Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
ARTICLE

DOI: 10.1002/zaac.201500096

The Reaction of Bunsen's Cacodyl Disulfide, $Me_2As(S)$-S-$AsMe_2$, with Iodine: Preparation and Properties of Dimethylarsinosulfenyl Iodide, Me_2As-S-I

Panayiotis V. Ioannou,*[a] Dimitris G. Vachliotis,[a] and Athanassios Chrissanthopoulos[b]

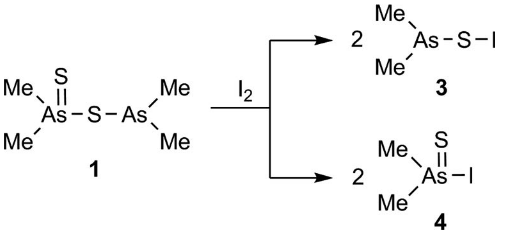
Keywords: Dimethylarsino dimethyldithioarsinate; Dimethylarsinosulfenyl iodide; Nucleophiles; Arsenic, Iodine

Abstract. Bunsen's cacodyl disulfide, $Me_2As(S)$-S-$AsMe_2$ (**1**), reacted with iodine giving the novel dimethylarsinosulfenyl iodide, Me_2As-S-I (**3**) although theoretical calculations indicated that the As^V compound $Me_2As(S)$-I (**4**) was more stable in the gas phase. The oily product was stable neat and as a solution in $CDCl_3$ at +4 °C and –20 °C for at least 15 d. Light, H_2O, H_2O_2, and Zn dust, but not NaI or Ag, decomposed it. Compound **3** did not interact with Ph_3N, with Ph_2NH and $PhNH_2$ it interacted but not reacted. **3** was decomposed by piperidine, with pyridine and 4-dimethylaminopyridine it interacted and produced Me_2As-SS-$AsMe_2$ (**2**) and I_2 that formed charge transfer complexes Base·I_2, whereas Et_3N decomposed **3**, and $3Et_3N{\cdot}2I_2$ was isolated. **3** was desulfurized by Ph_3P and $(Me_2N)_3P$ completely, and by $(PhO)_3P$ and $(PhS)_3P$ partially. The reactions of **3** with $(Me_2N)_3P$, $(PhS)_3P$, and $(EtO)_3P$ were complicated. From the As^{III} nucleophiles, only Ph_3As was bound, while $(PhS)_3As$ reacted slowly in a complicated manner with **3**. No interaction of **3** with MeOH or PhOH was observed but NaOH, Ag_2O, and PhONa decomposed it. Thiophenol produced traces of Me_2As-SPh (**10**) and sodium thiophenolate attacked mainly at As^{III} of **3**. Thus, externally stabilized sulfenium ions of the type Me_2As-S-Nu^+I^- were not obtained.

Introduction

In a previous publication[1] we summarized the nucleophilic (towards many heavy metal cations) and electrophilic (towards a variety of nucleophiles of group 15 and 16 of the periodic Table) reactions of Bunsen's cacodyl disulfide $Me_2As(S)$-S-$AsMe_2$ (**1**). Metal cations split **1** giving complexes $(Me_2As(S)\text{-}S)_xM$, whereas nucleophiles either bind or split or desulfurize **1**. Another aspect of **1** is that it shows internal redox chemistry by being equilibrated to an extent of approx. 10 % with the true disulfide Me_2As-S-S-$AsMe_2$ (**2**) when dissolved in an inert solvent.[2] Group 17 elements have not been examined for their ability to react with **1**. A reaction of **1** with, e.g., I_2 can conceivably give the hitherto unknown compounds **3** or **4** [Equation (1)], where I_2 oxidizes the sulfur atoms and the arsenic atom of **1**, respectively.

In the dimethylarsine-*As*-sulfenyl iodide or dimethylarsinosulfenyl iodide (**3**) the –SI group is linked to As^{III}. Going up in group 15, compounds of the type R_2P-SX (dialkylphosphine-*P*-sulfenyl halides) seems to be unknown, while there are a few compounds, e.g. $(EtO)_2P(O)$–SX, where the –SX group is linked to P^V.[3,4] Dialkylamine-*N*-sulfenyl halides, R_2N-SX, are known but not widely studied.[4,5] The dimethylthioarsinyl iodide (**4**) should either not exist or be highly unstable because of the operation of the inert pair effect that will convert **4** to **3**.



(1)

In this paper we describe the preparation of Me_2As-S-I (**3**) as well as an overview on its stability under various conditions, its reactivity towards oxidizing and reducing agents, and its behavior towards nucleophiles of group 15, i.e. compounds of N, P^{III}, and As^{III}, as well as of group 16, i.e. O and S^{II}, hoping to get stable adducts of the type Me_2As-S-Nu^+I^-, by analogy to phosphine-stabilized arsenium salts, $R_2As{:}^+{:}PR'_3I^-$.[6]

Results and Discussion

Preparation and Properties of Me_2As-S-I (3)

Bunsen's cacodyl disulfide (**1**) reacted smoothly with iodine in dry dichloromethane, initially giving an orange suspension that cleared to a very pale yellowish solution. However, in all preparation a small amount (approx. 40 mg·mmol^{-1} **1**) of a brown sticky solid formed that did not subsequently react. Its identity is unknown and its IR (KBr) showed a broad, strong

---

* Prof. Dr. P. V. Ioannou
Fax: +30 2610 997118
E-Mail: ioannou@chemistrty.upatras.gr
[a] Department of Chemistry
University of Patras
26504 Patras, Greece
[b] Department of Chemistry
National and Kapodistrian University of Athens
15771, Athens, Greece

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201500096** or from the author.

band at 3446 cm^{-1} and non-informative somewhat broad bands in the region 1645–670 cm^{-1}. Removal of the CH_2Cl_2 solvent should be done at low temperatures (approx. 15 °C) on a rotary evaporator only, otherwise the yields diminish drastically. Also, even a brief (approx. 1 min) drying in vacuo diminishes the yields to approx. 50–60 %. Under the conditions described in the Experimental Section, the yields of **3** were 77–92 %. Product **3** was obtained from a yellowish solution in CH_2Cl_2 as a red-orange to cherry-red mobile liquid, having an unpleasant odor, and by ^{1}H NMR in $CDCl_3$ the very pale yellowish solution showed the presence of 0.5–2 % CH_2Cl_2.

