Synthesis, Spectroscopic, and Structural Characterization of Organyl Disulfanides and a Tetrasulfanide

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One-Step Synthesis, Isolation and Characterization of Various Polysulfanide Compounds

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Abstract: Various room-temperature-stable monoorganylpolsulfanides of the form $X^+RS_n^-$ ($n \geq 2$) were synthesized in a simple and versatile one-step process starting from sodium thiolates and elemental sulfur. The compounds were characterized by X-ray crystal structure analysis, NMR spectroscopy, microelemental analysis and electrospray mass ionization spectrometry including collision-induced dissociation experiments. While these salts are well-defined species as crystals, they undergo complex equilibria in solution. In one case, compounds ranging from $n = 1$ -8 have been observed in solution. Structural features, dynamics in solution as well as thermochromic properties of one of the compounds, $PPh_4^+ PhS_2^-$, are investigated in detail by temperature- and pressure-dependent X-ray crystal structure analysis. The experimental data is complemented by periodic boundary density functional theory calculations on the crystal structures, as well as energy decomposition analyses.

INTRODUCTION

Monoorganylpolsulfanides RS_n^- ($n \geq 2$) have been observed as transient species in the context of reactions involving polysulfides of the form RS_nR .^{1, 2} A few examples are the oxidation of thiolates by elemental sulfur to form RS_nR -type molecules, reactions of inorganic polysulfides S_n^{2-} with alkylhalides, and desulfurization of RS_nR species by strong nucleophiles.³ In the context of this kind of reactions, Paris and coworkers have performed several studies on the formation and equilibria of RS_n^- compounds by spectroelectrochemical means. Due to the instability of these compounds and their tendency to undergo sulfur exchange reactions in solution, no compounds, with only one exception, of this form have been isolated. They have only been observed and investigated in dimethylacetamide (DMA) solutions.^{1, 2, 4-6} The single exception was prepared as a metal-containing 2:1 salt $[M(N\text{-methylimidazole})_6](PhS_2)_2$ for $M = Mn$ and Ni .⁷ Given the paucity of experimental data and the lack of accessible pure compounds of this kind, it is no surprise that the fundamental chemistry of the monoorganylpolsulfanide species is still poorly understood.

The limited understanding has been specifically acknowledged in chemical biology, where the importance of monoorganylpolsulfanides, especially perthiolates (RS_2^-), has been recently recognized.⁸ In biochemical systems, they most often appear as cysteine or glutathione perthiolate species of the form $CysSS^-$ or GSS^- , respectively. Due to the lower pK_a value of $RSSH$ species ($pK_a \sim 6.2$) compared to the closely related RSH thiols ($pK_a \sim 7.6$), perthiolates, in contrast to thiols, predominantly appear in the deprotonated form under physiological conditions. One example of a protein with a cysteine perthiolate group is the enzyme rhodanese. It detoxifies cyanide (CN^-) by converting it to thiocyanate (SCN^-) with the help of a cysteine perthiolate species.^{9, 10} Further examples include the SoxAX protein involved in thiosulfate oxidation¹¹ as well as the adenylyl- and sulfurtransferase MocS3.¹²

Organylpolsulfanide species are further involved as intermediates in the production of the gasotransmitter H_2S in living systems. This occurs enzymatically in nature^{13, 14} and can also be

achieved artificially by using the right chemical tools, called H₂S releasing compounds,^{13, 15-18} with diallyl trisulfide being the most commonly used example. H₂S has been found to have a plethora of roles e.g. in processes like vasodilation¹⁹, neurotransmission²⁰, apoptosis²¹ and, in addition, therapeutic potential.²² Easy access to small polysulfanide compounds might not only offer new candidates for artificial H₂S release but might also allow further mechanistic studies on the subject.

In this work we present a simple one step synthesis as well as the characterization, including crystal structure analyses, of various X⁺PhS₂⁻ salts (X⁺ = PPh₄, bis(triphenylphosphine)iminium (PNP), NEt₄), of an alkyl variant PPh₄⁺*t*-BuS₂⁻ as well as of the even more exotic tetrasulfanide salt PPh₄⁺PhS₄⁻ salt. Synthesis, structural aspects, properties and stability of this unusual class of compounds are discussed. The experimental results are complemented by DFT calculations.

RESULTS AND DISCUSSION

During our studies on homolytic substitution reactions in sulfonium groups²³, we stumbled upon a perthiolate species, namely PPh₄⁺PhS₂⁻, as a reaction side product, inspiring the search for a clean synthesis and isolation of such compounds. Stirring of sodium thiophenolate with one equivalent of tetraphenylphosphonium chloride and one equivalent of elemental sulfur in acetonitrile (MeCN) for a few hours at room temperature (r.t.) under inert atmosphere formed a dark green solution. Filtration and treatment of the filtrate with diethyl ether (Et₂O) and subsequent cooling to -34 °C lead to the formation of moderately air-sensitive shiny orange crystals (Scheme 1). X-ray crystal structure analysis showed them to be the perthiolate species PPh₄⁺PhS₂⁻ ([Fig. 1](#)~~Fig. 1~~, **1a**).

R = Ph, *t*Bu

X = PPh₄, NEt₄, PNP

Scheme 1: Simplified reaction scheme for the synthesis of perthiolate salts.

The perthiolate anion can also be obtained as the yellowish NEt₄ or PNP salts by using the chloride salts of the respective cation as starting materials (crystal structures, see SI, crystallographic details section). Using more than one equivalent of sulfur leads to the oxidation of the formed PhS₂⁻ species by the excess sulfur, forming diphenyl disulfide and the known PPh₄⁺ S₇²⁻²⁴ salt as dark red crystals. As a transient species in this process, the exotic phenyltetrasulfanide PPh₄⁺ PhS₄⁻ ([Fig. 1](#)[Fig.-1](#), [2](#)) can be isolated as dark red crystals by careful fractional crystallization. This compound is stable at room temperature under inert atmosphere. The isolation attempts of PhS_n⁻ (n ≠ 1,2,4) using the corresponding equivalents of sulfur were unsuccessful, even though their formation was observed in mass spectrometric studies and NMR ([Fig. 7](#)[Fig.-7](#), [Fig. 8](#)[Fig.-8](#), [Fig. 9](#)[Fig.-9](#)). Applying the procedure for the synthesis of species **1a-c** with slight modifications to sodium 2-methyl-2-propanethiol, allowed the isolation of the alkyl-perthiolate species **3**. When starting with the sterically much less demanding sodium ethane thiolate we were not able to isolate any ethyl perthiolate species. As a side note, an attempt with an old 2-methyl-2-propanethiol bottle that contained the oxidized sodium tert-butylsulfonate delivered orange crystals that were identified to be the thiosulfonate salt *t*-BuSO₂S⁻ (SI, crystallographic details). This indicates that the procedure presented here also allows easy synthesis of thiosulfonate species. In this work, however, thiosulfonate synthesis is not further explored.

Fig. 1: Structures of the isolated polysulfanide compounds with numbering of relevant atoms.

