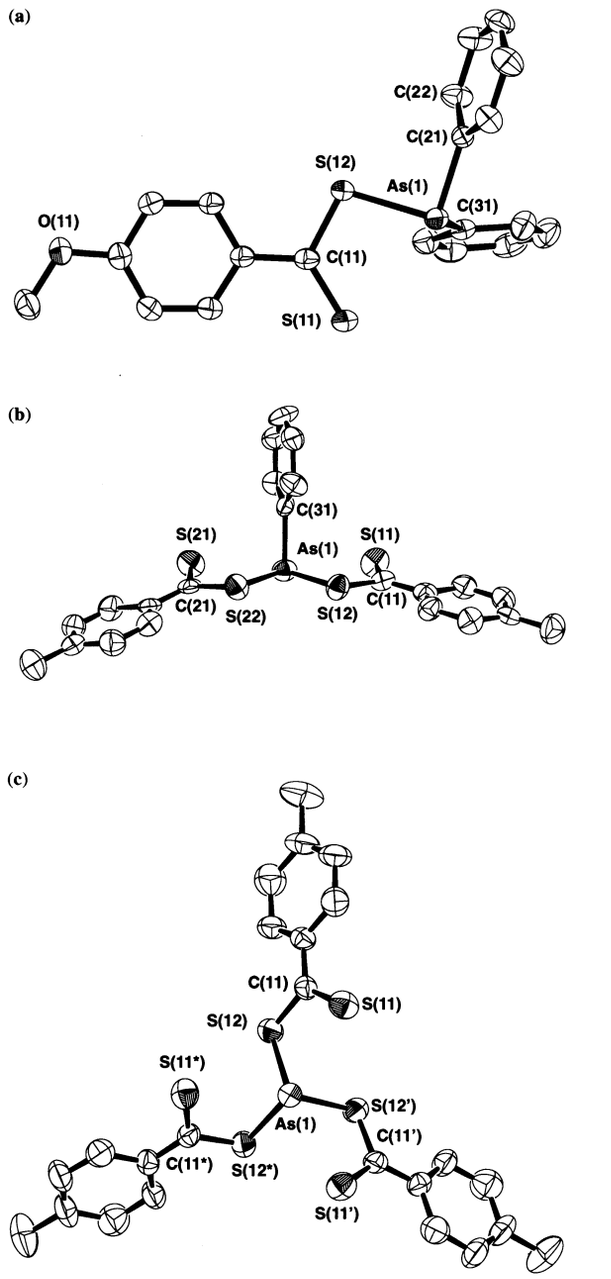


Fig. 1 Molecular structures of (a) (4-$CH_3OC_6H_4CS_2$)$AsPh_2$ **3g**, (b) (4-$CH_3C_6H_4CS_2$)$_2$AsPh **4e** and (c) (4-$CH_3C_6H_4CS_2$)$_3$As **5e**. The thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.

where the two CSSAs planes (C(11*)–S(11*)–S(12*)–As(1) and C(11)–S(11)–S(12)–As(1*)) are parallel, the distance between the planes being 1.37 Å and the distance between As(1*) and S(11) (or As(1)···S(11*)) is significantly short (3.939 Å), although greater than the sum of the van der Waals radii of both atoms. In contrast such a pairing of the molecules is not observed for the other compounds as shown in Fig. 3 (**b**) and also for the corresponding phosphorus isologues ((RCES)PPh_2, E = O or S).[12]

Structural comparison with the phosphorus isologues

In Table 1 the distances between the thiocarbonyl sulfur or carbonyl oxygen and the central arsenic atom are collected along with the C=E···P (E = O or S) distances of the corresponding phosphorus isologues. Interestingly, despite the large atomic radius of arsenic compared with that of phosphorus, the C=S···As distances are close to those in the corresponding phosphorus isologues. In addition, the C=O···As distance

Table 1 Distances between the thiocarbonyl sulfur or carbonyl oxygen and As or P in $(RCES)_xAsPh_{3-x}$ and $(RCES)_xPPh_{3-x}$

No.	R	E	x	Distance As···E/Å	R	E	x	Distance P···E/Å	Ref.
4e	4-$CH_3C_6H_4$	S	2	2.956(4) 2.958(4)	4-$CH_3C_6H_4$	S	2	2.965(3) 2.975(3)	14
6h	4-ClC_6H_4	O	1	2.943(3)	4-$CH_3C_6H_4$	O	1	2.917(3)	14
7g	4-$CH_3OC_6H_4$	O	2	2.708(3) 2.731(3)	4-$CH_3C_6H_4$	O	2	2.747(3) 2.784(3)	14
8e	4-$CH_3C_6H_4$	O	3	2.81(1)	4-$CH_3C_6H_4$	O	3	2.82(1)	14

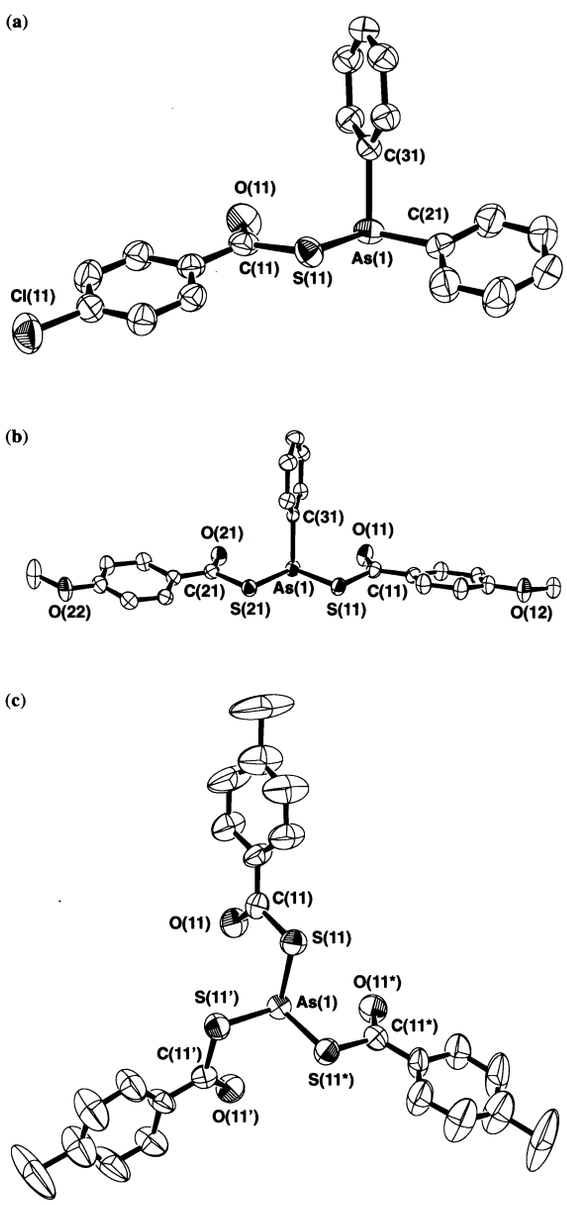


Fig. 2 Molecular structures of (**a**) (4-$ClC_6H_4COS)AsPh_2$ **6h**, (b) (4-$CH_3OC_6H_4COS)_2AsPh$ **7g** and (c) (4-$CH_3C_6H_4COS)_3As$ **8e**. Details as in Fig. 1.

