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To be cited as: *Chem. Eur. J.* 10.1002/chem.201802427

Link to VoR: http://dx.doi.org/10.1002/chem.201802427

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Chemistry - A European Journal 10.1002/chem.201802427

Sulfides and Disulfides of s-Triazine: Potential Thermal Thiyl Radical Generators

Carl-Christoph Höhne*,[a,b], Christian Posern[a], Uwe Böhme[a] and Edwin Kroke[a]

Abstract: A series of aliphatic and aromatic thioethers and dithioethers of s-triazine were synthesized to study their thermal properties, in particular the thermally induced thiyl radical generation ability. Four symmetric s-triazine sulfides of the type $(RS)_3C_3N_3$, namely 2,4,6-tris(phenylthio)- (**1**), 2,4,6-tris(para-tolylthio)- (**3**), 2,4,6-tris(ethylthio)- (**5**) and 2,4,6-tris(tert-butylthio)-1,3,5-triazine (**7**), as well as four symmetric s-triazine disulfides of the type $(RSS)_3C_3N_3$, namely 2,4,6-tris(phenyldithio)- (**2**), 2,4,6-tris(para-tolyldithio)- (**4**), 2,4,6-tris(ethyldithio)- (**6**) and 2,4,6-tris(tert-butyldithio)-1,3,5-triazine (**8**) were synthesized. All compounds were comprehensively characterized by ^{1}H and ^{13}C NMR, infrared and Raman spectroscopy as well as elemental analyses. Single-crystal X-ray diffraction analyses of **1**, **2** and **5** are discussed. The thermal behavior was studied by thermogravimetric analyses coupled with mass spectrometry (TGA-MS) and quantum chemical calculations. LOI flammability tests showed that the disulfides were the most promising radical generators, and were most likely to be suitable flame retardants for selected polymers.

Introduction

In a previous paper, we presented the first representatives of the new class of arylthio-substituted s-heptazines.[1] Arylthiocyamelurates are able to release thiyl radicals during thermal decomposition.[1] Thiyl radicals are known to be a species with flame retardant effects.[2–5] Our model arylthio-substituted s-heptazine molecule, triphenylthiocyamelurate $(C_6H_5S)_3C_6N_7$, decomposes thermally at around 393 °C.[1] This decomposition temperature could be too high for thermoplastics like polyethylene, polystyrene or polypropylene to achieve outstanding flame retardancy. Thiyl radical generation in the temperature range just above the polymer processing temperature between 200 °C and 300 °C should be more effective for these thermoplastics. Besides, it is known that almost all s-heptazine derivatives such as melem $C_6N_7(NH_2)_3$[6] and its derivatives like $C_6N_7(NR_2)_3$[6,7] or cymeluric acid $C_6N_7(OH)_3$[6] and related compounds such as the azide $C_6N_7(N_3)_3$[6,8] are significantly more stable than the corresponding s-triazine derivatives melamine $C_3N_3(NH_2)_3$[6], its derivatives $C_3N_3(NR_2)_3$[9], cyanuric acid $C_3N_3(OH)_3$[9] and $C_3N_3(N_3)_3$[8,10]. According to these hypotheses, we synthesized aryl- and alkyl-substituted thio- and dithio-s-triazines and studied their thermal properties and capacity for thermally induced thiyl radical formation.

Trithiocyanuric acid is well-known in the literature[11] and dates back to Hofmann[12] and Klason[13] in 1885. Aryl- and alkyl-substituted thiocyanurates are also known: in parallel to our study, Mehrotra and Angamuthu[14] studied the synthesis and the single crystal structure of eight aryl-substituted thiocyanurates. They showed that arylthiols - even sterically demanding arylthiols - react with cyanuric chloride with high yields in the range of 87% to 62%.[14] The thermal analysis of these compounds showed thermal stability at 230 °C to 280 °C.[14] The main decomposition step occurs below 400 °C. Most of them decompose or volatilize with one single decomposition step.[14] Further studies with arylthiocyanurates used as anti-cancer agents[15] or synthesized by C-S cross-coupling reactions of thiocyanuric acid and aryl halides[16] are reported. To the best of our knowledge, the first reported syntheses of aryl-substituted thiocyanurates were carried out by Klason[13] in 1886. He synthesized phenylthiocyanurate and p-tolylthiocyanurate from cyanuric chloride and sodium thiolates.[13] Hofmann[12] and Klason[13] also mentioned alkyl-substituted thiocyanurates, with methyl-[12,13], ethyl-[13] and n-pentyl-[13]substituents. Further examples are given in the literature.[12,17] Beside the substitution of the s-triazine core with three thio groups, substitution with mixed groups (thio-, oxy-, amino-) is also known.[18] One example is Irganox® 565 (BASF), an antioxidant with two octylthiol groups and one amino-2,6-di-tert-butylphenol group as an antioxidant group[19].

Hitherto, aryl- and alkyl disulfides of s-triazine are not further discussed in the literature. In Japanese patents the synthesis of 2,4,6-tris(isopropyldithio)-1,3,5-triazine by sulfenylation of thiocyanuric acid with *N*-cyclohexyl-*N*-isopropylthio-2-benzothiazolesulfonamide is mentioned[20], as is the reaction of thiocyanuric acid with chlorinated 2-propanethiol[21] and its use as scorch inhibitors[22] in polymers. A synthesis route for 2,4,6-tris(n-dodecyldithio)-1,3,5-triazine[23] and an application of 2,4,6-tris(n-octyldithio)-1,3,5-triazine[24] has been described in the literature.