STRUCTURAL FEATURES

X-ray crystal structures of compounds **1a-c**, **2** and **3** have been obtained together with the structure of PPh₄⁺ PhS⁻ for comparison ([Fig. 2](#)[Fig.-2](#) and SI, crystallographic details). Crystallographic tables can be found in the SI. [Tab. 2](#)[Tab.-2](#) shows selected bond lengths and

angles including diphenyl disulfide (PhSSPh) and 1,4-di-p-tolyltetrasulfane (MePhSSSSPhMe) as reference compounds. The most striking difference between the anions in compounds **1a-c** and the one in **2** is the C₂-C₁-S₁-S₂ dihedral angle. The PhS₂⁻ anions (**1a-c**) are in all cases almost planar exhibiting a C₂-C₁-S₁-S₂ dihedral angle around 180°. This suggests π -electron conjugation over the whole molecule. In contrast, the PhS₄⁻ anion (**2**) exhibits a C₂-C₁-S₁-S₂ dihedral angle of -129° indicating that the conjugation of the sulfur chain with the ring system is broken up. Instead, the p-electrons of the S₄ moiety seem to be “isolated” from the phenyl ring.

Fig. 2: Crystal structures of compounds **1-3** (50% probability ellipsoids). Hydrogen atoms as well as anion disorder for compound **3** (visible in SI, crystallographic details) are omitted for reasons of clarity.

Tab. 1: Selected bond lengths and dihedral angles of PPh₄⁺ PhS_n⁻ species and PPh₄⁺ t-BuS₂⁻, as well as of PhSSPh²⁵ and MePhSSSSPhMe¹⁸ for comparison.

compound	bond distances/Å				dihedral angles/°		
	C _{Ph} -S ₁	S ₁ -S ₂	S ₂ -S ₃	S ₃ -S ₄	C _{Ph,2} -C _{Ph,1} -S ₁ -S ₂	C _{Ph,1} -S ₁ -S ₂ -S ₃	S ₁ -S ₂ -S ₃ -S ₄
PPh ₄ ⁺ PhS ⁻	1.748	-	-	-	-	-	-
PPh ₄ ⁺ PhS ₂ ⁻ (1a)	1.767	2.043	-	-	-176.98	-	-
PPh ₄ ⁺ PhS ₄ ⁻ (2)	1.781	2.080	2.047	2.023	-128.56	-88.66	-87.97

PPh ₄ + <i>t</i> -BuS ₂ ⁻ (3)	1.847	2.067	-	-	-	-	-
PhSSPh ²⁵	1.788	2.023	-	-	-163.49	-	-
	1.789 (2nd ring)				179.92 (2nd ring)		
MePhSSSSPhMe ¹⁸	1.775	2.057	2.054	2.042	-104.68	-86.39	-82.79
	1.791 (2nd ring)				-136.97 (2nd ring)		

A computational study investigating the rotation around the C-S bond was performed. For purpose of method validation, four different functionals²⁶ (PBE0²⁷⁻²⁹, M06-L³⁰, B3LYP³¹⁻³⁴, TPSS^{35, 36}) together with the three different basis sets (def2-TZVPD^{37, 38}, aug-cc-pVTZ³⁹⁻⁴¹, 6-31G(2df,p)⁴²⁻⁴⁷) were applied. [Fig. 3](#) shows the results of C₂-C₁-S₁-S₂ dihedral angle scans in steps of 10° for the PhS₂⁻ anion and the PhS₄⁻ anion using the PBE0/def2-TZVPD method. Calculations applying the other methods yield qualitatively the same results (SI, Tab. S1, Fig. S1, Fig. S2). A high rotation barrier of 37 kJ mol⁻¹ was calculated for PhS₂⁻ indicating that the C-S bond has partial double bond character due to π -system conjugation. The distance between the terminal sulfur atom and the ortho ring proton (*d* = 2.64 Å computational, 2.68 Å experimental) makes a significant attractive electrostatic interaction between those two atoms unlikely. However, to exclude the possibility of the high barrier in the rotation around the C₁-S₁ bond in PhS₂⁻ anions originating from such an interaction, an angle scan on benzyl thiolate was performed (Fig. S3). In this molecule, no π -conjugation outside of the ring is possible, and the sulfur distance to the ortho proton (*d* = 2.58 Å) is similar as in PhS₂⁻. As expected the torsional barrier is much smaller, amounting to 2.6 kJ mol⁻¹.

For the PhS₄⁻ anion, the energetic cost for C-S bond rotation only amounts to 6 kJ mol⁻¹. This is a clear hint that the π -system of the ring is isolated from the sulfur chain. We note that also for PhS₄⁻ the dihedral angle scan would likely be symmetric if conformational sampling was performed at each point along the scan. This was not pursued as it would not raise the lowest barrier of rotation, and thus would not change the conclusion.

Fig. 3: Calculated energies for the rotation of 180° around the C-S bond for the PhS₂⁻ anion (top, maximum at 37 kJ mol⁻¹ for a dihedral of 90°) and the PhS₄⁻ anion (bottom, maximum at 6 kJ mol⁻¹ for a dihedral of -64°). Starting point is the ground state geometry. All numbers are electronic energies without zero-point-energy correction.

The difference in the rotation barrier and, connected to that, the difference in conjugation with the phenyl ring between PhS₂⁻ and PhS₄⁻ can be rationalized by qualitative molecular orbital (MO) theory. We start by modeling the MOs of PhS₂⁻ by considering the interaction between the MOs of benzene and the lone pairs of the S₂⁻ unit, which we model by ethylene-

like orbitals (Fig. 4). This qualitative picture explains the high rotational barrier by the in-phase basis orbital overlap between C₁ and S₁ in the HOMO, implying a double-bond like character between these atoms.

Fig. 4: A qualitative MO picture of the π -system of the PhS_2^- anion. The orbitals and interactions irrelevant for the analysis are grayed out. The MO describing the double-bond character between C and S is highlighted in orange.

In the case of PhS_4^- , the common staggered conformation of the RS_4^- chain results in the two sulfur lone pair orbitals (of S₁ and S₂) depicted above no longer being parallel. Instead, the lone pair on S₁ interacts with the adjacent σ -bond between S₂ and S₃. There are several ways to look at the effect of this change, and we discuss just one of them, for the sake of brevity. We can consider that in the case of PhS_4^- , the sulfur with the formal negative charge (S₄) no longer interacts directly through space with the lone pair of S₁, as it did in the case of PhS_2^- , but rather does it in a through-bond fashion (Fig. 5).⁴⁸ If we combine the two lone pairs in PhS_4^- , the resulting linear combinations remain at the non-bonding energy levels under the approximation of negligible through-space interaction. Mixing these linear combinations with the appropriate σ and σ^* orbitals then splits the orbital energies. In comparison to the through-

space interaction in PhS_2^- , the energy of the resulting HOMO is considerably lower. This in turn means that the interaction with the LUMO of the phenyl group is weaker. Hence, the double bond character is lesser, and the expected rotational barrier lower. For comparison, we also calculated the rotational barrier of PhSMe , where we expect the lone pairs to be of nonbonding character. It is similar to the barrier for PhS_4^- , amounting to 7 kJ mol^{-1} . From this we can conclude that the orbital splitting in PhS_4^- caused by the through bond interaction is indeed small, and the resulting orbitals close to non-bonding.

Fig. 5: A qualitative MO picture for the interaction of the lone pair on S_1 and the lone pair of the formally negatively charged outermost sulfur. Left: through-space interaction in PhS_2^- ; right: through-bond interaction in PhS_4^- . The orbital pairs that interact with each other have been colored green and purple for visualization.