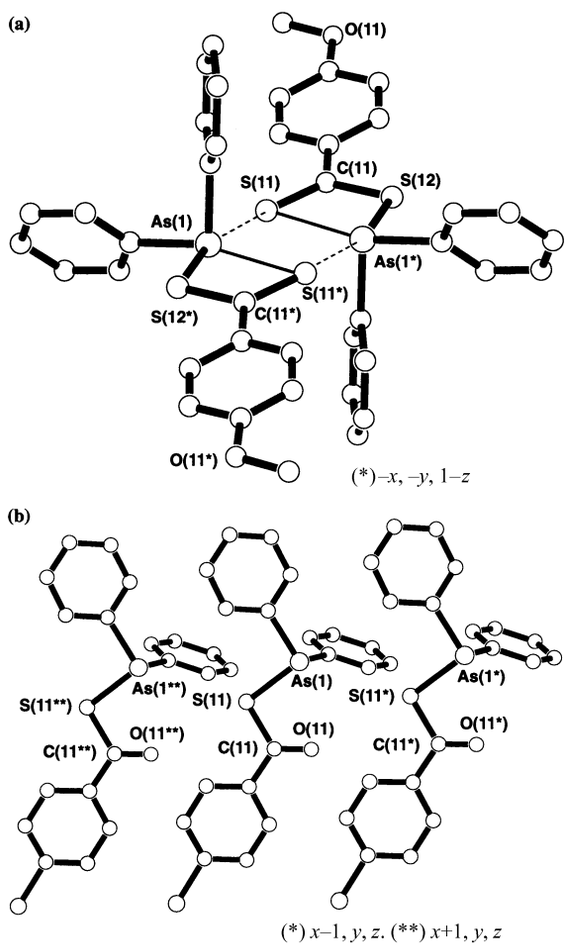


Fig. 3 Molecular arrangement of (**a**) (4-$CH_3OC_6H_4CS_2)AsPh_2$ **3g** and (b) (4-$ClC_6H_4COS)AsPh_2$ **6h**.

(av. 2.720(3) Å) in the bis(thiocarboxylate) **7g** is about 0.04 Å shorter than the C=O···P distance (av. 2.765(3) Å) in the corresponding phosphorus compounds. In the mono(thiocarboxylate) derivative **6h** ((4-$ClC_6H_4COS)AsPh_2$) the C=O···As distance (2.943(3) Å) is *ca.* 0.02 Å longer than that in the similar phosphorus compound ((4-$CH_3C_6H_4COS)PPh_2$).

Ab initio calculations

To elucidate the nature of these non-bonding attraction, *ab initio* geometry optimizations at the RHF/LANL2DZ level with the GAUSSIAN 94 program[15] were performed on the model compounds (acetylsulfanyl)dimethyl-phosphine **1′** and -arsine **2′** and dimethyl(thioacetylsulfanyl)-phosphine **1″** and -arsine **2″** for $(RCES)M(CH_3)_2$ (E = O or S; M = P or As) and bis(acetylsulfanyl)methyl-phosphine **3′** and -arsine **4′** and bis(thioacetylsulfanyl)methyl-phosphine **3″** and -arsine **4″** for $(RCES)_2MCH_3$ (E = O or S; M = P or As). The NBO (natural bond orbital) analyses showed that orbital interactions between

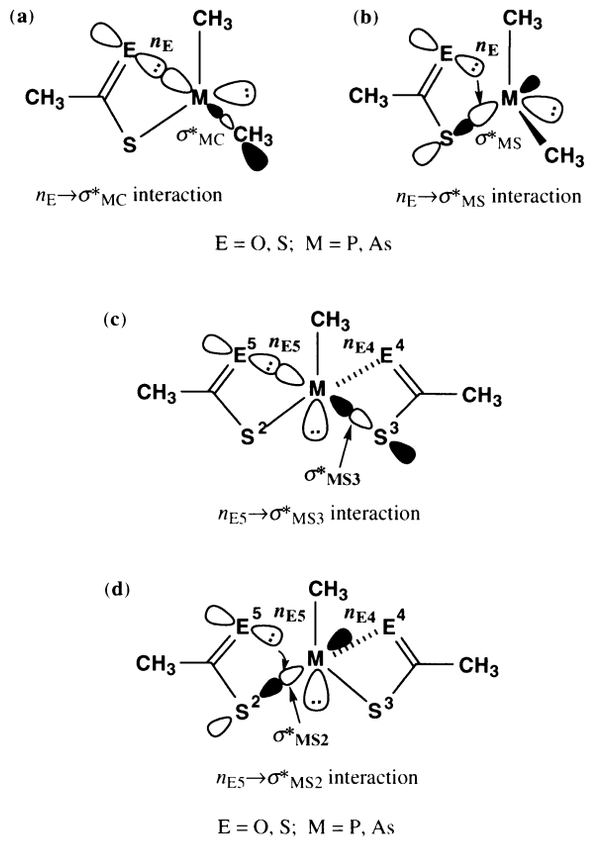
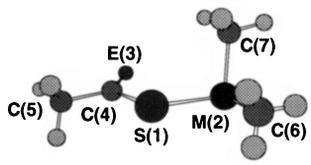


Fig. 4 Non-bonding attraction due to (**a**) the $n_E \rightarrow \sigma^*_{MC}$ and (b) $n_E \rightarrow \sigma^*_{MS}$ interactions in $(CH_3CES)M(CH_3)_2$ (E = O or S; M = P or As) and (c) the $n_{E5} \rightarrow \sigma^*_{MS3}$ and (d) $n_{E5} \rightarrow \sigma^*_{MS2}$ interactions in $(CH_3CES)_2MCH_3$ (E = O or S; M = P or As).