Disulfide bonds connecting two s-triazine rings have also been reported.[2,3,25,26] However, this bond type is not the subject of our present study.

To the best of our knowledge, a comprehensive discussion of the synthesis and characterization of s-triazines with a tri-fold substitution by aryl and alkyl disulfides and a corresponding comparison with s-triazine and s-heptazine monosulfides is missing in the literature. All these classes of compounds are considered as potentially promising halogen-free flame retardants.

Results and Discussion

Syntheses of s-thiotriazines

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For our study, we used the historical synthesis path[13]. Cyanuric chloride was reacted with the sodium salts of thiophenol, 4-methylthiophenol, ethanethiol and 2-methylpropane-2-thiol in the ratio of one-to-three to obtain 2,4,6-tris(phenylthio)-1,3,5-triazine (**1**), 2,4,6-tris(p-tolylthio)-1,3,5-triazine (**3**), 2,4,6-tris(ethylthio)-1,3,5-triazine (**5**) and 2,4,6-tris(tert-butylthio)-1,3,5-triazine (**7**), see Figure 1. All four compounds were characterized using ^{1}H and ^{13}C NMR spectroscopy, ATR-FTIR spectroscopy, Raman spectroscopy, elementary analysis and melting point. From compounds **1** and **5** single crystals were obtained and analyzed using a single-crystal X-ray diffraction technique. The thermal behaviour was studied by thermogravimetric analysis. The sodium salts of the four thiols were produced using elementary sodium.

Syntheses of s-dithiotriazines

In our study, we used the reaction of a chlorinated thiol with a second thiol to form a disulfide bond between these two thiols. Both, the sulfenyl chloride of thiocyanuric acid[26,27] and the synthesis of sulfenyl chlorides of aryl- and alkyl thiols[28] are known. Following the synthesis method described in the literature for 2,4,6-tris(isopropyldithio)-1,3,5-triazine[21], we used sulfenyl chloride of the aryl and alkyl thiols but used the sodium salt of thiocyanuric acid instead of thiocyanuric acid. Sodium thiocyanurate was reacted with sulfenyl chlorides of thiophenol, 4-methylthiophenol, ethanethiol and 2-methylpropane-2-thiol in the ratio of one-to-three to obtain 2,4,6-tris(phenyldithio)-1,3,5-triazine (**2**), 2,4,6-tris(p-tolyldithio)-1,3,5-triazine (**4**), 2,4,6-tris(ethyldithio)-1,3,5-triazine (**6**) and 2,4,6-tris(tert-butyldithio)-1,3,5-triazine (**8**) - see Figure 1. Compounds **2**, **4**, and **6** were characterized using ^{1}H and ^{13}C NMR spectroscopy, ATR-FTIR spectroscopy, Raman spectroscopy, elementary analysis and melting point. From compound **2** single crystals were obtained and analysed using the single-crystal X-ray diffraction technique. The thermal behaviour was studied by thermogravimetric analysis. The sulfenyl chlorides of the four thiols were produced using sulfuryl chloride. Purification is a frequent problem in triazine derivative synthesis. The raw product is obtained as a liquid with high viscosity caused by reactant-product and solvent-product interactions. Often repeated trituration of the liquid product with a volatile solvent removes impurities and solidification is achieved. However, the impurities of compound **8** remain, even after column chromatography.

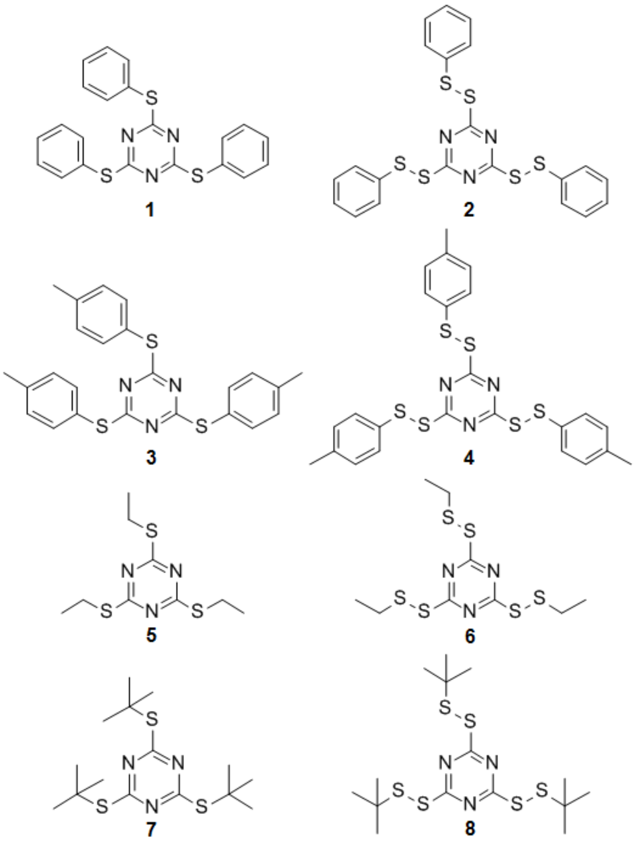

Figure 1 Aromatic (**1**-**4**) and aliphatic (**5**-**8**) s-thiotriazines and s-dithiotrianzines synthesised for this study.