Structurally the PhS_2^- anion is closely related to diphenyl disulfide (PhSSPh). The S-S bond length is slightly longer ($2.043 \text{ \AA}$ vs. $2.029 \text{ \AA}$), the S-C bond length slightly shorter ($1.767 \text{ \AA}$ vs. $1.788 \text{ \AA}$) while the C-S-S bond angles are almost identical (106° vs 105° and 106°). In PhSSPh the two C-C-S-S dihedrals ($\text{C}_2\text{-C}_1\text{-S}_1\text{-S}_2$ and $\text{C}_2'\text{-C}_1'\text{-S}_2\text{-S}_1$) are not the same for the two

rings. One amounts to -163° , the other one to 180° . Comparing this to the 177° in the PhS_2^- anion, one could conclude that diphenyl disulfide structurally resembles PhS_2^- with a second phenyl attached to the terminal sulfur atom.

Comparing the sulfur chain in the PhS_4^- anion with polysulfide dianions like S_7^{2-} ²⁴, S_6^{2-} ⁴⁹ and S_4^{2-} ⁵⁰ shows high similarity. The $\text{C}_1\text{-S}_1\text{-S}_2\text{-S}_3$ dihedral angle amounts to the familiar 89° and the $\text{S}_1\text{-S}_2\text{-S}_3\text{-S}_4$ dihedral to 88° , the bond angles are around the expected 110° , and the S-S bond length shortens when moving from the innermost sulfur atom attached to the ring to the terminal sulfur atom. This gradual change in bond length has been predicted by calculations for HS_4^- , and has been explained by hyperconjugation.⁵¹ Comparison with the published crystal structure of 1,4-di-p-tolyltetrasulfane (MePhSSSSPhMe)¹⁸ does not show any big deviations, except that the S-S bond lengths differ less from each other in 1,4-di-p-tolyltetrasulfane.

Comparing the aryl species **1a** to its alkyl equivalent **3** shows a much shorter C-S bond length ($1.767 \text{ \AA}$ vs. $1.847 \text{ \AA}$) and a slightly shorter S-S bond for the former ($2.043 \text{ \AA}$ vs. $2.067 \text{ \AA}$). These observations are both in line with the qualitative MO analysis. The shorter C-S bond length in **1a** likely results from the bonding interaction of the π^* orbital of the sulfur lone pairs and the LUMO of the phenyl group ([Fig. 4](#)); this interaction does not exist in **3**. This interaction can also explain the shorter S-S bond length in **1a**—as electrons are delocalized from the π^* orbital, the bonding is strengthened. In any case, both C-S bond lengths lie in the normal range for phenyl-sulfur bonds and quaternary-carbon-sulfur bonds, respectively.

OXIDATION OF THE COMPOUNDS

All polysulfanide compounds are somewhat air sensitive as crystals and very air sensitive in solution. Compound **1b** is in general much less stable than its two relatives **1a** and **1c**, be it to heat or to air. While **1a** and **1c** turn into a white powder after weeks in air, **1b** after much shorter time formed a melt from which interestingly the triply oxidized tetraethyl ammonium S-phenyl

sulfurothioate ($\text{NEt}_4^+ \text{PhS}_2\text{O}_3^-$ salt, **4**, [Fig. 10](#)) crystallized as X-ray quality crystals together with diphenyl disulfide.

Oxidation of **1b** seems to destroy conjugation of the sulfur system with the ring. The S-SO₃ group is turned out of the ring plane in the crystal structure. The C₂-C₁-S₁-S₂ dihedral angle changes from -171° in the almost planar reduced molecule to 103° in the oxidized form. Computationally the dihedral stays planar also in the oxidized form (180°). However, rotation around the C-bond only costs 7 kJ mol⁻¹ (Fig. S4).

Fig. 6: Crystal structure (50% probability ellipsoids) of the oxidation product of **1b** (**4**). Hydrogen atoms as well as the counter ion PPh_4^+ are omitted for clarity. Full picture can be seen in the SI.

DYNAMICS IN SOLUTION

Dissolving the pure orange crystals of compound **1a** or the yellow ones of compounds **1b** and **1c** in acetonitrile-d₃, pyridine-d₅, dimethyl formamide-d₇ or dimethyl sulfoxide-d₆ for NMR analysis lead to the formation of deeply blue-to-green solutions at room temperature. This suggests chemical reaction upon dissolving. Cooling down to -34 °C turned the solutions orange again in a reversible process, suggesting further a shift in equilibrium. It is known from the literature that this kind of molecules forms complex equilibria in solution.^{1,2,7} The intense blue-

to-green color at r.t. can be explained by the presence of the strongly colored $S_3^{\cdot-}$ radical that is formed together with diphenyl disulfide by the reactions shown in [Scheme 2](#).^{1,2,7} This process, however, only happens to a very limited extent. The ^1H -NMR spectra in MeCN-d_3 show almost no diphenyl disulfide, but its formation was confirmed by GC-MS analysis from MeCN. Instead equilibria between various $\text{PhS}_n^{\cdot-}$ ($n = 1-4$) species are observed at r.t., as indicated by broad peaks (Fig. S10).

Scheme 2: Formation of $S_3^{\cdot-}$ radicals and diphenyl disulfide from $\text{PhS}_2^{\cdot-}$.

Cooling to $-40\text{ }^\circ\text{C}$ allows resolution of these peaks, slowing down the equilibria reactions ([Fig. 7](#)). Under those conditions $\text{PhS}_n^{\cdot-}$ species ($n = 1-4$) can be observed with relative abundances of 25% for $\text{PhS}^{\cdot-}$, 54% for $\text{PhS}_2^{\cdot-}$, 14% for $\text{PhS}_3^{\cdot-}$ and 3% for $\text{PhS}_4^{\cdot-}$. The missing 4% of aromatic signals could not be assigned unambiguously. They could involve species of longer sulfur chains as well as diphenyl polysulfides.

Fig. 7: ^1H -NMR spectrum (aromatic region) of **1a** (top) and **1b** (bottom) in MeCN-d_3 at $-40\text{ }^\circ\text{C}$. The strong peaks downfield in the top spectrum stem from the PPh_4 cation. The colored bars at the bottom indicate which peak belongs to which species as confirmed by 2D-NMR.

Using NMR solvents like chloroform- d , methylene chloride- d_2 , chlorobenzene- d_5 , methanol- d_4 , nitromethane- d_3 did not lead to the formation of blue-to-green solutions but the stability issues of the sulfanides, including decomposition, seemed to be even worse, impeding the recording of clean NMR-spectra (Fig S11-S13). Pure compound **2** is also not stable in solution, forming complex equilibria as well. While at room temperature the spectrum of **2** in MeCN- d_4 only shows two broad peaks for the anion indicating exchange (Fig. S16), at $-40\text{ }^{\circ}\text{C}$ the PhS_4^- signals as also seen in **1a** are observed as the main peaks (Fig. 8). Further, three aromatic signals (**A**, red) belonging to a second molecule as confirmed by 2D NMR, that is not PhS_n^- ($n = 1-4$), and not diphenyl disulfide, appeared. Judging from the ESI-MS spectra (Fig. S6), the most probable assignment is the PhS_5^- anion. There also exist three more broad peaks (**B**, blue) belonging to species that are in exchange in the NMR time regime even at $-40\text{ }^{\circ}\text{C}$. They might stem from further PhS_n^- species. To circumvent the equilibration reactions in solution, we took ^{13}C solid state NMR spectra of the pure compounds **1a** and **2**, which may be found in the SI (Fig. S19).

Fig. 8: ^1H -NMR-spectrum (aromatic region) of **2** in MeCN- d_3 at $-40\text{ }^{\circ}\text{C}$. The strong peaks downfield stem from the PPh_4 cation. The colored bars at the bottom of the spectrum indicate which peak belongs to which species as confirmed by 2D NMR.