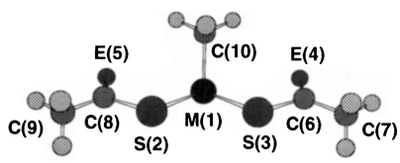
the n orbital (n_O) on the carbonyl oxygen and the σ^*_{MC} orbitals in **1′** and **2′** (Fig. 4a) are present, but their values are close to each other (Table 2). Interactions between the n_S and σ^*_{MS} orbitals (Fig. 4b) are also appreciable for **1″** and **2″** together with interactions between the n_S and σ^*_{MC} orbitals. The contour maps of the n_E and σ^*_{MS} orbitals in the molecular plane C(=S)–S–M (E = O or S; M = P or S) for the model compounds were depicted by using the MOLDEN 3.6 program.[14] Indeed, the overlaps between the n_S and σ^*_{MS} orbitals are present for **1″** and **2″**.

In the case of the bis derivatives (**3′**, **3″**, **4′** and **4″**) the interactions between the n orbitals (n_E) on the carbonyl oxygen or thiocarbonyl sulfur and σ^*_{MC} are absent. Instead, the orbital interactions between n_{E5} and σ^*_{MS3} and between n_{E4} and σ^*_{MS2} (Fig. 4c) are large. Those between n_{E5} and σ^*_{MS2} and between n_{E4} and σ^*_{MS3} (Fig. 4d) are also appreciable for **4′**, **3″** and **4″**, but small. The contour maps of the n_E and σ^*_{MS} orbitals in the molecular planes C(=E)–S–M–S–C(=E) (E = O or S; M = P or As) for **4′**, **3″** and **4″** obtained by using the MOLDEN 3.6 program[14] showed the expected overlaps between the n_E and σ^*_{MS} orbitals. The stabilization energies of the arsenic compounds **2′**, **2″**, **4′** and **4″** are larger than those of the corresponding phosphorus compounds **1′**, **1″**, **3′** and **3″**, respectively. In addition, the stabilization energies of the dithiocarboxylic acid derivatives **1″**–**4″** are greater than those of the corresponding thiocarboxylic acid derivatives **1′**–**4′**, respectively. The former tendency may be understood in the terms of their orbital levels: the lower energy level of the σ^*_{AsS} orbitals compared with that of σ^*_{PS}. Also, the latter can also be understood in terms of the lower energy level of the n_O orbitals (−0.93201, −0.46778 au for **2′**; −0.94975, −0.48359 au for **2″**) compared with that of the n_S orbitals (−0.66262, −0.31594 au for **4′**; −0.67753, −0.33772 au for **4″**). These non-bonding orbital interactions between n_E and σ^*_{MS} in the bis derivatives **4** and **7** may facilitate the two dithio- or thio-carboxylate groups being in the same direction

Table 2 NBO analysis of $(CH_3CES)M(CH_3)_2$ and $(CH_3CES)_2MCH_3$ (E = O or S; M = P or As) at RHF/LANL2DZ levels of theory



$(CH_3CES)M(CH_3)_2$			ΔE^a/kcal mol^{-1}	
No.	E	M	$n_E \rightarrow \sigma^*_{MC6}$	$n_E \rightarrow \sigma^*_{MS}$
1′	O	P	0.55	—
2′	O	As	0.77	—
1″	S	P	1.46	0.62
2″	S	As	2.22	0.84



$(CH_3CES)_2MCH_3$			ΔE^a/kcal mol^{-1}		
No.	E	M	$n_E \rightarrow \sigma^*_{MC10}$	$n_E \rightarrow \sigma^*_{MS2}$	$n_E \rightarrow \sigma^*_{MS3}$
3′	O	P	—	1.77 (E4)	— (E4)
			—	— (E5)	1.77 (E5)
4′	O	As	—	2.84 (E4)	0.64 (E4)
			—	0.64 (E5)	2.84 (E5)
3″	S	P	—	4.97 (E4)	1.57 (E4)
			—	1.57 (E5)	4.97 (E5)
4″	S	As	—	8.25 (E4)	2.50 (E4)
			—	2.50 (E5)	8.25 (E5)

[a] Stabilization energy associated with delocalization.

(see Figs. 1b and 2b). The atomic charges (0.73) of the As in the arsenic compounds (**2′**, **2″**, **4′** and **4″**) are larger than those in the phosphorus compounds (0.63 for **1′** and **1**; 0.53 for **3′** and **3″**), suggesting that electrostatic interactions may contribute to the short C=E · · · As distances.

Spectra

In Table 3 the thiocarbonyl and carbonyl stretching frequencies, thiocarbonyl and carbonyl carbon chemical shifts and the visible spectral data are collected. It is noted that the thiocarbonyl stretching frequencies of compounds **3**–**5** appear at 1170–1250 cm^{-1}. The carbonyl stretching frequencies for **6**–**8** are observed at 1610–1690 cm^{-1} and show a low frequency shift in the order **7** < **8** < **6**, which is consistent with the C=O · · · As distance. The thiocarbonyl carbon chemical shifts of **4** and **5** are observed in the region δ 214–257, and those of **3** show an upfield shift of 3–5 ppm compared with those of **4** and **5**. The carbonyl carbon chemical shifts of **6**–**8** appear at δ 190–208, and that of the *t*-C_4H_9 derivative **6b** shows a downfield shift relative to those of the other derivatives. In the electronic spectra the absorptions of **4** due to the n–π* transitions of the C=S group show hypsochromic shifts compared with those of the mono **3** and tris derivatives **5**.

Reactions of compounds 3–5 or 6–8 with piperidine

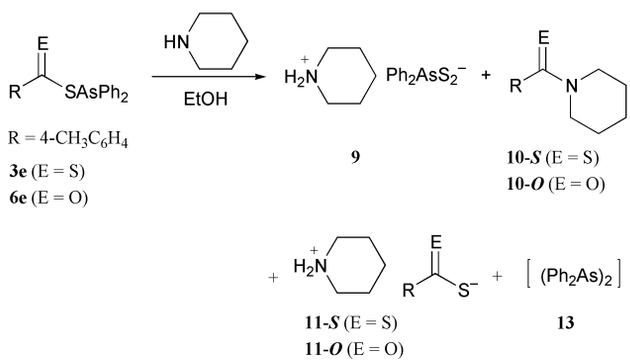
Expecting formation of a piperidinium diphenylthioarsenate(III) salt $(H_2NC_5H_{10})^+Ph_2AsS^-$, the reactions of (4-methylthiobenzoylsulfanyl)diphenyl- **3e** and (4-methylbenzoylsulfanyl)-diphenyl-arsine **6e** with piperidine were examined (Table 4). When **3e** or **6e** and two equivalents of piperidine were refluxed in ethanol, piperidinium diphenyldithioarsinate **9** was