The IR (neat) of the oil showed the symmetric and asymmetric bending of the Me groups at 1430 and 1252 cm^{-1}, the rocking bands of $AsMe_2$ at 899 and 838 cm^{-1}, and the asymmetric and symmetric As–C stretching at 582 and 572 cm^{-1}, respectively, but could not reveal an expected very strong band at 478–488 cm^{-1}[2,7] attributable to As=S stretching, if the oil is compound **4**, because of noise. Its IR (CCl_4), in the noisy region 700–400 cm^{-1}, again did not show an expected very strong band at 478–488 cm^{-1}. If the oil is compound **3**, the expected As–S stretching is expected at 389 cm^{-1},[2] a region not reached by our instrument. An IR spectrum was obtained by adsorbing the oily product on KBr and brief (otherwise the product evaporates) grinding. The yellowish disc gave a spectrum, whose bands were at the same position as that obtained as a film and, moreover there was only one weak, somewhat broad, band at 486 cm^{-1}, a band at about the same position that the As=S of **1** absorbs strongly (see Supporting Information for the spectra). Because theoretically the As=S stretching of **4** at 530 cm^{-1} is very strong, the absence in the actual spectrum indicates that the product was **3** and not **4**.

In order to further establish the structure of the product we performed theoretical calculations, at MP2(full)/6-311** level of theory, which indicated that **4**, as isolated molecule in the gas phase, was more stable by 45.14 kJ·mol^{-1} than **3**. Thus, it is probable that **4** rearranges to **3** in the condense phase most likely due to the inert pair effect.

The possibility that **4** was hydrolyzed by water in KBr, giving the compounds $Me_2As(S)–O–As(S)Me_2$ (**8**) and $Me_2As(S)–OH$ (**9**) (see stability of **3**) was dismissed because the As=S stretching in **8** was found at 482/523 cm^{-1},[7] while in **9** was calculated to be at 528 cm^{-1} (see Supporting Information) and there was no band at approx. 520 cm^{-1} in the actual spectrum.

Although the Me_2As^V protons in **1** resonate at approx. 2.0 ppm and the Me_2As^{III} protons in **1** and **2** at approx. 1.5 ppm,[1,8] the Me_2As protons of **3** resonated at 2.026 ppm in $CDCl_3$ and at 1.980 ppm in CD_3OD (Figure 1). It should be noted that the iodide Me_2As-I (**6**) resonated at 2.016 (this work) or 2.01[9] in $CDCl_3$, at 1.98 in CD_3OD,[6] at 2.00 as neat liquid,[10] while it resonated in the expected region, i.e. at δ = 1.46 ppm, in benzene.[11] The origin of the downfield shift of the methyl protons of **6** and **3** is still unknown.

The reaction of I_2 with Bunsen's disulfide can involve I_2+**1** and/or I_2+**2**. In the first case **1** has inherently electrophilic and nucleophilic properties, and there will be a *nucleophilic* attack on the positively polarized iodine atom, $^{\delta+}I–I^{\delta-}$. The attacking atom should be **c** as shown in Figure 2 and not **a** or **b** because the latter case do not give quantitatively **3** without further rearrangements. The same occurs if I_2 attacks at the As^V **d** with the negatively charged iodine atom. In the second case, as I_2 reacts with **2**, the equilibrium between **1** and **2** shifts towards **2**. Based on the mechanisms proposed for the reaction of halogens with disulfides, i.e. nucleophilic attack of the electrons of the S–S bond at $X–X$[12] and nucleophilic attack of the electrons of sulfur at $X–X$,[13,14] it seems that both are possible with **2**, as shown in Figure 2. The formation of **4** can be visualized as a concerted reaction of iodine atoms with arsenic atoms of **1**.

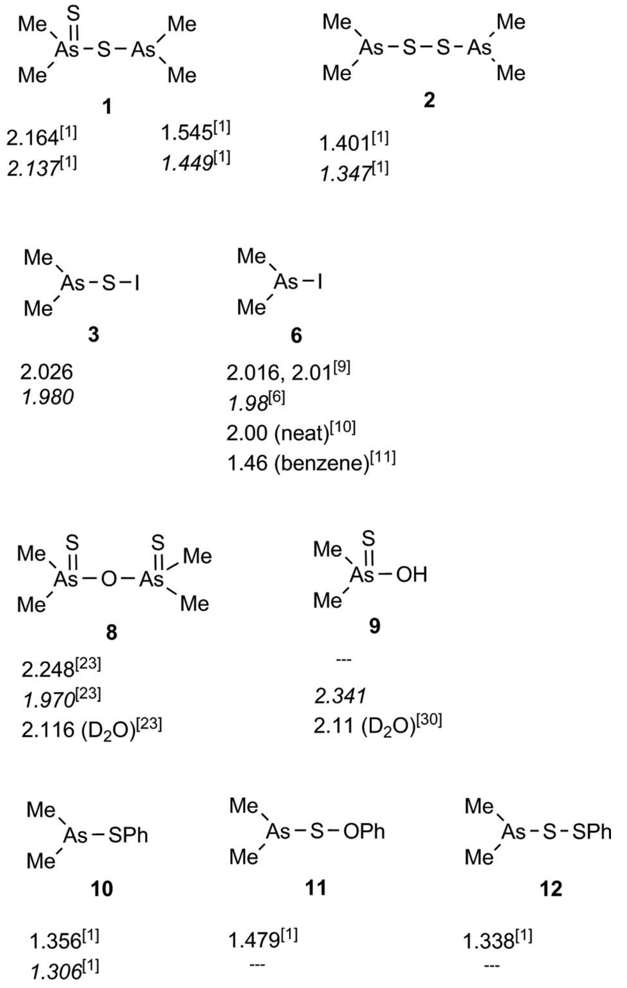


Figure 1. Formulae of the compounds encountered in this work showing the Me_2As proton shifts in $CDCl_3$ and in CD_3OD (italics). The δ values have a range of less than ±0.002 ppm of the quoted values.