As a way to investigate the equilibria in solution in more depth, electrospray-ionization mass spectrometry (ESI-MS) measurements were performed. Fig. 9 shows the dynamics of the sulfur chains in acetonitrile (MeCN) for compound **1a**. In solution, various species of PhS_n^- ($n=1-5$) are in equilibrium with each other. Furthermore, the S_3^- radical is observed. For

compound **2** the ESI-MS spectrum looks quite similar to **1a**, except for higher intensities for PhS_n^- species with larger n . Spraying from methanol instead of MeCN allowed detection of species with n up to 9 (Fig. S9), although with low intensities for high n . The presence of $M+16$ ($+O$) or $M+48$ ($+3 O$) species indicate that the compounds are reacting with oxygen during the spray process.

Dissolving the pure dark red crystals of **3** in MeCN, does not form blue-to-green solutions but yellow-to-red solutions, indicating that no S_3^- radical anions are formed. However, also here $^1\text{H-NMR}$ (Fig. 10) as well as ESI-MS measurements (Fig. 11) show formation of equilibria with species of various numbers of sulfur atoms. In ESI-MS $t\text{-BuS}_n^-$ ($n = 1\text{-}5$) could be observed, while in $^1\text{H-NMR}$ $t\text{-BuS}_n^-$ ($n = 1\text{-}4$) could be assigned by the help of DOSY (Fig. S18) spectra and 2D NMR. In contrast to **1** and **2**, sharp peaks are measured for **3** at r.t., indicating slower exchange reactions. It can be observed over the time period of days, how the $t\text{-BuS}_2^-$ peak shrinks from a relative intensity of 85% of all $t\text{-Bu}$ group carrying species after 30 minutes in solution to 58% after 2 days in solution. It mainly converts to $t\text{-BuS}^-$ and $t\text{-BuS}_3^-$ (see experimental details section). There also exist peaks of further $t\text{-Bu}$ -containing species in the NMR spectra (Fig. S20, species V-Z), each of them with a relative intensity of less than 1%. We were not able to assign the minor species unambiguously. They could be oxidized or protonated species, or possibly, $t\text{-BuS}_n^-$ with $n > 4$.

Fig. 9: ESI-MS spectrum of **1a** sprayed from MeCN. Bottom: full scan from m/z =50-300. Unlabeled peaks with $M^+ + 48$ are species oxidized during the spray process of the form PhS_nO_3^- determined by the isotope pattern. Especially pronounced is the PhS_3O_3^- anion at m/z = 221 (Fig. S8). Individual peak intensities vary with spray settings and do not reflect actual concentration ratios. Top: isotope patterns of PhS_n^- ($n = 2-5$) species.

Fig. 10: Aliphatic region of the ^1H -NMR spectrum of $\text{PPh}_4^+ t\text{-BuS}_2^-$ in MeCN at r.t. after 2 days in solution. Except for $t\text{-BuS}_4^-$, peaks with lower intensity than 1% of all tert-butyl signals are

not assigned here (for full description see Fig. S20). The gray Et₂O triplet at δ 1.12 ppm persisted even after a week of drying under high vacuum.

Fig. 11: ESI-MS spectrum of **3** sprayed from MeCN. Bottom: full scan from $m/z = 50$ -300. Individual peak intensities vary with spray settings and do not reflect actual concentration ratios. Top: isotope patterns of $t\text{-BuS}_n^-$ ($n = 2$ -5) species.

COLLISION-INDUCED DISSOCIATION STUDIES

Collision-induced dissociation studies of PhS_n^- compounds show characteristic fragmentation patterns ([Fig. 12](#), top, for PhS_8^- , for PhS_n^- $n = 1$ -9, see Fig. S9). For all compounds all fragments going from PhS_{n-1} to PhS_1 are observed at collision offsets of 40 V. Loss of neutral disulfur S_2 is the preferred fragmentation channel (except for $n = 5$, where S_3^- radical anion formation is favored). Further, cleavage of neutral trisulfur S_3 is observed. It cannot be determined unambiguously from our data whether the appearance of the daughter ions of the form PhS_{n-4} to PhS_1 is a result of consecutive S_2 and S_3 losses, or the loss of neutral S_n species ($n \geq 4$). However, given that we are working at low pressures of collision gas (0.1 mTorr), and

that all the S_n fragments are stable species themselves, our observation suggests that indeed S_n species ($n \geq 4$) are formed. Least favorable is the loss of a single sulfur atom S. This only occurs in a tiny fraction of the fragmentations. Depending on the sulfur chain length of PhS_n^- anions S_2^- - S_6^- anions are also observed. For $t\text{-Bu}S_n^-$ compounds (Fig. 12 bottom, Fig S8.), similar fragmentations occur. In addition, however, there are also species formed from reactions with the *tert*-butyl group.

Fig. 12: CID-spectrum of PhS_8^- (top) and $t\text{-Bu}S_5^-$ (bottom) measured at a collision offset of 40 V.

TEMPERATURE AND PRESSURE DEPENDENT X-RAY CRYSTAL STRUCTURES

Compound **1a**, in contrast to the other phenylperthiolate compounds **1b** and **1c**, shows pronounced, fully reversible, thermochromic properties. At room temperature, the crystals of **1a** are shiny orange, while those of **1b** and **1c** (as well as $PPh_4^+ PhS^-$) are bright yellow. Upon cooling, crystals of **1a** gradually turn yellow; upon heating they become dark red (Fig. 13). It has been shown a long time ago that certain polysulfides can exhibit thermochromic properties caused by thermal broadening.⁵² Lamar Field explains the effect this way: “Increased

population of the higher vibrational levels of the ground state leads to broadening and flattening of the absorption curve so that just enough extension occurs in the tails of bands to produce a yellow colour”.⁵³ However, if this effect was the reason for the thermochromism in **1a**, compounds **1b** and **1c** were expected to also show pronounced thermochromic properties, which is not the case.

Fig. 13: Fully reversible thermochromic properties of compound **1a** (left) at room temperature, after cooling with liquid nitrogen (LN₂), after heating to 100 °C and after heating close to the decomposition temperature (heat gun). As a comparison non-thermochromic **1b** (middle) and **1c** (right) are shown. **1b** decomposes already at moderate temperatures.

Several experiments were performed to investigate the origins of this peculiarity. As observed by the naked eye, the color changes happen without delay as the temperature is changed. Moreover, the changes seem to be gradual instead of discrete, hinting against a phase transition as the cause. A differential scanning calorimetry (DSC) study of **1a** between 100 K and 373 K confirmed that no phase transitions in the crystals take place, as no peaks were observed (Fig. S21). X-ray crystal structure analyses of **1a** at various temperatures between 100 K and 300 K (Fig. 15) showed increasing disorder in the anion upon heating, starting from unmeasurable < 2% at 100 K to around 15% at 300 K. The disorder resembles a formal flip of the anion by 180° (or a rotation around the C-S bond overlaid with a tilt); temperature changes barely influence the cation.