Table 3 Spectral data of compounds **3**, **4**, **5**, **6**, **7** and **8**

$(RCS_2)_xAsPh_{3-x}$ R	ν(C=S)[a]/cm^{-1} mono **3**	bis **4**	tris **5**	$\delta_{C=S}$[b] mono **3**	bis **4**	tris **5**	λ_{max}[c]/nm mono **3**	bis **4**	tris **5**
C_6H_5	1218	1238	1241	229.0	231.0	234.2	527	506	511
4-$CH_3C_6H_4$	1227	1241	1243	227.8	230.3	234.1	527	505	511
4-$CH_3OC_6H_4$	1264	1265	1249	226.2	228.1	231.0	518	498	505
4-ClC_6H_4	1224	1237	1241	227.0	228.9	232.7	533	507	510
1-Naph	1238	1227	1229	233.4	235.4	239.3	494	495	500
$(RCOS)_xAsPh_{3-x}$ R	ν(C=O)[a]/cm^{-1} mono **6**	bis **7**	tris **8**	$\delta_{C=O}$[b] mono **6**	bis **7**	tris **8**			
C_6H_5	1644	1639	1631	192.1	192.8	190.3			
4-$CH_3C_6H_4$	1644	1626	1639	191.7	192.4	192.5			
4-$CH_3OC_6H_4$	1629	1628	1627	190.5	191.1	191.3			
4-ClC_6H_4	1655	1612	1660	190.8	191.6	191.7			

[a] As KBr disc. [b] In $CDCl_3$. [c] In CH_2Cl_2.

Table 4 Reactions of **3e** and **6e** with piperidine

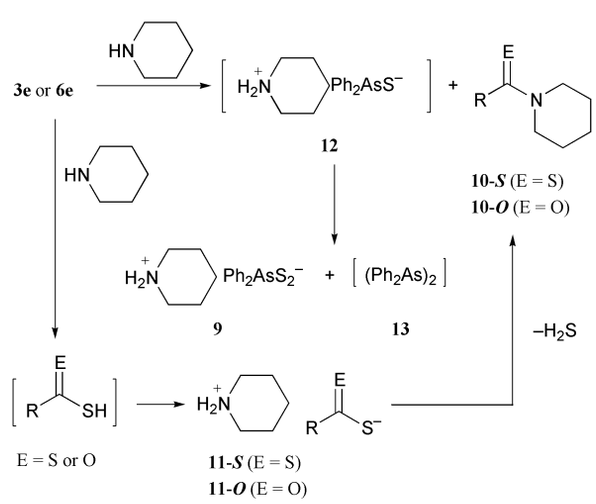


Entry	Compound	**4e** or **7e**: piperidine[a]	t/h	T/°C	Yield[b] (%) **9**	**10**	**11**	**13**
1	**3e**	1:1	9	20	7	44 (**10-*S***)	31 (**11-*S***)	0
2	**3e**	1:2	9	78	38	69 (**10-*S***)	0 (**11-*S***)	0
3	**6e**	1:1	3	20	5	83 (**10-*O***)	17 (**11-*O***)	0
4	**6e**	1:1	12	20	10	90 (**10-*O***)	0 (**11-*O***)	0
5	**6e**	1:2	12	78	42	88 (**10-*O***)	0 (**11-*O***)	11

[a] Mole ratio. [b] Isolated yields.

obtained in yields of 38 and 42%, respectively, together with *N*-4-methylthiobenzoylpiperidine **10-*S*** or *N*-4-methylbenzoylpiperidine **10-*O*** (entries 2 and 5). The reaction with an equivalent of piperidine in EtOH at 20 °C resulted in a significant decrease in **9**. Instead, the corresponding thioamide **10-*S*** or amide **10-*O*** was obtained in good yields along with **11-*S*** or **11-*O*** (entries 1 and 3). A plausible mechanism for the formation of **9** is shown in Scheme 2, where piperidine attacks the thiocarbonyl or carbonyl carbon in **3e** and **6e** to form piperidinium diphenylthioarsenate salt **12**, which further disproportionates to give **9** and tetraphenyldiarsane, while piperidine attacks the As to form dithio- or thio-carboxylic acids which further react with piperidine to give **11-*S*** and **11-*O***. We have observed that **11-*S***[5a,b] and **11-*O***[16] gradually decompose at room temperature to **10-*S*** and **10-*O***, respectively, with the evolution of hydrogen sulfide.

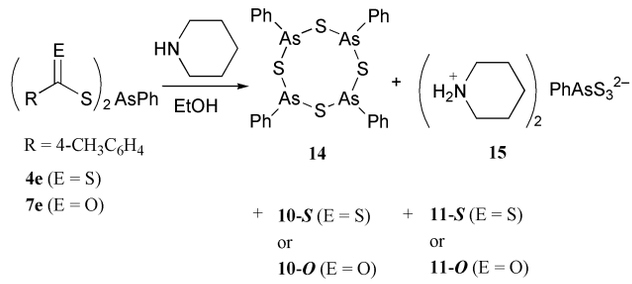
In contrast to the results with compounds **3e** and **6e**, the reaction of bis(4-methylthiobenzoylsulfanyl)phenylarsine **4e** under the same conditions gave di(piperidinium) phenyltrithioarsonate **15** in 14% yield along with **10-*S*** (Table 5, entry 1). The reaction with four equivalents of piperidine at 78 °C in ethanol led to a significant increase in the yield of **15** (entry 3). Formation of **11-*S*** was not observed. On the other hand, reflux



Scheme 2

of **7e** and two equivalents of piperidine in ethanol gave 2,4,6,8-tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14**[17] (hereafter called cyclic tetramer) and **11-*O*** in 63 and 27% yields,

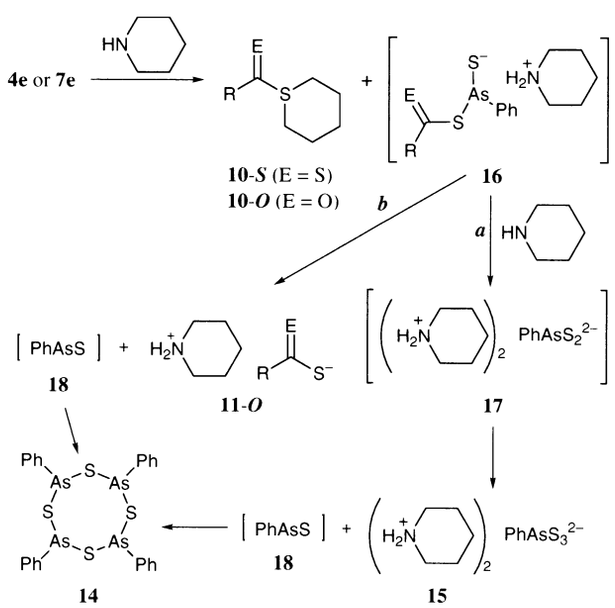
Table 5 Reactions of compounds **4e** and **7e** with piperidine