Reactivity of Me_2As-S-I (3)

From the sulfenyl halides proper, *R*–S*X*, the chlorides, *R*SCl, have been mostly studied,[3] although sulfenyl iodides may have biological importance.[15,16] The sulfenyl halides show dual reactivity (i.e. they are "electromeric"[17]). Thus, in nucleophilic reactions the nucleophile attacks at sulfur expelling the halide anion. Less frequently the sulfenyl halide releases a positive halogen or reacts via free radicals.[17]

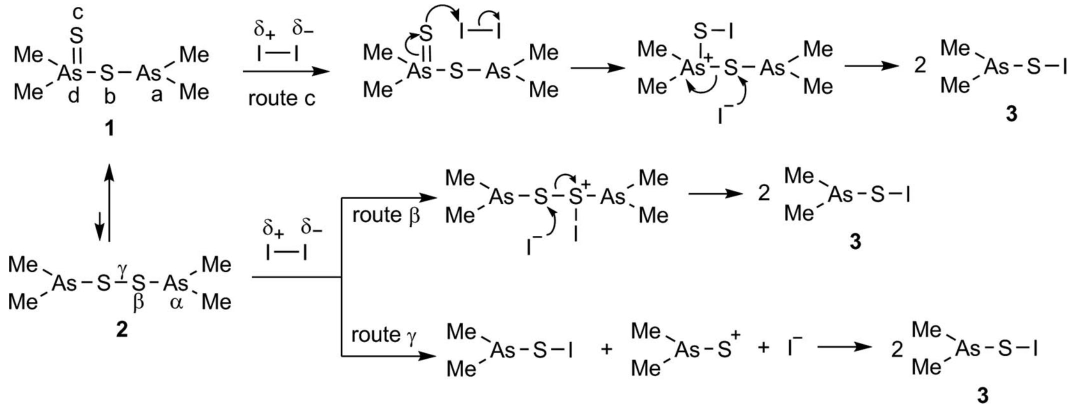
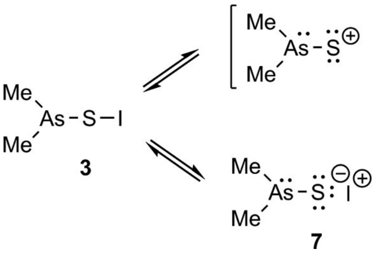


Figure 2. Probable mechanisms for the formation of **3** from **1** and **2**.

The sulfenyl halides, *R*–S*X*, can be considered to be polarized as $RS^{\delta+}–X^{\delta-}$ [18] and in the limit the (solvated) sulfenium ion, $R–S^+$,[19] can be obtained. A stabilized sulfenium was detected in a crystalline complex.[20] Therefore, the reactions of sulfenyl halides can be viewed from the sulfenium ion perspective.



(2)

The sulfenyl iodide **3** can be considered to be similarly polarized $Me_2As–S^{\delta+}–I^{\delta-}$ and it can give the novel sulfenium ion in resonance with the "arsenium" ion **5** [Equation (2)], i.e. the sulfenium ion can be *intra*molecularly stabilized. **5** has been previously postulated.[21,22] Based on this consideration, the reverse polarization to give **7** [Equation (2)], is not expected unless the iodonium I^+ is strongly stabilized by a Lewis base.

Reactions of $Me_2As–S–I$ (3): Conditions and the Identification of the Products

The stability of **3** under various conditions, its redox properties, and the nucleophilic substitution of its iodine by group 15 and 16 nucleophiles were studied by ^1H and ^{31}P NMR spectroscopy. In some cases the reactions were worked up and also run on a preparative scale.

The identification of the species in solution (Figure 1) was based on the accumulated data on compounds having Me_2As^{III} and $Me_2As(S)$– groups[1,8,21–23] and the shifting of the *Me*$_2$As protons on binding of a nucleophile to **3**, although it was not so profound. The position of the sharp singlets in some cases was not fixed probably indicating a fast exchange between **3** + Nu and $Me_2As–S–Nu^+I^-$. The shifting of the aromatic protons in some nucleophiles upon binding to **3** corroborated such a binding. For phosphorus(III) nucleophiles, the binding or reaction was studied by ^{31}P NMR as well, and assignment of the singlets was based on literature data.[24–26]

Stability of Me_2As-S-I (3)

Sulfenyl iodides, *R*–SI, are rare because of their high reactivity and not for their inherent instability.[27] They undergo a facile disproportionation to disulfide and I_2[28] that can be suppressed by very bulky flanking groups.[29] The new $Me_2As–S–I$ (**3**) seems to be quite stable. Thus, attempted distillation at reduced pressure (20 Torr) gave no distillate and a black oil remained. When neat **3** was stored at +4 °C or at –20 °C, it was stable for at least 15 d. As a solution in $CDCl_3$, **3** was stable at +4 °C for at least 15 d and at –20 °C for at least 40 d. On TLC (petroleum ether) it was decomposed producing S_8. A sample of **3** in $CDCl_3$ left in daylight for 2 d gave six new singlets in the ^1H NMR spectroscopy. Compound **2** was not detected. *Field* et al.[15] reported that brief UV irradiation of $Me_3C–SI$ gave the disulfide and I_2 and the reverse reaction did not take place.

As sulfenyl halides are not stable in the presence of water and they are hydrolyzed to $RSO_2–SR$ and *RSSR*[17] via *R*SOH, which acts as a S nucleophile to itself,[27] so **3** in CD_3OD is partly hydrolyzed by H_2O (1:3 molar ratio of **3** to H_2O) in 1 h to give $Me_2As(S)–O–As(S)Me_2$ (**8**).[21] With more water (1:13 molar ratio) in 3 h **3** and **8** reacted giving $Me_2As(S)–OH$ (**9**)[30] resonating at 2.341 ppm. **9** in D_2O resonates at δ = 2.11 ppm[21,30] and in CD_3OD/D_2O 3:1 at 2.056.[8] A probable mechanism for the formation of **8** may involve the internally stabilized sulfenium cation **5** as a key species.[22]

Redox Properties of Me_2As-S-I (3)