The change in the ratio of the secondary orientation (disorder) with temperature has two contributions: a) the relative energy of the two orientations changes with temperature; b) the effect of configurational entropy changes with temperature. Regarding contribution a), in general, unit cell dimensions grow upon heating: while at 100 K the unit cell volume amounts to 2450.12 (3) Å³, it increases to 2526.20 (3) Å³ at 300 K for **1a**. The change in volume influences the contact distances between the ions in the crystal (Fig. S22). As a result, the secondary orientation could become disfavored at 100 K, and therefore not occupied. Regarding effect b), disordered structures are known to be stabilized by configurational entropy.⁵⁴ The probability of the system being in a disordered state i with degeneracy g_i that is higher in energy by ΔE_i in a canonical ensemble can be calculated according to Boltzmann distribution:

$$p_i = \frac{g_i \cdot e^{-\frac{\Delta E_i}{kT}}}{\sum_{j=1}^N g_j \cdot e^{-\frac{\Delta E_j}{kT}}} \quad (1)$$

To probe the possible range of energies and ratios of the secondary orientation in the crystal, we used Eq. (1) under the approximation that the anions are independent and non-interacting. This approximation is crude, but acceptable in this case, because the anions are separated from each other by the cations, which do not undergo significant structural changes upon cooling. This leads to three main simplifications: 1) the system is represented by a vector of lattice sites, which can be occupied by either the primary or the secondary orientation; 2) the energy of the state, ΔE_i , is assumed to behave additively, i.e., the energy is calculated by multiplying ΔE_s , the energy per single orientation change, by the number of secondary orientations; 3) the degeneracy is calculated by the binomial distribution:

$$g_i = \frac{n!}{k! (n - k)!} \quad (2)$$

where n is the number of lattice sites and k is the number of secondary orientations. The most probable ratio between primary and secondary orientation was calculated for several lattice sites and ΔE_s values (Fig. 14, Python code in the SI.)

The ratio was found to converge to a stable value at around 100 sites. Comparing these results to the experimentally observed ratios (15% at 300 K and <2% at 100 K) suggests that the average ΔE_s of the two orientations is between 4 and 6 kJ mol⁻¹.

Fig. 14: Ratio calculations at different ΔE values and temperatures. Left: the most probable ratio of the secondary orientation, calculated at different values of lattices sites. Right: Boltzmann distribution, calculated with 1000 lattice sites.

The ΔE_s value of the two orientations of the anion in **1a** was also investigated by DFT calculations with periodic boundary conditions. Both orientations were optimized with the unit cell parameters of the 300 K crystal structure and the 100 K crystal structure. The electronic energy difference of the optimized structures was calculated with several methods ([Tab. 2](#)[Tab. 2](#)). Because each unit cell holds 4 anions, the average ΔE_s value is a quarter of the calculated

energy—about 8–8.5 kJ mol⁻¹ at 300 K and about 9–9.5 kJ mol⁻¹ at 100 K. Thus, the secondary orientation becomes approximately 1 kJ mol⁻¹ less favored as the unit cell shrinks. This indicates that the secondary orientation is indeed relatively less stable at 100 K, or in a more general sense, in the smaller unit cell measured at 100 K.

The average energy for changing the orientation of a single anion was also calculated by flipping only one, two or three anions in the unit cell (SI, Tab. S4). These calculations suggest a slightly higher value of approximately 9–11 kJ mol⁻¹ for ΔE_s . This indicates that the approximation of independent anions, as introduced for statistical modelling, is expectedly not exact. However, the similar magnitude of the ΔE_s value from different calculations as well as the crude statistical treatment strongly suggest that the anion in **1a** is approximately 4–11 kJ mol⁻¹ less stable in the second orientation than in the primary orientation.

Tab. 2: The energy differences between the unit cell with the primary and the secondary orientation with the experimental unit cell parameters determined at 300 K and 100 K. Positive energy values mean that the secondary orientation is less stable. All values are given in kJ mol⁻¹.

Method	ΔE_{cell}		ΔE_s		$\Delta \Delta E_s^a$
	300 K	100 K	300 K	100 K	
PBE-D3(BJ)/DZVP ^b	32.5	35.6	8.1	8.9	0.8
PBE-D3(BJ)/TZV2P ^c	32.9	36.5	8.2	9.1	0.9
HSE-D3(BJ)/DZVP ^b	34.2	38.5	8.6	9.6	1.0

^aThe difference between 300 K and 100 K ΔE_s . ^bDZVP-MOLOPT-GTH basis set. ^cTZV2P-MOLOPT-GTH basis set.

The interpretative origin of the relative stability was investigated with energy decomposition analysis (EDA) by the absolutely localized molecular orbitals (ALMO) method. It has the following components:

$$\Delta E_{\text{Total}} = \Delta E_{\text{FRZ}} + \Delta E_{\text{POL}} + \Delta E_{\text{COV}} (+ \Delta E_{\text{DISP}}) \quad (3)$$

ΔE_{POL} is the energy associated with intrafragment polarization in the presence of the other fragments. ΔE_{COV} is the interfragment polarization (charge transfer) energy, and ΔE_{DISP} the D3 dispersion energy. ΔE_{FRZ} includes the following components:

$$\Delta E_{\text{FRZ}} = \Delta E_{\text{ELSTAT}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{DISP}} \quad (4)$$

The ΔE_{DISP} term, which can be separately accessed as the D3 energy difference, can be subtracted from the ΔE_{FRZ} term, so that it becomes $\Delta E_{\text{ELSTAT}} + \Delta E_{\text{Pauli}}$ —i.e., the sum of the stabilizing electrostatic interaction and the destabilizing Pauli repulsion. The ΔE_{DISP} term can then be listed as a separate energy contribution as indicated in the parentheses in Eq. (3). The analysis was performed for both orientations in the 300 K and 100 K unit cells ([Tab. 3](#)~~Tab. 3~~). It appears that the decrease of the stability of the secondary orientation at 100 K originates from the interplay of the electrostatic interaction and Pauli repulsion, balanced by the increased stability from charge transfer.

Tab. 3: The difference between the energy components of the primary and secondary orientation in the experimental unit cell determined at 300 K and 100 K. Calculated with PBE-D3(BJ)/TZV2P-MOLOPT-GTH. All values are given in kJ mol⁻¹.

Component	300 K	100 K	Δ^a
FRZ (-DISP)	32.0	39.5	7.5
POL	0.0	-0.6	-0.6
COV	-3.0	-9.7	-6.7
DISP	6.4	7.7	1.3
TOTAL	35.4	36.9	1.5

^aThe difference between 300 K and 100 K energy components.

Fig. 15: Left: X-ray crystal structure of the asymmetric unit of **1a** at r.t. showing the two orientations (blue: primary, red: secondary). Right: PhS_2^- anion in thermochromic **1a** (left window) and non-thermochromic **1c** (right window) at 100 K and 300 K. While for **1a** at 100 K almost no disorder in the anion is observed ($< 2\%$), the ratio between the two orientations at 300 K is around 85:15 (black-yellow: blue-orange). For **1c** no increase in anion disorder is observed at elevated temperature.

The interactions between the anion and the cation were further investigated by Hirshfeld surface analysis^{55, 56}. The normalized contact distance (d_{norm}) maps imply moderately strong intermolecular interactions in the crystal structure for both orientations of the anion at r.t. (Fig. 16).

Fig. 16: Hirshfeld surface mapping d_{norm} shown from both sides of the anion for the primary anion orientation (top) and the secondary orientation (bottom). Red areas correspond to contact distances shorter than the sum of van der Waals radii (Σr^{vdW}), blue to distance longer than Σr^{vdW} sum, and white to contacts around the Σr^{vdW} .

The main interactions are found between the ring protons of the PPh_4^+ cation and the perthiolate moiety (Fig. S22) as well as between the PPh_4^+ protons and the center of the phenyl ring of the PhS_2^- anion. For the primary orientation, five shorter-than van der Waals contacts were found; three of them including the two sulfur atoms and two the anion ring π -system. Only three contacts exist for the secondary orientation. Two of them point exclusively on the terminal sulfur atom while the third one includes the anion ring π -system. An X-ray crystal structure measurement of non-thermochromic **1c** as a reference measurement showed no increased disorder at 300 K (Fig. 15Fig. 15) and therefore no significant changes in short contacts upon heating. A connection between thermochromic properties of **1a** and the crystal dynamics is therefore likely.