Entry	Compound	**4e** or **7e**: piperidine[a]	*t*/h	*T*/°C	Yield[b] (%) **10**	**11**	**14**	**15**
1	**4e**	1:2	5	20	35 (**10-*S***)	0 (**11-*S***)	0	14
2	**4e**	1:2	2	78	38 (**10-*S***)	0 (**11-*S***)	4	24
3	**4e**	1:4	5	78	84 (**10-*S***)	0 (**11-*S***)	16	65
4	**7e**	1:2	15	78	70 (**10-*O***)	27 (**11-*O***)	63	0
5	**7e**	1:2	3	20	56 (**10-*O***)	40 (**11-*O***)	66	0

[a] Mole ratio. [b] Isolated yields.

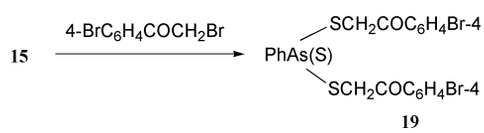
respectively (entry 4). The reactions at room temperature led to a decrease in **10-*O*** and to an increase in **11-*O*** (entry 5). One plausible mechanism for the formation of **14** and **15** is shown in Scheme 3, where piperidine attacks initially at the thiocarbonyl



Scheme 3

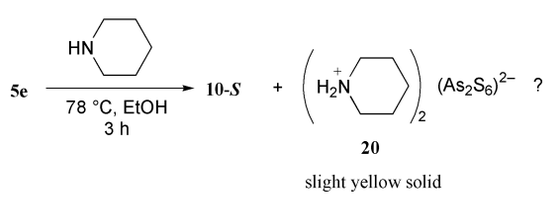
carbon in **4e** or carbonyl carbon in **7e** to form **10-*S*** or **10-*O*** and unstable piperidinium salts **16** (E = S or O), respectively. In the case of dithiocarboxylic acid derivative **4e** the thiocarbonyl carbon is further attacked by piperidine to form the dithioarsenate dianion **17** which disproportionates to give **15** and phenylthioxoarsine **18** which further tetramerizes to give **14** (path *a*). In this reaction, the formation of a cyclic trimer of **18** was not observed. In the case of the thiocarboxylic acid derivative **7e** the As–S bond of **16** (E = O) is cleaved to give **11-*O*** and **18** (path ***b***). The processes for the disproportionation of **17** to give **15** and for tetramerization of **18** to **14** are not clear at this time. The structures of **9**, **14** and **15** were determined by ^{1}H and ^{13}C NMR, elemental analysis and and by X-ray structural analysis. In addition, **15** was converted into 4-bromophenacyl ester **19** (Scheme 4).

The reaction of tris(4-methylthiobenzoylsulfanyl)arsine **5e** with piperidine under reflux in ethanol gave **10-*S*** along with



Scheme 4

traces of a white solid with mp >300 °C and a slightly yellow solid **20** with mp 142–145 °C (Scheme 5). The structure of



Scheme 5

20 was deduced as $(H_2NC_5H_{10}^+)_2(As_2S_6)^{2-}$ on the basis of elemental analysis and the IR and ^{1}H NMR spectra which show characteristic absorption bands of piperidinium salts as observed for **9** and **15**.

Structures of salts 9 and 15 and the cyclic tetramer $(PhAsS)_4$ 14

The ORTEP drawings of the salts **9** and **15** are shown in Fig. 5a and b, respectively. The structure determined for **9** shows that it exists as a dimer in the solid state, in which the distances S(1)···N(1*) 3.225(3) and S(2)···N(1) 3.473(3) Å are close to the sum of the van der Waals radii of both atoms (3.26 Å),[11] clearly indicative of the presence of N–H···S hydrogen bonding between the molecules. In the dimer a 12-membered ring is formed by the hydrogen bonding (Fig. 5a). The two As–S bond lengths (As(1)–S(1) 2.128(1), As(1)–S(2) 2.101(1) Å) are intermediate between the sum of their single (2.25 Å)[18] and double-bond covalent bond radii (2.05 Å),[18] suggesting delocalization of the negative charge on the AsS_2 moiety of **9**. The angles around the As atom (103.3(1)–116.27(4)°) are close to tetrahedral, thus yielding a distorted tetrahedral structure.

In compound **15** the three As–S bond distances are in the range 2.135(3)–2.151(2) Å, indicative of their covalent radii having values intermediate between those of single and double bonds,[18] and suggesting delocalization of the negative charges on the AsS_3 group. The bond angles around the central As atom are S(1)–As(1)–S(2) 111.69(9), S(1)–As(1)–C(1) 105.8(2), S(1)–

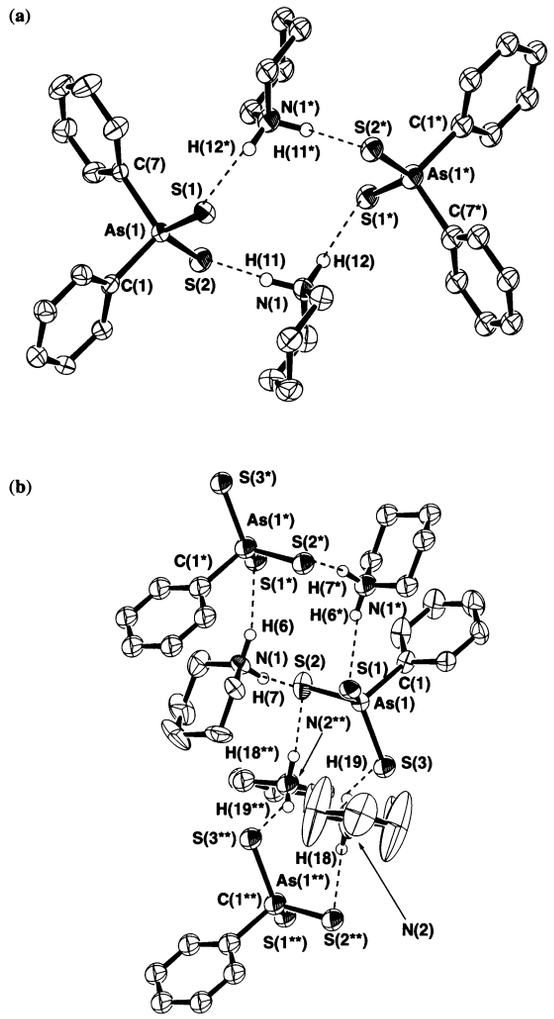


Fig. 5 Molecular structures of (a) piperidinium diphenyldithioarsinate **9** and (b) di(piperidinium) phenyltrithioarsonate **15**. Details as in Fig. 1.