Addition of one equivalent of 30 % aqueous H_2O_2 to a solution of **3** (+**8**) in CD_3OD gave at once a brown solution, indicative of I_2, whose ^1H NMR showed absence of **3** and the presence of two singlet signals at 1.911 and 1.931 ppm having intensities 4:6, respectively, that could not be assigned. Adding one more equivalent of H_2O_2 changed only the intensities to 9:6. Sulfenyl halides are progressively oxidized to sulfinyl and sulfonyl halides giving eventually sulfonic acids.[17]

While zinc dust with sulfenyl halides gave disulfides, *RSSR*,[17] it gave with **3** (+**8**) in CD_3OD two prominent sharp singlet signals at 1.274 and 1.349 ppm, with a 6:6.3 integrations, and other five minor singlet signals at approx. 2 ppm. The singlet at 1.274 could not be assigned but the singlet at 1.349 ppm can be due to the disulfide **2** probably stabilized towards formation of **1** by complexation with ZnI_2 as in the case of **2** and $AlCl_3$.[23] The less electropositive Ag (as silver wool) did not react with **3** in $CDCl_3$ or $CDCl_3/CD_3OD$ 1:1 after 24 h.

Addition of an equimolar quantity of dry NaI to **3** (+**8**) in CD_3OD, a light orange solution was formed and ^1H NMR showed only the singlet signals due to **3** and to **8**. The disulfide **2** and I_2 were not produced although they were expected based on the behavior of sulfenyl halides.[17]

Reactions of Me_2As-S-I (3) with Nitrogen Nucleophiles

Triphenylamine and **3** in $CDCl_3$ did not react because the lone pair on nitrogen atom is on a p atomic orbital[31] and, being involved in p_π interaction with the phenyl groups is not available for donation to acids e.g. HF, HCl, $HClO_4$.[32]

Diphenylamine and **3** under 2:1 stoichiometry did not react in $CDCl_3$ (24 h) but interacted as the shifting of *Me_2*As singlet to 2.001 ppm indicated and **2** was not detected. In dry ether or ether/pentane $Ph_2NH{\cdot}HI$ was not precipitated out. Under 1:1 stoichiometry ^1H NMR revealed only binding (singlet at 2.007 ppm). The non-reactivity of Ph_2NH towards **3** may, in part, be due to being a nearly planar molecule.[33] It should be noted that Me_3C–SI reacted with piperidine, giving the expected sulfonamide.[15] In contrast, piperidine and **3** under a 2:1 stoichiometry in dry ether in less than 1 h gave a white odorous solid (118 %), which was piperidine hydroiodide (by ^1H NMR). From the ether supernatant malodorous oil was isolated that by ^1H NMR ($CDCl_3$) exhibited singlet signals at 1.401, 1.738, 1.910, and 2.034 ppm with integrations 0.6:1.0:1.0:0.25. The signals could not be assigned except the one at 1.401 ppm, which can be due to **2** and/or Me_2As–S–$AsMe_2$.[8]

Aniline and **3** under a 3:2 molar ratio in $CDCl_3$ did not react after 24 h at room temperature but only interacted. No solid precipitated running the reaction in dry ether or ether/pentane. However, *n*-butylamine was reactive towards triphenylmethyl sulfenyl iodide[34] and the sterically protected aromatic sulfenyl iodides reacted with excess benzylamine giving sulfenamides.[29]

Pyridine and **3** in $CDCl_3$ under 1:1 to 1.5:1 molar ratios interacted as the ^1H NMR spectra showed. Approx. 0.02 molecules of **2** per molecule of **3** were detected implying the formation of a 1:1 charge transfer complex $py{\cdot}I_2$[35] giving a solution with a very pale yellowish color. When the $CDCl_3$ solution was evaporated, dried, and treated with ether, traces of an off-white solid was obtained that by ^1H NMR in CD_3OD had the *Me_2*As protons at 2.115 ppm and the aromatic protons well downfield (8.10, 8.64 and 8.87 ppm) approaching those of py·HCl implying the formation of $Me_2As\text{-}S\text{-}py^+I^-$.

4-Dimethylaminopyridine (DMAP) and **3** reacted in $CDCl_3$ under 1:1 stoichiometry. In 1 h, 0.14 molecules of complexed **3**, resonating at 1.981 ppm, were left and two singlet signals at 1.400 and 1.354 ppm appeared that merged in 24 h to one at 1.398 ppm assigned to **2** (0.40 molecules). The production of **2** in greater amounts than with pyridine implies the formation of a stronger 1:1 charge transfer complex $DMAP{\cdot}I_2$[36] and the absence of signals due to **1** indicates inhibition of the reversion of **2** to **1**.

A likely mechanism for the formation of **2** from **3** in the presence of pyridine or DMAP is based on the equilibria of Equation (2). If the base acts on **5**, then an externally stabilized sulfenium **5** will be present. The base, however, can promote the formation of iodonium I^+, as in the case of sulfenyl halides,[17] that can be stabilized as, e.g. py_2I^+.[37] The reaction of cation **5** with anion **7** will give the observed **2** and combination of I^- and I^+ will give I_2 forming charge transfer complexes, Base·I_2.

Triethylamine and **3** in $CDCl_3$ behaved quite differently compared to pyridine and DMAP. Under 1:1 molar ratio, the clear colorless solution, in 1 h, contained "protonated" Et_3N and only 0.04 molecules of complexed **3**, 0.03 molecules of **2**, 0.02 molecules of an unknown species at 1.852 ppm, and 0.90 molecules of an unknown species at 1.299 ppm were seen. The later singlet is in-between the singlets of cacodyl (Me_2As–$AsMe_2$) at δ = 1.11 ppm[38] and Me_2As–S–$AsMe_2$ or **2** at 1.399 ppm.[8] Working up gave a white, needle-like solid, not suitable for X-ray analysis, that was analyzed as $3Et_3N{\cdot}2I_2$. Its IR (KBr) did not match the spectrum of $Et_3N{\cdot}HCl$ in KBr or perfluorinated paraffin oil[39] nor $Et_3N{\cdot}HI$ in the same solvent.[39] In $CDCl_3$ the solid gave a yellow solution that revealed a "protonated" nitrogen with the *CH_3* protons as one triplet (at 1.474 ppm) but the C*H_2* protons appeared as two quartets of equal intensities (at 3.173 and 3.186 ppm). The formation of $3Et_3N{\cdot}2I_2$ was reproducible in other runs, as the elemental analyses revealed. The constitution of $3Et_3N{\cdot}2I_2$ could not be formulated based either on the work done[40–42] on the strong but unstable complex formed from Et_3N and I_2 nor the X-ray analysis of $py{\cdot}2I_2$.[43] It is of interest that the reaction of **3** with Et_3N has produced I_2 virtually without producing **2**. Therefore, another atom from **3** should be reduced and, since sulfur having oxidation number of zero was expelled as S_8, it remains As^{III} to be reduced, probably to cacodyl, Me_2As–$AsMe_2$.