The influence of the structure on the color was investigated by time-dependent DFT (TDDFT) calculations with periodic boundary conditions (Tab. 4). The large difference between the PBE and HSE results is expected, as non-hybrid functionals often underestimate the band gap in solids. Based on the observed crystal colors of orange and yellow, the crystals are assumed to absorb in the green and violet parts of the color spectrum, respectively. Accordingly, the lowest excitation energies should be around 2.5–3 eV, which is significantly higher than the lowest HSE calculated excitation energy. The character of the excitation was investigated by visual observation of the molecular orbitals participating in it. There are several near-degenerate excitations, which are combinations of the excitations of an electron from the near-degenerate set of S-S π^* orbitals (HOMO of the system) to the near-degenerate set of phosphonium LUMOs (Fig. S5). This indicates that the lowest excitation corresponds to a charge-transfer excitation, which could be a further reason for the inaccuracy of the TDDFT result.⁵⁷ The lower excitation energy of the charge-transfer excitation in the secondary orientation may also be connected to the stronger apparent charge transfer interaction in that orientation as implied by EDA (Tab. 3).

Regardless of the absolute value, the relative difference between the lowest excitation energy in the primary and secondary orientation is consistent within all the methods. It indicates that the UV/Vis absorption is red-shifted in the secondary orientation, in line with the experimental color change. The excitation energy of the primary orientation itself is also red-shifted by 0.05 eV in the 300 K cell compared to the 100 K cell (SI, Tab. S5), possibly enhancing the effect of the color change.

Tab. 4: The lowest excitation energies of the primary and secondary orientation in the experimental 300 K unit cell.

Method	Primary	Secondary	Δ^a
PBE/DZVP ^b	1.06	0.91	-0.15
PBE/TZV2P ^c	1.14	1.00	-0.14
HSE/DZVP ^b	1.95	1.81	-0.14

^aThe difference between the excitation energy in the primary and the secondary orientation.

^bDZVP-MOLOPT-GTH basis set. ^cTZV2P-MOLOPT-GTH basis set. All values are given in eV.

Given these findings, we wondered how increased pressure would influence crystals of **1a**. Would the shrinking of the unit cell under pressure also make the secondary orientation disappear? Using a diamond anvil cell, measurements were performed at room temperature at pressures of 0.5 GPa, 1.5 GPa and 3.5 GPa using Daphne Oil as pressure-transmitting medium.

⁵⁸ The first two pressures did not alter the crystal phase, while at 3.5 GPa the sample underwent a phase transition from monoclinic to triclinic symmetry. Therefore, only measurements at 0.5 GPa (CCDC- 1987818) and 1.5 GPa (CCDC-1987760) were considered (Fig. 17) for our comparison.

Fig. 17: C₁-S₁-S₂ atoms overlay of crystal structures of **1a** at various pressures. Red: ambient pressure, black: 0.5 GPa, cyan: 1.5 GPa. The red crosses show the secondary orientation only visible at ambient pressure. Note the shrinking of the unit cell as seen by closer PPh₄⁺ packing at high pressures.

At those pressures the unit cell volume shrinks to 2442.1 (6) Å³ and 2200.5 (6) Å³, respectively. Like at 100 K, the shrinking of the unit cell by increased pressure causes the secondary

orientation to vanish (Fig. 18). This observation also qualitatively agrees with the calculations, which show a similar decrease in the stability of the second orientation in the 0.5 GPa cell as in the 100 K cell (SI, Tab. S3). The respective value is approximately 0.5–1.0 kJ mol⁻¹, which is too small to explain the observed disappearance of the second orientation. Understanding the origin of this discrepancy is beyond the scope of this study, and was not further pursued.

Fig. 18: X-Ray crystal structures of the anion in **1a** and unit cell volume at various pressures. The secondary orientation present at ambient pressure (blue-orange) vanishes at elevated pressures. Cations have been omitted for clarity. Full structures can be seen in the SI.

The influence of high pressure on the color of the compound could not be investigated, since for small crystals of the size that fit into the diamond anvil cell, the color, as determined by the naked eye, is very close to yellow already at ambient conditions. The orange color is perceptible only for larger crystals (Fig. S24) which have a sufficiently long optical path length. However, based on the observation that the secondary orientation is not populated under pressure, alongside with comparative calculations (Tab. S5 and S6), the color under pressure is assumed to be similar to the color at low temperatures.

A further hint for the increased crystal dynamics of **1a** at room temperature can be found in solid state NMR studies (Fig. S19). Interestingly, measurements on **1a** revealed an unusually

long T1 relaxation time, much longer than for closely related **2**. This is somewhat surprising given the similarity of the compounds. The phenomenon can be explained by assuming very different dynamics in the two crystals.

CONCLUSION

In this study various well-defined aryl and alkyl polysulfanide salts of the form $X^+RS_n^-$ were synthesized via an easy one-step procedure and characterized by X-ray crystal structure analysis, NMR spectroscopy, electrospray-ionization mass spectrometry and elemental analysis. Stirring of an aryl or alkyl sodium thiolate salt, elemental sulfur and the chloride salt of a preferably well-crystallizable cation like PPh_4^+ or PNP^+ in acetonitrile at room temperature allowed the isolation of perthiolates salts $X^+RS_2^-$ ($R = Ph, t-Bu$) in a pure form by crystallization. Fractional crystallization further gave access to an organyl tetrasulfide species $PPh_4^+PhS_4^-$. Characterization of those compounds proved them to be well-defined in the solid state but unstable in solution. Crystal structure analyses revealed similarities to the known diorganyl polysulfides but also differences in between species with different sulfur chain lengths. The most striking example is the putative presence of π -conjugation over the whole anion in PhS_2^- but the absence of the same kind of conjugation in PhS_4^- as well as $PhS_2O_3^-$ as shown by DFT studies, and explained by qualitative MO theory. In solution, complex equilibria or decay were observed, depending on the solvent. Low temperature NMR investigations allowed for the observation and assignment of RS_n^- anions ($n = 1-4$), while in ESI-MS species with n up to 8 were discovered. Furthermore, temperature- and pressure-dependent X-ray crystallography were applied to investigate the thermochromic properties of one of the perthiolate compounds, $PPh_4^+PhS_2^-$, and to gain insights into its crystal dynamics in general. It was shown that lower temperature as well as elevated pressure eliminate disorder in the crystal. With the additional help of differential scanning calorimetry and periodic boundary condition DFT calculations, thermochromism has been hypothesized to be connected to this very effect.

Having this new and easy method in hand to isolate monoorganypolysulfanides in a pure form, we not only hope to inspire the synthesis of more of these compounds, but also to enable the development of model systems for pethiolate enzymes and polysulfanide reactions in general. We further hope that our investigations on the behavior and peculiarities of these compounds might spark new ideas on open mechanistic questions of reactions related to monoorganypolysulfanides.

METHODS

COMPUTATIONAL DETAILS

Density functional theory (DFT) angle scan studies were performed using the Gaussian 09d1 program.⁵⁹ A method validation study was conducted to assess a suitable method (see SI, method validation). It turned out that all the methods applied (PBE0²⁷⁻²⁹, M06-L³⁰, B3LYP³¹⁻³⁴, TPSS^{35, 36, 60}) together with the three different basis sets (def2-TZVPD^{37, 38}, aug-cc-pVTZ³⁹⁻⁴¹, 6-31G(2df,p)⁴²⁻⁴⁷) yielded qualitatively similar results. PBE0 results combined with def2-TZVPD basis-set are shown here. For the numerical integration, an ultrafine grid was chosen. Energies for the angle scans are electronic non-zero-point-corrected energies.