NMR spectroscopy

As reported[14] for tris-arylthiotriazines, the NMR spectra of thiotriazines and dithiotriazines indicate a C3 symmetry at common solution NMR conditions. ^{13}C NMR spectroscopy was used to study the electronic effects (indicated by a chemical shift) of the sulfide bond and the disulfide bond on the aryl group.

The ^{13}C NMR spectra for the aryl derivatives (**1**-**4**) are shown in Figure 2 and the signals of the phenyl group of **1** and **2** are shown in Figure 3.

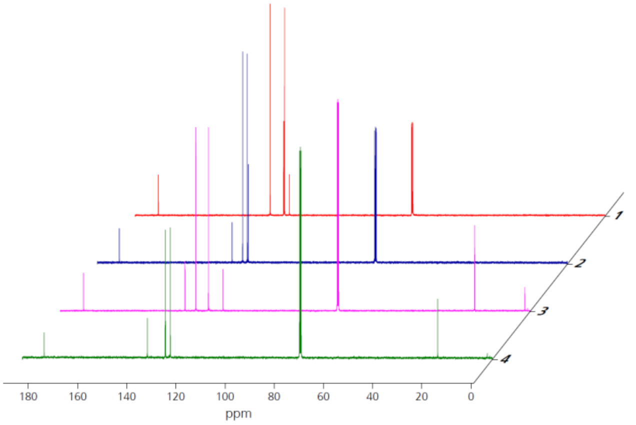

Figure 2. ^{13}C NMR spectra of **1**-**4**.

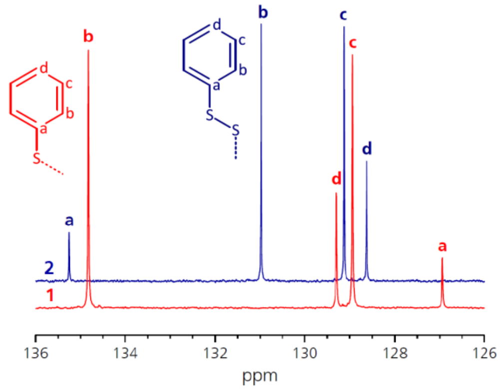

Figure 3. ^{13}C NMR signals of the phenyl groups of **1** (red) and **2** (blue). The ^{13}C NMR signal assignment by 2D NMR measurements are given in the supporting information.

All four aryl derivatives show one peak of the triazine core at about 180 ppm. In comparison to the aryl thiotriazines, this signal is shifted downfield by 0.7 ppm for the aryl dithiotriazines. The pattern of the ^{13}C NMR phenyl group shifts of **1** and **2** in Figure 3 show a different electronic character for the (mono)sulfide and disulfide bond. In comparison to **1**, the ^{13}C NMR signals of the phenyl core carbon atoms of **2** on position b and d are shifted upfield and the signals a and c are shifted downfield. This suggests that in the (mono)sulfide, the sulfide substituent creates an –M effect on the phenyl group. However, the main effect of the disulfide substituent is an -I effect on the phenyl group due to the partially positive sulfur atom of the disulfide bond caused by strong lone pair interactions between the two sulfur atoms[29].

ATR-FTIR and Raman spectroscopy

As expected, the ATR-FTIR and Raman spectra of the thiotriazines and dithiotriazines are quite similar. The main differences can be seen at the Raman spectra around 500 cm^{-1}, a typical area for disulfide bonds[30]. Figure 4 shows the ATR-FTIR and Raman spectra of **1** and **2**. Table 1 shows the Raman signals for the dithiotriazines at about 500 cm^{-1}.

Table 1. Raman signals for **2**, **4** and **6** indicating the disulfide bond.

#	**2**	**4**	**6**
Wave number [cm^{-1}]	537	533	529
	503	494	496
	464	466	465

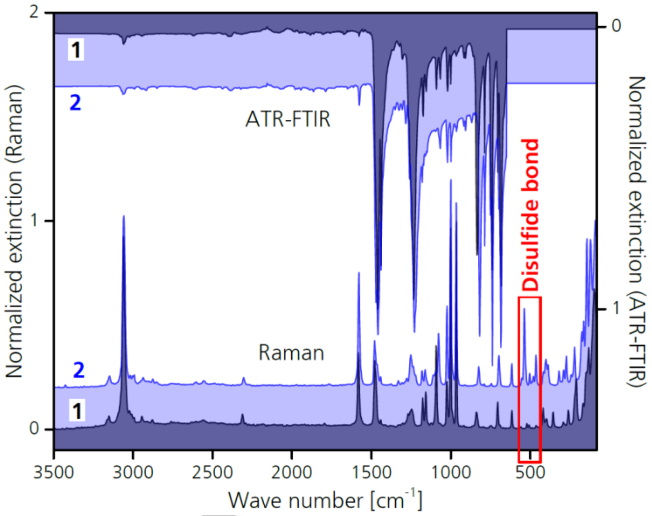

Figure 4. ATR-FTIR (top) and Raman (bottom) spectra of **1** and **2**.

Description of crystal structures (1, 2, 5)

Single crystals of compound **1**, **2**, and **5** were grown by cooling crystallization from n-heptane. Single crystal X-ray diffraction analysis of these crystals allows access to the structural parameters.