Summarizing, although tertiary amines reduce sulfenyl halides to disulfides and the salt of the radical cation $R_3N^{\cdot+}$,[44] **3** and py or DMAP gave the disulfide **2** and I_2 but with Et_3N the nature of the arsenic-containing species is not certain. If base is to be used for promotion of reactions of **3**, pyridine must be the base of choice (see also reference[18]).

Reactions of Me_2As-S-I (3) with Phosphorus Nucleophiles

The reaction of equimolar quantities of **3** and triphenylphosphine in $CDCl_3$, in 1 h, resulted in the production of Me_2AsI (**6**), $Ph_3P{=}S$ by ^1H and ^{31}P NMR {43.9 ppm; literature value

–42.6 ppm[24]} and 0.07 molecules of **2** per molecule of **6**. Under similar condition the non-fissionable phosphite $(PhO)_3P$, in 6 h, produced only 22 % **6** giving $(PhO)_3P{=}S$ as estimated from the ^{31}P spectrum,[24] and from the ^1H NMR spectrum **2** (0.08 molecules) was present per (**3** plus **6**) both resonating at 2.015 ppm as one singlet. With $(PhO)_3P$ aromatic sulfenyl chlorides gave ArSSAr and $(PhO)_3PCl_2$, whereas aliphatic sulfenyl chlorides were desulfurized to $(PhO)_3P{=}S$ and *R*Cl.[45] Ph_3P did not react with **6**.[46] Our results with Ph_3P and $(PhO)_3P$ on **3** are in line with their effect on **1**, where Ph_3P desulfurized **1** in 5 min, while $(PhO)_3P$ reacted slowly[8] and on S_8, where Ph_3P reacted slowly, while $(PhO)_3P$ did not react at all.[47]

Tris(phenylthio)phosphine[48] in $CDCl_3$ reacted slowly (>24 h) with **3** giving, by ^{31}P NMR, $(PhS)_3P{=}S$ (at δ = 93.1 ppm; literature value –91.1 ppm[25]) but most $(PhS)_3P$ had not reacted (δ = 133.1 ppm; literature value –130.5 ppm[25]). The overall reaction was complicated because the ^1H NMR spectra showed, that **2** was produced in 1 h but in 24 h had reacted and $Me_2As–SPh$ (**10**) was present at 1.353 ppm,[1] arising by an unknown mechanism. The prominent singlet at 2.019 ppm could be due to {**3** and **6**}.

There are no reports on the reaction of sulfenyl halides with the more nucleophilic than Ph_3P, tris(dimethylamino)phosphine. In $CDCl_3$ **3** was quickly (< 1 h) desulfurized by $(Me_2N)_3P$, some **2** was produced but it seems that **6** reacted further giving singlet signals at 1.208, 1.246, and 1.83 ppm. In the ^{31}P NMR spectrum, apart from the $(Me_2N)_3P{=}S$ signal at δ = 82.3 ppm (literature value –77.5 ppm[24]), two singlet signals at δ = 49.7 and 26.3 ppm were present, the latter close to the $(Me_2N)_3P{=}O$ signal (literature value –23 ppm[24]).

The mechanism of desulfurization of **3** by the above P^{III} nucleophiles most likely involves the formation of the quasi-phosphonium intermediate $Me_2As–S–PAr_3{}^+I^–$ followed by attack of $I^–$ on As^{III} to give $Me_2As–I$ (**6**). The production of **2** can be explained as in the case of nitrogen nucleophiles.

Even more complicated was the reaction of **3** with the fissionable nucleophile $(EtO)_3P$. Thus in $CDCl_3$, in 1 h, apart from $(EtO)_3P$, $CH_3CH_2–I$, **2**, and a compound having H–P proton (6.817 ppm, *J* 692 Hz) were detected. In the ^{31}P spectrum six signals were present at –27.6, 14.6, 18.8, 23.1, 53.0, and 81.2 (major) ppm. $(EtO)_3P{=}S$ was not present at (–)68.1 ppm,[24] implying that $(EtO)_3P$ did not desulfurize **3** but reacted in an Arbuzov-type manner, like the reactions of trialkyl phosphites with sulfenyl halides.[4,17,45] A very small amount of the expected Arbuzov product, $Me_2As–S–P(O)(OEt)_2$, was detected at approx. 20 ppm, which being based on the chemical shift of $(ClPhS)P(O)(OEt)_2$ at –21 ppm.[49] The major singlet at 81.2 is found within the range of 50–100 ppm for thiophosphoryl compounds[26,49] but its identity remains unknown.

Reactions of Me_2As-S-I (3) with Arsenic Nucleophiles

There are no reports in the literature on the reaction of sulfenyl halides with arsenic(III) nucleophiles. In contrast to Ph_3P, the homologous Ph_3As in $CDCl_3$ did not react with **3** in 1 h. A small amount (ca. 0.08 molecules) of **2** was present in the solution. A weak binding cannot be excluded because *Me_2*As protons were at 2.013 ppm.

Tris(phenylthio)arsine, $(PhS)_3As$, reacted slowly and in a complicated way with **3** in $CDCl_3$. After 24 h at room temp., the ^1H NMR spectrum showed in the aromatic region $(PhS)_3As$, absence of PhSSPh and presence of signals some of them attributable to $Me_2As–SPh$ (**10**). In the aliphatic region there was a singlet at 1.353 ppm due to **10**[1] and another singlet of equal intensity at 2.021 ppm. **2** was not detected. TLC (petroleum ether) showed three spots that could not be assigned and one spot due to S_8. The production of **10** is difficult to explain.