The periodic boundary condition calculations were performed with CP2K 7.1.⁶¹⁻⁶³ Density functional theory with the mixed Gaussian and plane wave basis set approach as implemented in the QUICKSTEP module⁶⁴ was employed. The Perdew-Burke-Ernzerhof (PBE)⁶⁵ and the Heyd-Scuseria-Ernzerhof (HSE)⁶⁶⁻⁶⁸ functionals were used with the D3 dispersion correction⁶⁹ and the Becke-Johnson damping function,⁷⁰ as parametrized for the PBE or PBE0 functionals, respectively. The MOLOPT type basis sets⁷¹ were used together with the Goedecker-Teter-Hutter (GTH) pseudopotentials optimized for the PBE functional.⁷²⁻⁷⁴

The excitation energies of the 10 lowest states were calculated with the time-dependent DFT (TDDFT) formalism as implemented in CP2K.⁷⁵ The orbitals were visualized by requesting a molden file print-out from CP2K, and converting the orbitals of interest to cube files with MultiWFN.⁷⁶ The cube files were visualized with Chemcraft.⁷⁷

The absolutely localized molecular orbitals (ALMO)⁷⁸⁻⁸⁰ were used to decompose the total energy into interpretable components.

Further details about the periodic boundary calculations as well as input examples are provided in the SI.

EXPERIMENTAL SECTION

Unless stated otherwise, all experiments were conducted under N₂ or Ar atmosphere using standard Schlenk and glovebox techniques. Starting materials were purchased from commercial suppliers and used without further purification unless stated otherwise. MeCN was dried by refluxing over calcium hydride and subsequent distillation. Et₂O was dried by refluxing over Na/benzophenone and subsequent distillation. NMR solvents were degassed by three freeze-pump-thaw cycles and dried over 3 Å molecular sieves activated by applying vacuum (10⁻² mbar) for 12 h -16 h at 700 °C -800 °C.

Solution phase NMR spectra were recorded either on a Bruker AVIII 300 MHz, a Bruker Neo 400 MHz or if needed a Bruker Neo 500 MHz or even a Bruker DRX 600 MHz instrument. Residual peaks of the deuterated solvents were used as internal standard (¹H-NMR: MeCN-d₃: 1.94 ppm; pyridine-d₅: 8.74 ppm, 7.58 ppm, 7.22 ppm; dimethylformamide-d₇: 8.03 ppm, 2.92 ppm, 2.75 ppm; dimethyl sulfoxide-d₆: 2.50 ppm; CDCl₃: 7.26 ppm, CD₂Cl₂: 5.32 ppm; chlorobenzene-d₅: 7.14 ppm, 6.99 ppm, 6.96 ppm; methanol-d₄: 3.31 ppm; nitromethane-d₃: 4.33 ppm⁸¹). All shifts are reported in ppm. All assignments were double checked by standard 2D-NMR methods.

ESI-MS studies were conducted on a Thermo Finnigan TSQ Quantum instrument with a flow rate of 5 µl min⁻¹. The measurements were conducted at spray voltages from 3000 V to 4000 V at a capillary temperature of 473 K. Argon was used as collision gas in collision-induced dissociation (CID) experiments at a pressure of 0.1 mTorr.

Elemental analyses were performed on a Leco TruSpec Micro instrument for C, H and N determination and on a HEKAtech EUROVector instrument for S determination.

Tetraphenylphosphonium thiophenolate was synthesized according to Zhou et al.⁸² and subsequently investigated by X-ray crystal structure determination (Fig. 2, CCDC-1965771 for CuK α).

Phenyl perthiolate salts:

Sodium thiophenolate (90% purity), 1 equivalent of the chloride salt of the desired cation and 1/8 equivalents of S₈ were suspended in MeCN (15 ml) and stirred at r.t. for 1 h 30 min. Subsequently, the solution was filtered and treated with diethyl ether to initiate crystallization. The solution was stored at -34 °C, yielding yellow or orange crystals. The crystals were filtered off, the filtrate treated with more diethyl ether and put at -34 °C again, yielding a second portion of identical crystals. NMR: the anion equilibrates among several polysulfides in solution, see results and discussion section and SI.

¹H-NMR (500 MHz, CD₃CN, -40 °C): Anion: PhS⁻: δ 7.12-7.07 (m, covered under PhS₂⁻, 2H) δ 6.71 (t, J = 7.6 Hz, 2H) δ 6.50 (t, J = 7.3 Hz, 1H). PhS₂⁻: δ 7.48 - 7.43 (m, 2H) δ 7.11-7.06 (m, 2H) δ 6.80 (tt, J = 7.2, 1.2 Hz, 1H). PhS₃⁻: δ 7.61-7.57 (m, 2H) δ 7.29-7.25 (m, 2H) δ 7.13 - 7.08 (m, covered under PhS₂⁻, 1H). PhS₄⁻: δ 7.82 - 7.79 δ (m, 2H) δ 7.32-7.27 (m, covered under PhS₃⁻, 2H) δ 7.23-7.19 (m, 1H). ¹³C NMR (126 MHz, CD₃CN-*d*₃, -40 °C). PhS⁻: δ 141.79 δ 133.80 δ 127.32 δ 117.53. PhS₂⁻: δ 150.59 δ 127.94 δ 124.44 δ 121.39. PhS₃⁻: δ 158.62 δ 129.00 δ 127.19 δ 125.58. PhS₄⁻: δ 139.18 δ 130.12 δ 129.31 δ 127.24.

Further characterization details for X⁺ PhS₂⁻ compounds are listed in the section for the specific compounds.

Tetraphenylphosphonium perthiophenolate PPh₄⁺ PhS₂⁻ (1a): amount of starting materials: sodium thiophenolate (500 mg, 3.4 mmol, 90% purity), PPh₄Cl (1276 mg, 3.4 mmol), S₈ (109 mg, 0.43 mmol); product: orange crystals at r.t. (thermochromic) (1340 mg, 2.73 mmol, 80% yield). NMR: see “phenyl perthiolate salts”. Elemental analysis: Calc. for C₃₀H₂₅PS₄: C, 74.97%; H, 5.24%; N, 0.00 %; S, 13.34%. Measured: C, 75.00%; H, 5.30%; N, 0.01%; S,

13.53%. Mass spectrum and crystal structure (CCDC-1965777 for CuK α at 100 K, CCDC-1969776 for CuK α at 300 K) see results and discussion section.

Tetraethylammonium perthiophenolate $\text{NEt}_4 \text{PhS}_2^-$ (**1b**): amount of starting materials: sodium thiophenolate (200 mg, 1.36 mmol, 90% purity), NEt_4Cl (225 mg, 1.36 mmol), S_8 (44 mg, 0.17 mmol); product: shiny yellow crystals, much more air sensitive than **1a** and **1c** (208 mg, 0.43 mmol, 56%). NMR: see “phenyl perthiolate salts”. Elemental analysis: Calc: C, 61.94; H, 9.28; N, 5.16. Measured: C, 61.79%; H, 9.08%; N, 5.14%. Crystal structure: CCDC- 1965778 for CuK α , CCDC-1965779 for MoK α .