Compound **1** crystallizes with two crystallographically independent molecules in the monoclinic space group *I2/c* with an angle β = 100.740(3)°. The alternative setting C2/c has a larger angle β of 133.022°. The crystal structure of **1** was already reported.[14] Data from our structure determination are included here for comparison with the other structures (see Figure 5 and supporting information).

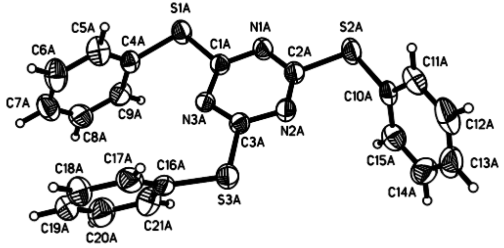

Figure 5. One crystallographically independent molecule of **1**. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50 % probability level.

The bond lengths and angles in the C_3N_3 core are in the expected range[31] for all three structures. The bond lengths from the triazine carbon to the sulfur atom are 1.75 Å (mean value) in **1**. The S-C-bonds to the phenyl groups in **1** are somewhat longer with a mean value of 1.771 Å. The ipso-carbon atoms of the phenyl groups of **1** are nearly in plane with the triazine unit. This is indicated by the torsion angles of -2.4° to 7.9° (see Table S2). The phenyl groups themselves are orientated perpendicularly to the triazine plane of **1**.

The molecular structure of **2** is shown in Figure 6 and numeric values for bond lengths and angles as well as further information on the structure analysis are listed in the supporting information. The bond lengths from the triazine carbon atoms to the sulfur atoms are somewhat longer in **2** than in **1**, with a mean value of 1.769 Å. The S-C-bonds to the phenyl groups in **2** have a mean value of 1.782 Å.

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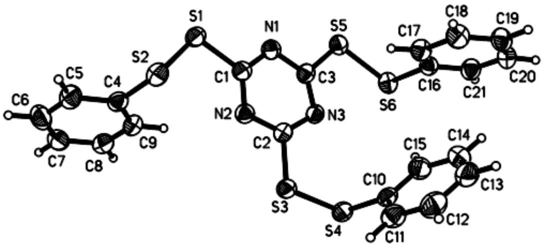

Figure 6. Molecular structure of **2**. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50 % probability level.

Differences between structures **1** and **2** arise mainly from the different orientation of the substituents at the triazine unit. The sulfur-sulfur bond in **2** adds additional flexibility for possible orientations of the phenyl groups. All six sulfur atoms lie nearly in plane with the triazine core with a maximal deviation of 8.6° for the torsion angle N2-C1-S1-S2. The phenyl groups are rotated out of this plane with torsion angles C-S-S-C around ± 90°.

The molecular structure of **5** is shown in Figure 7 and numeric values are listed in the supporting information. The bond lengths from the triazine carbon atoms to the sulfur atoms are similar to those in **1** with a mean value of 1.748 Å. The S-C-bonds to the ethyl groups in **5** have a mean value of 1.815 Å. These bonds are longer than all other C-S-bonds discussed in this paper. The reason is the lower electronegativity of the ethyl group in comparison to the phenyl groups. The ethyl groups are in plane with the triazine unit with torsion angles N-C-S-C close to 0°. Only one methyl function (C7) of the ethyl group –C6-C7 is out of the triazine plane.

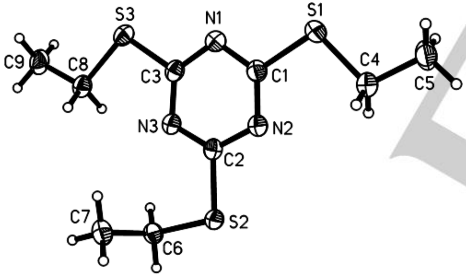

Figure 7. Molecular structure of **5**. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50 % probability level.

Intermolecular interactions of compound **2** are shown in Figure 8. The molecules of crystalized **2** form double layers connected by S(lp)···$\pi_{\text{Triazine ring}}$ interaction with a distance ($D_{S(lp)\cdots\pi}$) of 3.528 Å. One of the three phenyl groups is located in the double layer by S(lp)···$\pi_{\text{Phenyl ring}}$ interaction with a distance ($D_{S(lp)\cdots\pi}$) of 3.443 Å. Both other phenyl groups are located in the area between two double layers.

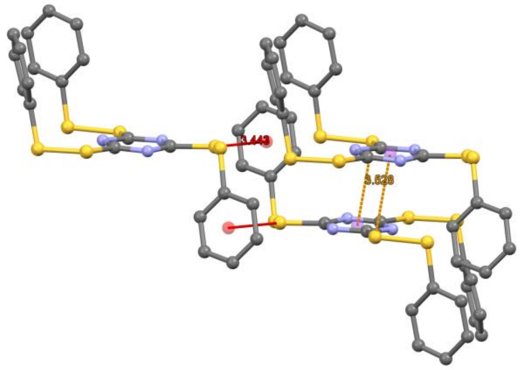

Figure 8. Intermolecular interaction of **2** (carbon: grey, nitrogen: light blue, sulfur: yellow, hydrogen: not drawn, center of triazine ring: purple, center of phenyl ring: red; distance: [Å]).

Intermolecular interactions of compound **5** are given in Figure 9 and Table 2. Two molecules of **5** are connected by intermolecular S(lp)···π interaction with a distance ($D_{S(lp)\cdots\pi}$) of 3.524 Å. These dimers are connected to an adjacent dimer by hydrogen···$\pi_{\text{triazine ring}}$ interaction with a distance ($D_{H\cdots\pi}$) of 2.726 Å. The out of plane methyl function (C7) is located between the S(lp)···π connected molecule dimers.