Reactions of Me_2As-S-I (3) with Oxygen and Sulfur Nucleophiles

While sulfenyl halides with NaOH gave disulfides and thiosulfonic acid esters, $Ar–SO_2–SAr$, or sodium arylsulfinate, $Ar–SO_2Na$, depending on the stoichiometry,[17] **3** and NaOH (1:1 molar ratio) in CD_3OD reacted (30 min to 24 h) giving four singlet signals at 1.274 (main), 1.560, 1.738, and 1.910 ppm, none of which could be assigned. The disulfide **2** was not detected.

Silver oxide reacted slowly with **3** (1:2 molar ratio) in $CDCl_3$ producing in 24 h the yellow AgI and a clear, colorless solution containing two main singlet signals at 1.403 ppm, most likely due to the disulfide **2**, and at 1.853 ppm that could not be assigned.

Methanol or phenol in stoichiometric amounts or excess to **3** in $CDCl_3$ did not interact after 2 d at room temperature. These findings are in line with the reports that sulfenyl chlorides react with alcohols and phenols when heated or when their alkali metal salts are used.[5] So, despite the shortcoming of $CDCl_3$ as a solvent in the presence of PhONa, we tried its reaction with **3**. After 30 min shaking most PhONa had reacted (a few needles floating), **3** had reacted and the main singlet was at 1.478 ppm due to expected $Me_2As–S–OPh$ (**11**), a very small singlet at 1.401 ppm due to **2** and six small singlets in the regions 1.255–1.342 and 1.810–2.004 ppm were seen. After 8 h, most **11** had reacted and the spectrum contained singlet signals of **2** and of unknown compounds at 1.255, 1.876, 1.981, and 1.991 ppm. As some “monothioperoxide” derivatives of sulfenyl halides are unstable,[5] **11** was not stable and decomposed giving more **2** and other non identifiable, by ^1H NMR, compounds.

Thiophenol and **3** in $CDCl_3$ after 24 h at room temperature produced only 0.05 molecules of $Me_2As–SPh$ (**10**). However, sodium thiophenoxide in $CDCl_3$ shaken with **3** gave a yellowish precipitate (impure NaI) and a colorless solution containing **10**, $Me_2As–SSPh$ (**12**), **2** and **1** in a molar ratio of 1.0:0.06:0.01:0.03, respectively. A small singlet at 2.038 ppm could not be assigned. TLC (petroleum ether) showed the presence of S_8 and three other spots. These results indicate that $PhS^–$ attack mainly at the As^{III} of **3** and the S_8 came from NaSI. However, the formation of **1** and **2** cannot be explained.

Conclusions

The novel, quite stable sulfenyl iodide **3** having the –SI group linked to As^{III} was prepared in good yields from Bunsen's cacodyl disulfide (**1**) and iodine. It was reactive towards H_2O and redox reagents, but not NaI, indicating that it did not easily produce I^+. An overview of the reactivity of **3** towards nitrogen, phosphorus, arsenic, oxygen, and sulfur nucleophiles was given. Each group of nucleophiles behaved differently and even the various members in each group showed variable reactivity, e.g. from non reactivity with Ph_3N to complete decomposition with piperidine and Et_3N. The reactions, in general, gave by-products that made the isolation of pure products difficult because of the small scales used. In any case, externally stabilized sulfenium cations of the type $Me_2As–S–Nu^+I^–$ could not be isolated.

Experimental Section

Bunsen's cacodyl disulfide (**1**) was prepared according to *Zingaro* et al.[2,8,50] The sources and purity of the nucleophiles (amines, phosphorus(III), arsenic(III), oxygen and sulfur(II) compounds) are described in a previous publication.[1] Solvents were kept over 4 Å molecular sieves. Silica gel 60 H (Merck) was used for thin layer chromatography, TLC.

TLCs were run on microslides and visualization was effected by iodine vapors. IR spectra were obtained with a Perkin-Elmer model 16PC FT-IR spectrometer. ^1H NMR spectra (400 MHz) and ^{31}P NMR spectra (162 MHz) were recorded with a Bruker DPX Avance spectrometer with either internal TMS (0.000 ppm) or external 84 % H_3PO_4 (δ = 0.00 ppm) as standards, respectively. Elemental analyses were obtained through the Centre of Instrumental Analyses, University of Patras, Patras, Greece.

Theoretical Calculations: Molecular orbital ab initio calculations based on Hartree-Fock (HF) and second order Møller-Plesset (MP2) perturbation theory as implemented in the Gaussian09 program package,[51] were utilized in the present study in order to calculate the structural details and the vibrational frequencies of $Me_2As–S–I$ (**3**), $Me_2As(S)–I$ (**4**), and $Me_2As(S)–OH$ (**9**) molecular units. The basis sets that were used are the Pople's 6-311G** split-valence triple-zeta basis set plus d polarization function on non-hydrogen and p polarization function on hydrogens.[52] Specific basis sets were obtained by use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library.[53] The geometries of all structural models were fully optimized at the MP2 all-electrons level of theory.

Preparation of Dimethylarsinosulfenyl Iodide (3): A solution of iodine (127 mg, 0.5 mmol) dissolved in dry dichloromethane (10 mL) in a oven-dried conical flask was added dropwise to vigorously stirred solution of Bunsen's disulfide (**1**) (137 mg, 0.5 mmol) dissolved in dry dichloromethane (5 mL) in an oven-dried spherical flask. The orange suspension, containing some brown solid, was stirred at room temperature for 3 h giving a clear yellowish solution and a small amount of beige solid. Concentration to approx. 3 mL (rotary, 13 °C) gave a yellow solution (plus the solid) that was treated with 3 drops of aqueous sodium thiosulfate by stirring vigorously for 5 min. Filtration (Pasteur pipette plugged with cotton having on top anhydrous sodium sulfate) gave a pale yellow solution that was evaporated (rotary, 13 °C) to give a red-orange oil (241 mg, 91 %) that by ^1H NMR contained approx. 2 % CH_2Cl_2, soluble in ether and pentane. C_2H_6ISAs (M_r 263.95): calcd. C 9.10, H 2.29, S 12.15 %; found C 9.46, H 2.31, S 11.73 %. **IR** (neat): $\tilde{\nu}$ = 3015 m, 2976 m, 2900 m, 2788 w, 1403 vs, 1252 s, 899 vs, 874 s, 838 vs, 763 w, 582 vs, 572 vs cm^{-1}. **^{1}H NMR** ($CDCl_3$, TMS): δ = 2.026 (s), 5.301 (s, CH_2Cl_2). **^{1}H NMR** (CD_3OD, TMS): δ = 1.980 (s), 5.484 (s, CH_2Cl_2), 1.970 [s, due to *Me*$_2$As(S)–O–As(S)*Me*$_2$ (**8**)[21]].