As(1)–S(3) 112.0(1), S(2)–As(1)–C(1) 106.7(2), S(2)–As(1)–S(3) 113.6(1) and S(3)–As(1)–C(1) 106.5(2)°, indicating a distorted tetrahedron. As in **9**, the distances between S and N (3.195(8)–3.339(8) Å) of **15** are close to the sum of their van der Waals radii (3.35 Å), indicating the presence of N–H···S intermolecular hydrogen bonding.[11] Thus, **15** exists as a polymer in which a 12-membered ring was formed by the hydrogen bonding (Fig. 5b) and is the first example of an organoarsenic trithionate in which two negative charges are delocalized on the AsS_3 moiety.

The ORTEP drawing of cyclic tetramer **14** is shown in Fig. 6. The crown ring structure is similar to that of the tetramer $(PhAsS)_4$ prepared by treating phenylarsine with thionyl chloride,[19] and closely resembles those in the analogous methyl cyclo-tetramer[20] and *cyclo*-S_8.

Experimental

General

Melting points were determined by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on JASCO grating IR-G and Perkin-Elmer FT-IR 1640 spectrophotometers, ^1H (400 MHz) and ^{13}C NMR spectra (100 MHz) on JEOL JNM-α400 spectrometers in $CDCl_3$ containing Me_4Si as an internal standard, the ^1H spectrum (60 MHz) of compound **19** on a Hitachi R-24 and UV and visible spectra on Hitachi 124 and 330 spectrophotometers. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University and Bernhardt Analytisch Laboratorium.

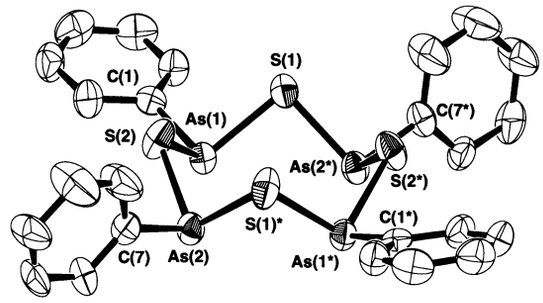


Fig. 6 Molecular structure of 2,4,6,8-tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14**. Details as in Fig. 1.

Materials

All solvents were dried and distilled prior to use. Arsenic(III) chloride was obtained from Aldrich. Chlorodiphenylarsine[21] and dichlorophenylarsine[22] were prepared by heating triphenylarsine[23] with arsenic(III) chloride under argon at 250 °C for 5–10 h. Piperidinium carbodithioates[5b] and potassium carbothioates[24] were prepared according to the literature procedures. Piperidine and 4-bromophenacyl bromide were commercial grade.

X-Ray crystallography

Measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). All the structures were solved and refined using the TEXSAN® crystallographic software package.[25] All crystal samples were cut from the grown crystals, mounted on a glass fiber, and coated with an epoxy resin. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [Ψ scans[26] (**3g**, **4e**, **5e**, **6h**, **7g**, **8e** or **14**) and DIFABS[27] (**9** or **15**)] were also applied. The structures were solved by direct methods using SHELXS 86[26] for **3g**, **6h**, **7g**, **9**, **14** or **15**, SAPI91[28] for **4e** or **8e** and MITHRIL 90[29] for **5e** and expanded using DIRDIF, 94.[30] Scattering factors for neutral atoms were from Cromer and Waber[31] and anomalous dispersion[32] was used. A full-matrix least-squares refinement was executed, with non-hydrogen atoms being anisotropic for **3g**, **4e**, **5e**, **6h**, **7g**, **8e**, **9**, **14** or **15**, and using SHELXL 93 for **8e**.[33] The final least-squares cycle included fixed hydrogen atoms at calculated positions, for which each isotropic thermal parameter was set to 1.2 times that of the connecting atoms. Crystal data and data collection parameters are summarized in Table 6. The bond lengths and angles and torsion angles are deposited as ESI supplementary data.

Preparation of single crystals at 25 °C. Compound **3g** (0.060 g) from dichloromethane (1.5 mL) and hexane (1.1 mL) for 8 days, **4e** (0.130 g) from dichloromethane (1.0 mL) and hexane (0.6 mL) for 6 days, **5e** (0.095 g) from dichloromethane (4.3 mL) and hexane (3.0 mL) for 6 days, **6h** (0.090 g) from dichloromethane (2.0 mL) and hexane (2.0 mL) for 4 days, **7g** (0.140 g) from dichloromethane (1.5 mL) and hexane (1.1 mL) for 1 week, **8e** (0.070 g) from dichloromethane (0.5 mL) and hexane (2.8 mL) for 4 days, **9** (0.035 g) from dichloromethane (3.5 mL) and hexane (2.8 mL) for 1 week, **14** (0.032 g) from dichloromethane (0.5 mL) and hexane (0.7 mL) for 3 days and **15** (0.051 g) from dichloromethane (1.5 mL) and hexane (3.0 mL) for 5 days.

CCDC reference number 186/2321.

See http://www.rsc.org/suppdata/dt/b0/b008702p/ for crystallographic files in .cif format.