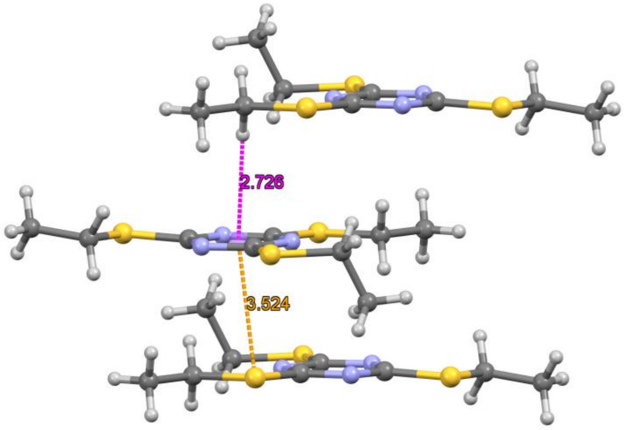

Figure 9. Intermolecular interaction of **5** (carbon: grey, nitrogen: light blue, sulfur: yellow, hydrogen (calculated): white, center of triazine ring: purple; distance: [Å]).

Table 2 Distances of intermolecular interactions of **2** and **5**.

#		Centroid	Plane
2	S-Ph	3.443	3.386
	S-Triazine core	3.528	3.436
5	H-Triazine core	2.726	2.720
	S-Triazine core	3.524	3.499

Thermal behaviour

For application, for example as flame retardants, the melting point (mp) of a new compound is important. In polymer processing materials are often easier to process if they are liquid at processing temperatures, e.g. because blending or infiltration of fibre reinforcements are more feasible.

The four aryl triazines are solids at room temperature. Their mps are given in Table 3. Both dithiotriazines **2** and **4** melt at lower temperatures than their thiotriazine analogs **1** and **3**. The alkyl triazines **5** and **7** are liquid at room temperature but **5** do

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not recrystallize at room temperature after melting. Like **6** and **8**, compound **5** is a liquid with high viscosity at room temperature.

Table 3. Melting point (mp) of compounds **1**-**7**.

#	1	2	3	4	5	6	7
mp [°C]	97-98	93-94	116-117	95-96	23-25	<23	147
Literature	97[13]		114[13]		27[13]		

The thermal behaviour of the derivatives, especially the derivatives of the disulfides, is of great interest for future applications. It is known, that organic disulfides act as thiyl radical generators. However, in one of our previous studies we were able to show the thermally initiated thiyl radical generation of the s-heptazine analog (triphenyl thiocyamelurate) of **1**.[1] On the basis of this knowledge, we started thermal studies with alkyl and aryl thiocyanurates and dithiocyanurates. Table 4 shows the results of TGA measurements.

Table 4. TGA results of compounds **1**-**7**.

#	Onset temperature [°C]	Mass loss [%]
1	291	total
2	223	41.4
	297	39.1
	567	10.0
	at 995	4.8 (residual mass)
3	349	total
4	240	74.1
	504	9.4
	at 995	11.3 (residual mass)
5	231	total
6	228	78.8
	565	19.2
	at 995	2.0 (residual mass)
7	219	total

Table 5. Temperature at which compounds **1**-**7** reach a 2.0 % mass loss.

#	1	2	3	4	5	6	7
T [°C]	223	210	283	217	158	184	157

In contrast to thiocyamelurates[1], the thiocyanurates **1**, **3**, **5** and **7** (see Figure 10) show just one thermal effect – the complete transition into the gaseous phase. All four aryl and alkyl thiocyanurates decompose above 210 °C. Incorporation into polymeric materials with low processing temperatures like polyethylene and polypropylene seems to be possible.

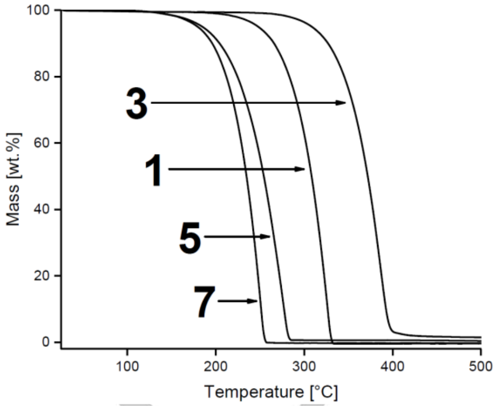

Figure 10. TGA of the compounds **1**, **3**, **5** and **7**.

However, for the dithiocyanurates **2**, **4**, and **6** a stepwise thermal decomposition is observed (see Table 4). The main decomposition products detected by TGA-MS measurements are shown in Figure 11, Figure 12 and Figure 13. All three Figures show important MS signals observed during the thermal decomposition which indicate the release of expected molecule fragments. Due to large differences in the MS signal intensity, four separate MS plots are shown for each component.