Stability of Me_2As-S-I (3): The stability of **3** as a neat liquid and as a solution in $CDCl_3$ was studied by ^1H NMR under various conditions of temperature, daylight and sunlight, and on TLC. The hydrolytic stability of **3** was studied by ^1H NMR in CD_3OD by adding various amounts of H_2O.

Oxidation and Reduction of Me_2As-S-I (3): To freshly prepared solutions of **3** in CD_3OD, 30 % H_2O_2, dry sodium iodide, Ag wool or zinc powder under various stoichiometries were added and the NMR tubes shaken. The progress of the reactions was followed by ^1H NMR spectroscopy.

Reaction of Me_2As-S-I (3) with Various Nucleophiles: The reactions of **3** (approx. 50 µmol) in $CDCl_3$ (approx. 0.6 mL) with various nucleophiles were followed by ^1H NMR and sometimes they worked up or were done in a preparative scale (approx. 0.2 mmol).

Reaction of Me_2As-S-I (3) with Diphenylamine: To a solution of **3** (20 mg, 76 µmol) in $CDCl_3$ (0.6 mL) was added diphenylamine (12.8 mg, 76 µmol) and the clear solution after 20 h was examined by **^{1}H NMR** ($CDCl_3$, TMS): δ = 2.011 (s, 6 H, *Me*$_2$As), 6.922 (t, *J* = 7.2 Hz, 2 H, *p*–Ph–*H*), 7.066 (d, *J* = 8.0 Hz, 4 H, *m*–Ph–*H*), 7.259 (t, *J* = 8.0 Hz, 4 H, *o*–Ph–*H*).

Running the reaction under 1:2 molar ratio of **3** to Ph_2NH in $CDCl_3$, after 24 h the ^1H NMR showed a singlet at 2.001 ppm and the aromatic signals at 6.917 (t), 7.055 (d), 7.253 (t), i.e. slightly upfied from the corresponding signals of free Ph_2NH.

Running the 1:2 reaction in dry ether, nothing precipitated after 48 h stirring. Addition of dry pentane did not cause any precipitation.

Reaction of Me_2As-S-I (3) with Triethylamine: In a NMR tube containing a solution of **3** (37 µmol) in $CDCl_3$ (0.6 mL) was syringed in dry triethylamine (5.2 µL, 37 µmol) and the clear, colorless solution, after 1 h, examined by ^1H NMR contained "protonated" Et_3N (at δ = 1.46 and 3.15 ppm) and singlet signals at 1.299 (integration 6.00), 1.401 (0.21 due to **2**), 1.852 (0.13), and 1.980 (0.24 due to complexed **3**). Evaporation, drying in vacuo and treatment with ether gave 8.0 mg of an off-white solid, decomposing at 174–176 °C to bubbly orange oil. $3Et_3N\cdot 2I_2$ i.e. $C_{18}H_{45}N_3I_4$ (M_r 811.17): calcd. C 26.65, H 5.59, N 5.18 %; found C 26.80, H 5.38, N 4.62, S 0.00 %. **IR** (KBr): $\tilde{\nu}$ = 2972 vs, 2938 vs, 2794 s, 2760 vs, 2680 vs, 2478 s, 1466 vs, 1422 vs, 1398 vs, 1364 m, 1284 w, 1166 s, 1078 w, 1064 w, 1034 vs, 846 w, 802 m, 752 w, 466 w cm^{-1}. **^{1}H NMR** ($CDCl_3$, TMS, yellow solution): δ = 1.474 (t, *J* = 7.2 Hz, 9 H, CH_3), {3.173 (q, *J* = 7.2 Hz) and 3.186 (q, *J* = 7.2 Hz), 6 H, CH_2N^+}.

A preparative run in dry ether gave a white solid that washed with diethyl ether and dried in air to give 83 % of $3Et_3N\cdot 2I_2$, containing traces of S_8 by TLC (petroleum ether), soluble in acetone from which, by addition of ether, needles not suitable for X-rays were obtained.

Supporting Information (see footnote on the first page of this article): Experimental spectra of **1** and **3** and theoretical results and spectra of **3**, **4**, and **9**.

References

[1] P. V. Ioannou, D. G. Vachliotis, *Z. Anorg. Allg. Chem.* **2015**, *641*, 710–714.

[2] R. A. Zingaro, K. J. Irgolic, D. H. O'Brien, L. J. Edmonson Jr., *J. Am. Chem. Soc.* **1971**, *93*, 5677–5681.

[3] E. Kühle, *Synthesis* **1970**, 561–580.

[4] J. Michalski, B. Pliszka-Krawiecka, *J. Chem. Soc. C* **1966**, 2249–2252.

[5] E. Kühle, *Synthesis* **1971**, 617–638.

[6] K. A. Porter, A. C. Willis, J. Zank, S. B. Wild, *Inorg. Chem.* **2002**, *41*, 6380–6386.

[7] L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, M. N. Gibbons, D. B. Sowerby, *J. Organomet. Chem.* **1997**, *549*, 187–192.

[8] P. V. Ioannou, D. G. Vachliotis, T. D. Sideris, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2077–2084.

[9] C. R. Mitchell, R. A. Zingaro, *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 1–6.

[10] a) S. R. Jain, H. H. Sisler, *Inorg. Chem.* **1968**, *7*, 2204–2207; b) K. J. Irgolic, R. A. Zingaro, L. J. Edmonson Jr., *Phosphorus* **1975**, *5*, 183–187.

[11] A. L. Rheingold, E. J. Pleau, W. T. Ferrar, *Inorg. Chim. Acta* **1977**, *22*, 215–218.

[12] A. J. Parker, N. Kharasch, *Chem. Rev.* **1959**, *59*, 583–628.