Table 6 Crystal data and refinement parameters for compounds **3g**, **4e**, **5e**, **6h**, **7g**, **8e**, **9**, **14** and **15**

	3g	**4e**	**5e**	**6h**	**7g**	**8e**	**9**	**14**	**15**
Formula	$C_{20}H_{17}AsOS_2$	$C_{22}H_{19}AsS_4$	$C_{24}H_{21}AsS_6$	$C_{19}H_{14}AsClOS$	$C_{22}H_{19}AsO_4S_2$	$C_{24}H_{21}AsO_3S_3$	$C_{17}H_{22}AsNS_2$	$C_{24}H_{20}As_4S_4$	$C_{16}H_{20}AsN_2S_3$
M	412.40	486.55	576.71	400.75	486.43	528.53	379.41	736.35	420.52
Crystal system	Triclinic	Orthorhombic	Trigonal	Monoclinic	Triclinic	Trigonal	Monoclinic	Tetragonal	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$R\bar{3}$ (no. 147)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$R3c$ (no. 161)	$P2_1/n$ (no. 14)	$P4_2/n$ (no. 86)	$P\bar{1}$ (no. 2)
a/Å	10.464(2)	16.458(3)	18.846(1)	5.870(3)	11.304(2)	13.587(1)	9.8461(8)	16.4696(5)	10.500(2)
b/Å	11.022(3)	22.083(4)		8.373(3)	12.119(2)		12.9809(9)		11.643(3)
c/Å	8.916(2)	5.947(2)	4.855(1)	35.147(2)	8.725(1)	27.285(2)	14.2520(8)	9.971(1)	9.012(2)
α/°	96.09(2)				99.71(1)		96.757(6)		94.42(2)
β/°	92.36(2)			90.44(2)	101.91(1)				108.82(1)
γ/°	63.01(1)				110.14(1)				73.02(2)
U/Å^3	911.2(4)	2161.3(9)	1493.4(3)	1727.3(7)	1060.0(3)	4362.0(5)	1808.9(2)	2704.6(3)	997.2(4)
Z	2	4	2	4	2	8	4	4	2
μ(Mo-Kα)/cm^{-1}	20.98	19.64	15.67	22.44	18.26	18.72	21.04	52.22	20.18
T/K	193	296	296	296	193	296	193	296	193
Total reflections	4424	2867	2674	4352	5114	2396	4381	3512	4802
Unique reflections	4194		2290	3972	4880	1123	4147	3105	4575
No. observations	3432 ($I > 2\sigma(I)$)	1243 ($I > 2\sigma(I)$)	985 ($I > 1.4\sigma(I)$)	2587 ($I > 2\sigma(I)$)	3055 ($I > 2\sigma(I)$)	607 ($I > 2\sigma(I)$)	2774 ($I > 2\sigma(I)$)	1051 ($I > 2\sigma(I)$)	2344 ($I > 2\sigma(I)$)
No. variables	218	246	95	209	262	94	191	146	199
Residuals	$R = 0.032$	$R = 0.054$	$R = 0.084$	$R = 0.037$	$R = 0.040$	$R = 0.067$	$R = 0.037$	$R1 = 0.037$	$R = 0.066$
	$R_w = 0.035$	$R_w = 0.057$	$R_w = 0.102$	$R_w = 0.040$	$R_w = 0.041$	$R_w = 0.231$	$R_w = 0.039$	$wR2 = 0.135$	$R_w = 0.067$

Syntheses of thioacylsulfanyl- 3–5 and acylsulfanyl-arsines 6–8

Typical procedures are described in detail for the preparation of compounds **3e** and **6e**. Spectroscopic data of other thioacylsulfanyl **3**–**5** and acylsulfanyl-arsines **6**–**8** are deposited as ESI supplementary data.

(4-Methylthiobenzoylsulfanyl)diphenylarsine 3e. To a solution of piperidinium 4-methylbenzenecarbodithioate (0.269 g, 1.06 mmol) in CH_2Cl_2 (15 mL) was added Ph_2AsCl (0.264 g, 1.00 mmol) in CH_2Cl_2 (5 mL), and the mixture stirred at 20 °C for 1 h. After addition of CH_2Cl_2 (100 mL), the mixture was washed with water (3 × 90 mL), followed by drying over $MgSO_4$ (*ca*. 2 g) for 1 h. The solvent was removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in diethyl ether (5 mL), and allowed to stand in a refrigerator (−20 °C) for 24 h to give compound **3e** as red crystals 0.358 g (91%), mp 85–87 °C (Calc. for $C_{20}H_{17}AsS_2$: C, 60.60; H, 4.32. Found: C, 60.50; H, 4.36%). $\tilde{\nu}_{max}$/cm^{-1} (C=S) 1227 (KBr); λ_{max}/nm (CH_2Cl_2) 330 (ε/dm^3 mol^{-1} cm^{-1} 17 000) and 527 (170); δ_H($CDCl_3$) 2.22 (s, 3H, CH_3), 7.03 (d, J = 8.1, 2H), 7.24–7.27 (m, 6H), 7.49–7.53 (m, 4H) and 8.06 (d, J = 8.1 Hz, 2H); δ_C($CDCl_3$) 21.4 (CH_3), 127.1, 128.6, 128.6, 129.2, 133.0, 137.9, 141.9, 143.6 and 227.8 (C=S).

(4-Methylbenzoylsulfanyl)diphenylarsine 6e. To a solution of Ph_2AsCl (0.271 g, 1.02 mmol) in CH_2Cl_2 (20 mL), potassium 4-methylbenzenecarbothioate (0.196 g, 1.03 mmol) was added and the mixture stirred at 20 °C for 1 h. After addition of CH_2Cl_2 (100 mL), the mixture was washed with water (3 × 90 mL), followed by drying over $MgSO_4$ (*ca*. 2 g) for 1 h. The solvents were removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in CH_2Cl_2 (10 mL) and hexane (10 mL) and allowed to stand in a refrigerator (−20 °C) for 24 h to give compound **6e** as colorless crystals (0.358 g, 92%), mp 96–99 °C (Calc. for $C_{20}H_{17}AsOS$: C, 63.16; H, 4.51. Found: C, 62.95; H, 4.61%). $\tilde{\nu}_{max}$/cm^{-1} (C=O) 1644 (KBr); δ_H($CDCl_3$) 2.39 (s, 3H, CH_3), 7.21 (d, J = 8.1, 2H), 7.34–7.38 (m, 6H), 7.56–7.60 (m, 4H) and 7.94 (d, J = 8.1 Hz, 2H); δ_C($CDCl_3$) 21.7 (CH_3), 128.4, 128.8, 129.2, 129.4, 133.2, 134.8, 138.5, 144.5 and 191.7 (C=O).