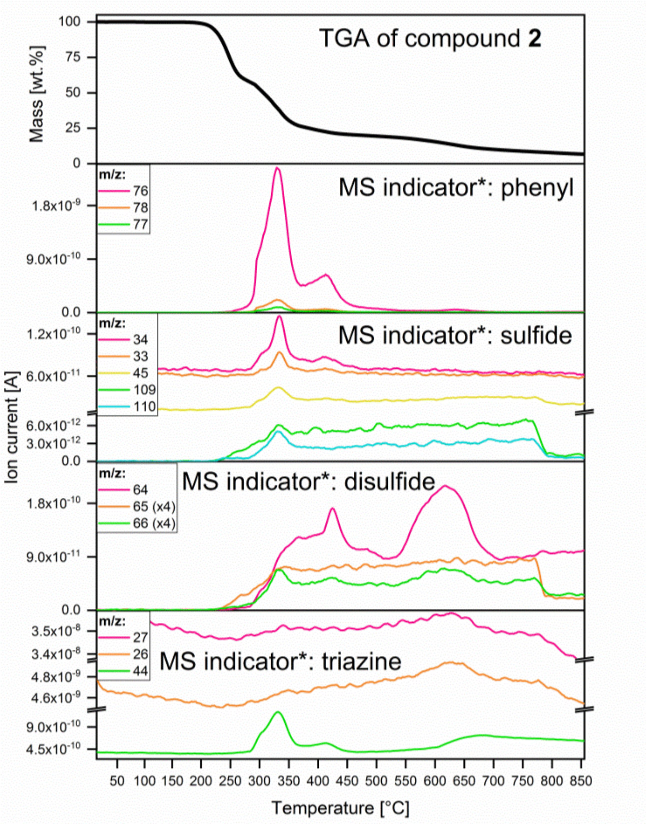

Figure 11. TGA-MS results of **2** (* smoothed signals).

The thermal decomposition of **2** shows three decomposition steps. During the first and second decomposition step at 223 °C and 297 °C, a mass loss of around 40 % for each step is observed. An explanation for this mass loss is the formation of a sulfide bridged triazine network ($C_3N_3S_{1,5}$, mass loss: 75 %) with the release of phenyl sulfide and phenyl disulfide. The third decomposition step at 567 °C, with a mass loss of 10 %, is assumed to be the incomplete decomposition of this CNS network. The TGA-MS analysis of the decomposition steps shows no MS signal for the first decomposition step. We assume that phenyl sulfide is released during the first decomposition step. In the gaseous phase, diphenyl disulfide is formed and precipitates at the walls of the TGA unit. Due to the mass loss of about 41 %, the release of two phenyl sulfide groups per molecule seems to be plausible. At the temperature of the second decomposition step, the released components and the residue of **2** decompose. For the second decomposition step MS fragments of the phenyl group (m/z: 76 ($C_6H_4^+$), 77 ($C_6H_5^+$) and 78 ($C_6H_6^+$)), MS fragments of the phenyl sulfide group (m/z: 33 (SH^+), 34 (SH_2^+), 45 (CHS^+), 109 ($C_6H_5S^+$) and 110 ($C_6H_6S^+$)) and MS indicators for the formation of disulfides (diphenyl disulfide) (m/z: 64 (S_2^+), 65 (S_2H^+) and 66 ($S_2H_2^+$)) are observed. Between 300 °C and 800 °C, a constant release of phenyl sulfide (m/z: 109, 110) and disulfide (m/z: 65, 66) is measured. This observation supports the assumption that diphenyl disulfide is formed and precipitates on the TGA chamber walls during the first decomposition step. For the third decomposition step, indicators for the decomposition of a CNS network are observed; m/z: 26 (CN^+), 27 (HCN^+), and 44 (CS^+, $CN_2H_4^+$).

The MS analysis shows the release of all phenyl groups during the first and second decomposition step. The remaining carbon-nitrogen-sulfur material decomposes incompletely in the third decomposition step.

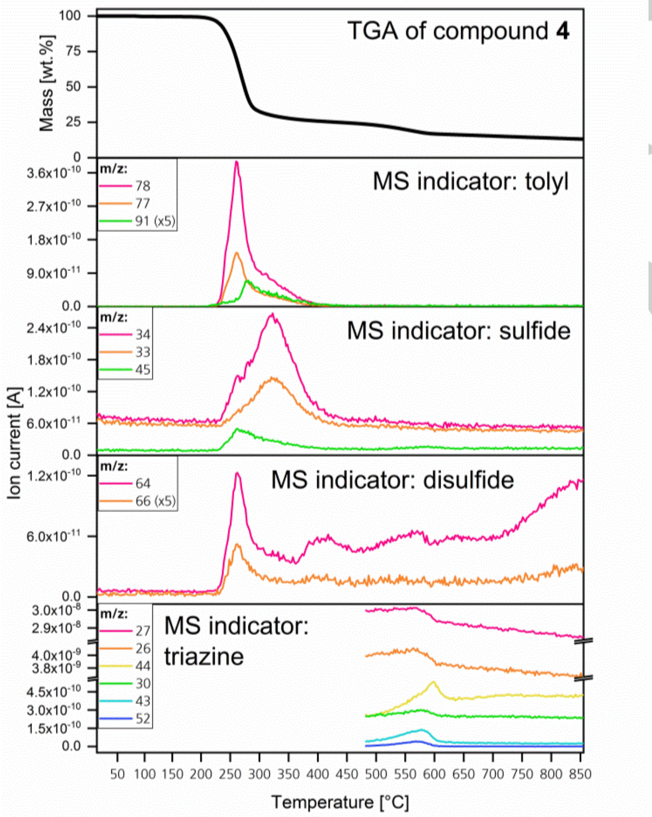

Figure 12. TGA-MS results of the aryl disulfide 2,4,6-tris(p-tolyldithio)-1,3,5-triazine (**4**).