[13] J. L. Kice, *Sulfur-Sulfur Bond*, in *Sulfur in Organic and Inorganic Chemistry*, vol. I, (Ed.: A. Senning), Marcel Dekker, N. York, pp 153–207, **1971**, cited by *Fair* and *Gupta* in Ref. [14].

[14] N. Fair, B. S. Gupta, *Prog. Polym. Sci.* **1985**, *11*, 167–200.

[15] L. Field, J. L. Vanhorne, L. W. Cunningham, *J. Org. Chem.* **1970**, *35*, 3267–3273.

[16] C. Wismach, P. G. Jones, W.-W. du Mont, G. Mugesh, U. Papke, H. B. Linden, M. Arca, V. Lippolis, *Eur. J. Inorg. Chem.* **2014**, 1399–1406.

[17] E. Kühle, *Synthesis* **1971**, 563–586.

[18] N. Kharasch, *J. Chem. Educ.* **1956**, *33*, 585–591.

[19] G. K. Helmkamp, D. C. Owsley, W. M. Barnes, H. N. Cassey, *J. Am. Chem. Soc.* **1968**, *90*, 1635–1638.

[20] M. Gressenbuch, B. Kersting, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1435–1437.

[21] P. V. Ioannou, D. G. Vachliotis, T. D. Sideris, *Z. Anorg. Allg. Chem.* **2009**, *635*, 329–336.

[22] P. V. Ioannou, *Main Group Chem.* **2014**, *13*, 243–250.

[23] P. V. Ioannou, G. M. Tsivgoulis, D. G. Vachliotis, *Main Group Chem.* **2009**, *8*, 151–161.

[24] E. Fluck, H. Binder, *Z. Anorg. Allg. Chem.* **1967**, *354*, 139–148.

[25] K. Moedritzer, L. Maier, L. C. D. Groenweghe, *J. Chem. Eng. Data* **1962**, *7*, 307–310.

[26] N. Muller, P. C. Lauterbur, J. Goldenson, *J. Am. Chem. Soc.* **1956**, *78*, 3557–3561.

[27] D. R. Hogg, *Sulfenic Acids and their Derivatives*, in *Comprehensive Organic Chemistry* (Eds.: D. Barton, W. D. Ollis), Pergamon Press, Oxford, **1979**, vol. 3, pp. 261–310.

[28] T. M. Klapötke, J. Passmore, *Acc. Chem. Res.* **1989**, *22*, 234–240.

[29] a) K. Goto, M. Holler, R. Okazaki, *Chem. Commun.* **1998**, 1915–1916; b) K. Goto, G. Yamamoto, B. Tan, R. Okazaki, *Tetrahedron Lett.* **2001**, *42*, 4875–4877.

[30] M. Fricke, M. Zeller, W. Cullen, M. Witkowski, J. Creed, *Anal. Chim. Acta* **2007**, *583*, 78–83.

[31] A. N. Sobolev, V. K. Belsky, I. P. Romm, N. Yu. Chernikova, E. N. Guryanova, *Acta Crystallogr., Sect. C* **1985**, *41*, 967–971.

[32] R. D. W. Kemmitt, R. H. Nuttall, D. W. A. Sharp, *J. Chem. Soc.* **1960**, 46–50.

[33] M. A. Rodriguez, S. D. Bunge, *Acta Crystallogr., Sect. E* **2003**, *59*, o1123-o1125.

[34] E. Ciuffarin, G. Guaraldi, *J. Org. Chem.* **1970**, *35*, 2006–2010.

[35] C. Reid, R. S. Mulliken, *J. Am. Chem. Soc.* **1954**, *76*, 3869–3874.

[36] J. M. Daisey, A. J. Sonnessa, *J. Phys. Chem.* **1972**, *76*, 1895–1901.

[37] S. G. W. Ginn, J. L. Wood, *Trans. Faraday Soc.* **1966**, *62*, 777–787.

[38] R. K. Harris, R. G. Hayter, *Can. J. Chem.* **1964**, *42*, 2282–2291.

[39] B. Chenon, C. Sandorfy, *Can. J. Chem.* **1958**, *36*, 1181–1206.

[40] P. Boule, *J. Am. Chem. Soc.* **1968**, *90*, 517–518.

[41] H. D. Bist, W. B. Person, *J. Phys. Chem.* **1969**, *73*, 482–489.

[42] T. F. Akhunov, F. A. Fatkullina, R. A. Karakhanov, D. L. Rakhmankulov, *J. Gen. Chem. USSR* **1983**, *53*, 624–627.

[43] O. Hassel, H. Hope, *Acta Chem. Scand.* **1961**, *15*, 407–416.

[44] N. J. Ioffe, M. I. Kalinkin, I. N. Rozhkov, I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 2070–2072; *English Translation* **1969**, 1929–1930.

[45] K. A. Petrov, G. A. Sokol'skii, B. M. Polees, *J. Gen. Chem. USSR* **1956**, *26*, 3765–3768.

[46] J. M. F. Braddock, G. E. Coates, *J. Chem. Soc.* **1961**, 3208–3211.

[47] J. R. Lloyd, N. Lowther, G. Zsabo, C. D. Hall, *J. Chem. Soc. Perkin Trans. II* **1985**, 1813–1817.

[48] G. M. Tsivgoulis, P. V. Ioannou, *Main Group Chem.* **2011**, *10*, 51–62.

[49] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, R. C. Jones, *J. Am. Chem. Soc.* **1956**, *78*, 5715–5726.

[50] M. W. Fricke, M. Zeller, H. Sun, V. W.-M. Lai, W. R. Cullen, J. A. Shoemaker, M. R. Witkowski, J. T. Creed, *Chem. Res. Toxicol.* **2005**, *18*, 1821–1829.

[51] *Gaussian 09*, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, **2009**.

[52] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648; J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys.* **1997**, *107*, 5016–5021; L. A. Curtiss, M. P. McGrath, J.-P. Blandeau, N. E. Davis, R. C. Binning Jr., L. Radom, *J. Chem. Phys.* **1995**, *103*, 6104–6113; M. N. Glukhovstev, A. Pross, M. P. McGrath, L. Radom, *J. Chem. Phys.* **1995**, *103*, 1878–1885.

[53] D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571–1586; K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.

Received: February 20, 2015
Published Online: May 7, 2015