Tetraethylammonium S-Phenyl sulfurothioate $\text{NEt}_4^+ \text{PhS}_2\text{O}_3^-$: Crystals of $\text{NEt}_4\text{PhS}_2^-$ (**1b**) were left standing at r.t. under air producing a melt. Out of the melt crystals formed that were suitable for X-ray crystal structure analysis (CCDC-1965782 for CuK α) (Fig. 6).

*Bis(triphenylphosphine)iminium perthiophenolate*MeCN* $\text{PNP}^+ \text{PhS}_2^- \cdot \text{CH}_3\text{CN}$ (**1c**): amount of starting materials: sodium thiophenolate (200 mg, 1.36 mmol), PNPCl (782 mg, 1.36 mmol), S_8 (44 mg, 0.17 mmol); product: yellow crystals (680 mg, 1.00 mmol, 74% yield). NMR: see “phenyl perthiolate salts”. Elemental analysis: C, 73.31%; H, 5.31%; N, 3.89%; S, 8.90%. Measured: C, 73.34%, H, 5.31%, N, 3.74%, S, 8.88%. Crystal structure: CCDC-1965780 for CuK α for 100 K, CCDC-1971844 for CuK α at 300 K.

Phenyl tetrasulfanide salt $\text{PPh}_4^+ \text{PhS}_4^-$ (**2**): Sodium thiophenolate (200 mg, 90% purity, 1.36 mmol), 1 equivalent of PPh_4Cl (511 mg) and 0.31 equivalents of S_8 (109 mg) were suspended in 15 ml of MeCN. The mixture was stirred at r.t. overnight. The dark suspension was filtered and the filtrate treated with diethyl ether to initiate crystallization. Subsequently it was stored at -34 °C, leading to the formation of orange and dark red crystals identified as **1a** and $(\text{PPh}_4)_2\text{S}_7$. The crystals were filtered off and the filtrate was treated with more Et_2O , leading again to the formation of the same crystals. The procedure was repeated 1-3 times in total until dark red crystal (hard to distinguish from $(\text{PPh}_4)_2\text{S}_7$ by eye) appeared (160 mg, 0.29 mmol, 22%). NMR: see results and discussion section ([Fig. 8](#)). Elemental analysis: Calc. for $\text{C}_{30}\text{H}_{25}\text{PS}_4$: C,

66.14%; H, 4.63%; N, 0.00%; S, 23.54%. Measured: C, 65.94%; H, 4.59%; N, 0.04%; S, 23.03%. Crystal structure: CCDC-1965791 for CuK α , CCDC-1965790 for MoK α .

Tert-butyl perthiolate salt $PPh_4^+ t-BuS_2^-$ (**3**): Sodium-2-methyl-2-propanethiolate (90%, 200 mg, 1.6 mmol) was dissolved in 10 ml of MeCN together with one equivalent of PPh_4Cl (602 mg) and 1/8 equivalent of elemental sulfur S_8 (51 mg). The suspension was stirred at r.t. for 1 h, then filtered and treated with diethyl ether to incipient crystallization. The filtrate was stored at $-34^\circ C$ leading to precipitation of a small amount of white powder. This powder was filtered off and the filtrate treated with some more diethyl ether and put back at $-34^\circ C$. Once again, a white precipitate appeared, which was filtered off again. After addition of some more diethyl ether, the solution was stored at $-34^\circ C$ in the freezer over the weekend, leading to the formation of dark red crystals. Those were filtered off, the filtrate treated with some diethyl ether and crystallized again at $-34^\circ C$ (202 mg, 0.44 mmol, 27%). 1H NMR (600 MHz, DOSY at 500 MHz, CD_3CN): When dissolved, the sulfur chain grows or shrinks. This happens slowly enough to allow peak separation. 2D NMR and a DOSY measurement allowed assignment of the relevant peaks. V, W, X, Y and Z are four species smaller than a 1% fraction of all compounds. They contain a *tert*-butyl group according to HMBC experiments but could not be assigned with certainty. Most likely they consist of oxidized or protonated species, or species of different sulfur chain lengths (Fig. S20). PPh_4^+ : δ 7.94-7.89 (m, 4 H, PPh_4^+) δ 7.77-7.72 (m, 8 H) δ 7.71-7.66 (m, 8 H). $t-BuS^-$: δ 1.29 (s, 9H), $D = 2.42 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 2%, 18% after two days). $t-BuS_2^-$: δ 1.18 (s, 9H), $D = 2.01 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 85%, 58% after two days). $t-BuS_3^-$: δ 1.34 (s, 9H), $D = 1.95 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 11%, 22% after two days). $t-BuS_4^-$: δ 1.36 (s, 9H), $D = 1.85 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 0.2%, 0.7% after two days). V: δ 1.39 (after 30 min: 0.5%, 0% after two days). W: δ 1.35 (s, 9H), $D = 2.34 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 0.6%, 0.5% after two days). X: δ 1.30 (s, 9H), $D = 2.02 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 0.8%, 0.7% after two days). Y: δ 1.25 (s, 9H), $D = 2.55 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 0%, 0.1% after two days). Z: δ 1.08 (s, 9H), $D = 2.01 \cdot 10^{-9} m^2 s^{-1}$ (after 30 min: 0%, 0.2% after two days). ^{13}C NMR (151 MHz,

CD₃CN-*d*₃): PPh₄⁺: δ 136.35 (d, *J* = 3.1 Hz) δ 135.70 (d, *J* = 10.3 Hz) δ 131.33 (d, *J* = 12.9 Hz) δ 119.08 (d, *J* = 89.9 Hz). *t*-BuS[·]: δ 46.76 δ 30.78. *t*-BuS₂[·]: δ 41.60 δ 29.97. *t*-BuS₃[·]: δ 48.42 δ 31.05. *t*-BuS₄[·]: δ 47.02 δ 31.31. V: signals too weak. W: δ 46.28 δ 31.20. X: δ 63.09 δ 25.49. Y: δ 47.02 δ 30.64. Z: δ 55.70 δ 23.68. Elemental analysis: Calc. for C₂₈H₂₉PS₂: C, 73.01%; H, 6.35%; N, 0.00% S, 13.92%. Measured: C, 73.05%; H, 6.47%; N, 0.13%; S, 14.14%. Crystal structure: CCDC-1966298 for CuKα.

CRYSTAL STRUCTURE DETERMINATION

Single crystals of the compounds were selected and mounted on an XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystals were kept at 100.0(1) K during data collection (unless stated otherwise). Using Olex2,⁸³ the structure was solved with the ShelXT⁸⁴ structure solution program using Intrinsic Phasing and refined with the ShelXL⁸⁵ refinement package using Least Squares minimization. Hirshfeld analysis was performed with CrystalExplorer17.⁸⁶ All structures can be found in the Cambridge Crystallographic Data base and the SI. Details concerning the pressure dependent X-Ray crystal structure determinations can be found in the SI.

ASSOCIATED CONTENT

Calculations with different methods, crystallographic details, low temperature NMR, NMR in different solvents, solid state NMR, additional ESI-MS spectra, collision-induced-dissociation spectra and DSC measurements can be found in the SI.

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Notes

The authors declare no competing financial interest.

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For Table of Contents Only

Synopsis: Various monoorganyl polysulfanide salts of the form $RS_n^- X^+$ have been isolated and subjected to X-ray crystal structure analysis. They were accessed via a

one-step synthesis from sodium thiolates and elemental sulfur. While stable as solids under inert atmosphere, those compounds enter complex equilibria when dissolved. The thermochromic properties of one specific compound were investigated by temperature- and pressure dependent X-Ray analyses as well as DFT periodic boundary calculations and traced back to crystal dynamics.