Compound **4** decomposes thermally in two steps. For the first decomposition step at 240 °C a mass loss of 74.1 % is measured up to a temperature of 400 °C. This mass loss is slightly more than expected for the release of three tolyl sulfide groups (mass loss: 68.0 %) but less than expected for the release of three tolyl disulfide groups (mass loss: 85.6 %). The formation of sulfur bridged s-triazine cores by releasing tolyl groups and 75 % of the sulfur (mass loss: 76.8 %) achieves the best match. For the second decomposition step at 504 °C a mass loss of 9.4 % is observed. The residue mass at 995 °C is 11.3 %. At the first decomposition step, the TGA-MS analysis of **4** (see Figure 12) shows the typical MS signals of the tolyl group (m/z: 77 ($C_6H_5^+$), 78 ($C_6H_6^+$) and 91 ($C_7H_7^+$)), fragments of the tolyl sulfide group (m/z: 33 (SH^+), 34 (SH_2^+) and 45 (CHS^+)) and fragments of the tolyl disulfide group (m/z: 64 (S_2^+) and 66 ($S_2H_2^+$)). For the second decomposition step, MS fragment signals of the triazine core are observed: m/z: 26 (CN^+), 27 (HCN^+), 30 ($N_2H_2^+$), 43 ($CN_2H_3^+$), 44 (CS^+, $CN_2H_4^+$) and 52 ($C_2N_2^+$).

The MS results show the release of all tolyl groups and most of the sulfur during the first decomposition step. The remaining carbon-nitrogen-sulfur material decomposes incompletely in the second decomposition step.

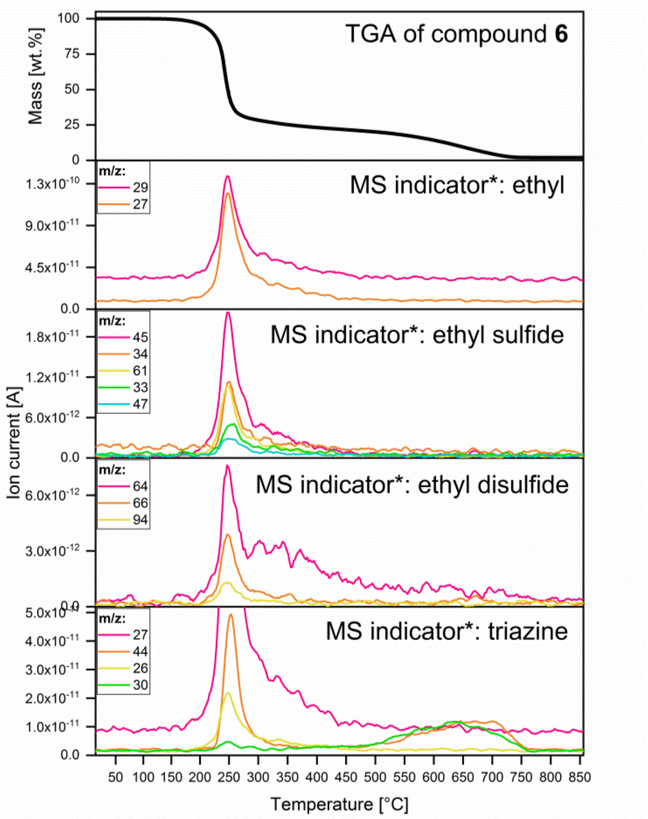

Figure 13. TGA-MS results of the alkyl disulfide 2,4,6-tris(ethyldithio)-1,3,5-triazine **6** (* smoothed signals).

The TGA of compound **6** shows two thermal decomposition steps. For the first decomposition step at 228 °C, a mass loss of 78.8 % is observed up to a temperature of 465 °C. According to the molecular structure of **6**, this mass loss corresponds to the calculated loss of three ethyl disulfide groups (mass loss: 78.2 %). The second decomposition step is observed at 565 °C. From 465 °C to 995 °C, a mass loss of 19.2 % is measured. The

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MS analysis of the first decomposition step shows typical MS signals for the ethyl group (m/z: 27 ($C_2H_3^+$) and 29 ($C_2H_5^+$)), the ethyl sulfide group (m/z: 33 (SH^+), 34 (SH_2^+), 45 (CHS^+), 47 (CH_3S^+) and 61 ($C_2H_5S^+$)) and MS indicator signals for the ethyl disulfide group (m/z: 64 (S_2^+), 66 ($S_2H_2^+$) and 94 ($C_2H_5S_2^+$)). MS indicator signals for the triazine core (m/z: 26 (CN^+) and 27 (HCN^+)) are overlapped by the ethyl group MS signals. In the second decomposition step, two MS signals are observed: 30 ($N_2H_2^+$) and 44 (CS^+, $CN_2H_4^+$). Due to the weakness of both of these signals, we assume that relatively stable fragments with a m/z > 120 are released. According to the MS results, in the first thermal decomposition step all ethyl groups and most of the sulfur is released from **6**. The MS results suggest the release of $EtS^{\bullet}$, $S^{\bullet}$ and $EtS_2^{\bullet}$ radicals from **6**. These radicals recombine in the gaseous phase leading to the observed MS species. The remaining carbon-nitrogen-sulfur material decomposes in the second decomposition step at 565 °C.