Reaction of compound 3e with piperidine (Table 4, entry 2)

A suspension of compound **3e** (0.198 g, 0.50 mmol) in ethanol (40 mL) was added dropwise to a solution of piperidine (0.085 g, 1.00 mmol) in ethanol (20 mL). This suspension was stirred at 78 °C for 9 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitates gave piperidinium diphenyldithioarsinate **9** as colorless needles (0.072 g, 38%). *N*-4-Methylthiobenzoylpiperidine **10-*S*** was obtained from this filtrate as yellow crystals (0.076 g, 69%). ^{1}H and ^{13}C NMR spectra were exactly consistent with those of authentic samples prepared by heating piperidinium 4-methylbenzenecarbodithioate. Piperidinium diphenyldithioarsinate **9**: mp 155–157 °C (Calc. for $C_{17}H_{22}AsNS_2$: C, 53.82; H, 5.84; N, 3.69. Found: C, 53.44; H, 5.70; N, 3.82%); $\tilde{\nu}_{max}$/cm^{-1} 3014, 2885, 1603, 1609, 1491, 1456, 1410, 1324, 1178, 1098, 1043, 1019, 961, 948, 881, 772, 718 and 699 (KBr); δ_H($CDCl_3$) 1.41–1.46 (m, 2H), 1.60–1.66 (m, 4H), 3.04–3.06 (m, 4H), 7.33–7.41 (m, 6H), 8.04–8.06 (m, 4H) and 9.02 (br, 2H, NH_2); δ_C($CDCl_3$) 22.3, 22.5, 44.2, 128.4, 129.7, 130.0 and 143.5.

Reaction of compound 6e with piperidine (Table 4, entry 3)

A suspension of compound **6e** (0.380 g, 1.00 mmol) in ethanol (40 mL) was added dropwise to a solution of piperidine (0.086 g, 1.01 mmol) in ethanol (20 mL). This suspension was stirred at 20 °C for 3 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL).

Filtration of the resulting precipitates gave piperidinium 4-methylbenzenecarbothioate **11-*O*** as a colorless solid (0.040 g, 17%). To the filtrate was added toluene (10 mL) and the mixture allowed to stand in a refrigerator (−20 °C) for 48 h. Filtration of the resulting precipitate gave **9** as colorless needles (0.019 g, 5%). *N*-4-Methylbenzoylpiperidine **10-*O*** was obtained from this filtrate as a colorless oil (0.168 g, 83%).

Reaction of compound 4e with piperidine (Table 5, entry 1)

A suspension of compound **4e** (0.487 g, 1.00 mmol) in ethanol (80 mL) was added dropwise to a solution of piperidine (0.173 g, 2.03 mmol) in ethanol (40 mL), and this suspension was stirred at 20 °C for 5 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitate gave di(piperidinium) phenyltrithioarsonate **15** as a colorless solid (0.057 g, 14%). Evaporation of the filtrate under reduced pressure gave **10-*S*** (0.149 g, 35%). Di(piperidinium) phenyltrithioarsonate **15**: mp 154–157 °C (Calc. for $C_{16}H_{29}AsN_2S_3$: C, 45.70; H, 6.95; N, 6.66. Found: C, 45.54; H, 6.87; N, 6.51%); $\tilde{\nu}_{max}/cm^{-1}$ 2950, 2710, 2500, 1579, 1455, 1441, 1308, 1078, 1039, 938, 872, 754, 703 and 651 (KBr); $\delta_H(CDCl_3)$ 1.59–1.65 (m, 4H), 1.82–1.88 (m, 8H), 3.23–3.25 (m, 8H), 7.33–7.35 (m, 3H), 7.42–7.44 (m, 2H) and 8.23 (br, 4H, NH_2); δ_C ($CDCl_3$) 22.6, 22.9, 44.8, 128.3, 129.8, 131.0 and 133.0.

Reaction of compound 7e with piperidine (Table 5, entry 5)

A suspension of compound **7e** (0.454 g, 1.00 mmol) in ethanol (80 mL) was added dropwise to a solution of piperidine (0.173 g, 2.03 mmol) in ethanol (40 mL), and this suspension was stirred at 20 °C for 3 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitate gave **11-*O*** as a colorless solid (0.190 g, 40%). The filtrate was added to ethanol (20 mL), and filtration of the resulting precipitate gave 0.162 g (66%) of 2,4,6,8-tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14** as a colorless solid which was recrystallized from dichloromethane–hexane. The compound **10-*O*** was obtained from this filtrate as a colorless oil (0.227 g, 56%). 2,4,6,8-Tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14**: mp 174–175 °C (lit.,[20] 175–176 °C) (Calc. for $C_{24}H_{20}As_4S_4$: C, 39.15; H, 2.74. Found: C, 39.32; H, 2.66%); $\tilde{\nu}_{max}/cm^{-1}$ 3042, 1571, 1475, 1429, 1179, 1062, 1019, 998, 728, 687 and 468 (KBr); $\delta_H(CDCl_3)$ 7.34–7.45 (m, 12H) and 7.77–7.87 (m, 8H); $\delta_C(CDCl_3)$ 129.0, 130.0, 131.6 and 142.3.

Reaction of di(piperidinium) phenyltrithioarsonate 15 with 4-bromophenacyl bromide (Scheme 4)

A two molar amount of 4-bromophenacyl bromide (0.139 g, 0.50 mmol) in ethanol (5.0 mL) was added to a suspension of compound **15** (0.105 g, 0.25 mmol) in ethanol (20 mL) and refluxed for 10 min. The solvent was evaporated and ether (50 mL) added, followed by washing with water (3 × 90 mL) and drying over Na_2SO_4 (*ca*. 2 g) for 1 h. The solvents were removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in CH_2Cl_2 (2.0 mL) and hexane (0.5 mL) and allowed to stand in a refrigerator (−20 °C) for 24 h to give di(4-bromophenacyl) phenyltrithioarsonate **19** as colorless crystals (0.027 g, 18%): mp 134–137 °C (Calc. for $C_{22}H_{17}AsBr_2O_2S_3$: C, 41.01; H, 2.66. Found: C, 41.35; H, 2.66%); $\tilde{\nu}_{max}/cm^{-1}$ (C=O) 1685 (KBr); $\delta_H(CDCl_3)$ 4.1 (s, 4H, CH_2) and 7.2–8.0 (m, 13H).

Reaction of compound 5e with piperidine (Scheme 5)

Tris(4-methylthiobenzoylsulfanyl)arsine **5e** (0.288 g, 0.50 mmol) and piperidine (0.128 g, 1.50 mmol) were refluxed in ethanol (50 mL) for 3 h. Filtration of the precipitates gave 0.006 g of a white solid (mp >300 °C) (As_xS_y?). The ethanol from the filtrate was removed under reduced pressure. To the residue ether (30 mL) was added. Filtration of the ether insoluble part gave 0.088 g of a slightly yellow solid **20** [mp 142–145 °C (decomp.) (Calc. for $C_{10}H_{24}As_2N_2S_8$: C, 20.76; H, 4.18; N, 4.84. Found: C, 20.43; H, 4.06; N, 4.92%); δ_H (DMSO-d_6) 1.1–3.2. Removal of the ether from the filtrate under reduced pressure gave **10-*S*** in 48% yield.

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