All three dithiocyanurates (**2**, **4**, and **6**) release all of their aryl/alkyl groups in the form of sulfides and disulfides between 220 °C and 350 °C. As thermally induced thiyl radical generators, the dithiocyanurates seem to be highly efficient.

Since for the thiocyanurates (**1**, **3**, **5** and **7**) no thermal decomposition is observed with the release of fragments (especially thiyl radicals) from the condensed phase, we expect thiocyanurates to have a lower ability to act as thermally induced thiyl radical generators, in particular with regard to flame retardancy.

Thermal thiyl radical generation

The potential formation of thiyl radicals takes place at temperatures between 200 °C and 300 °C. Due to the difficulty of measuring radicals at these temperatures, we chose the limiting oxygen index (LOI) flammability test as an indirect method to confirm the presence of thiyl radicals.

The interaction of thermally released radicals of a flame retardant with the thermally released radicals of the decomposing polymer influences the flammability[32,33]. Higher LOI values correlate with lower amounts of radicals in the gas phase[32]. Thermally released radical species are able to act as radical scavengers for free $HOO^{\bullet}$, $HO^{\bullet}$ and $H^{\bullet}$, species which promote polymer degradation[32].

To prove the existence of radical species, flammability tests can be used. As mentioned before, compounds which are able to release radicals by thermal degradation affect the flammability of polymers. Besides, flame retardant effects are attributed mainly to the physical and chemical effects shown in Table 6.

Table 6. Main physical and chemical flame retardant effects.

Physical effects	Chemical effects
A Dilution of the fuel source (polymer) with inert fillers	**E** Endothermic decomposition
B Dilution of the gas phase by inert gases	**F** Char formation
C Inhibition of heat and gas transfer by inert layer (char)	**G** Increased polymer degradation (drop-off effects)
D Enhanced melt dripping (drop-off effects)	**H** Radical scavenging

To observe thermally induced radical formation, flame retardant effects which are not caused by radical species have to be suppressed. Thermally induced radicals are mainly involved in the flame retardant effects **G** and **H**. To observe the flame retardant effects **A**, **B** and **E**, high amounts of flame retardant are required. By adding just a low amount (e.g. 1.0 wt.%) of a flame retardant, effects **A**, **B** and **E** are suppressed. Moreover, if a polyolefin with no char formation tendency, such as PP[33], is used in combination with a low additive amount, effects **C** and **D** are suppressed. Effects **D** and **G** are more pronounced in foams or foils and are suppressed by using bulky samples. Flame resistance observed in bulky PP samples containing 1.0 wt.% flame retardant is therefore attributed to effect **H** - radical scavenging.

To confirm the thermal thiyl radical formation, we used the LOI test with PP bulky samples which contain 1.0 wt.% of **1** or **2**. Table 7 shows the LOI test results. The LOI value is slightly increased by **1** (ΔLOI = 0.6 O_2%) and significantly increased by **2** (ΔLOI = 3.5 O_2%). The observed flame retardancy could be caused by 1) char formation, however the additive amount of 1.0 wt.% is too low for sufficient char formation, 2) fuel dilution by an inert filler, however **1** and **2** are incorporated with the same amount but the observed LOI value is not the same and 3) flame retarding effects of the triazine core, however the LOI value of **1** (higher triazine core proportion) is significantly lower than the LOI value of **2**. The substantially higher LOI value of **2** is therefore caused by radical scavenging. Since **2** differs only by one sulfur atom and the disulfide bond from **1**, the thermal decomposition of the disulfide bond and the release of thiyl radicals seem to be the appropriate explanation.

Table 7. LOI test result of PP containing 1 wt.% 1 or 2.

#	Additive content [wt.%]	LOI [O_2%]
PP-Std.	0.0	18.4 ± 0.15
PP + **1**	1.0	19.0 ± 0.15
PP + **2**	1.0	21.9 ± 0.30

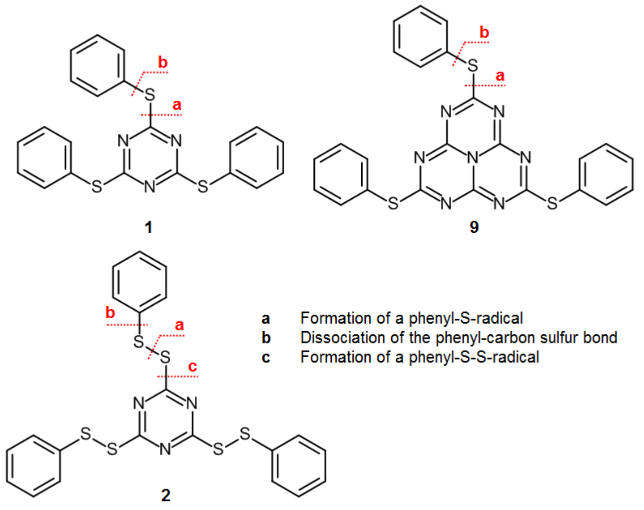
Flame retardant effects of disulfides attributed to thermally induced thiyl radical release are known in the literature[2–5]. LOI test results with bulky PP samples of several organic disulfides are reported[2,3]. The highest LOI value is observed for 2,2'-dithiobis(benzothiazole) (DTBB) with 20.6 O_2% (1.0 wt.% of DTBB; ΔLOI = 3.6 O_2%)[3]. In comparison to these results, dithiocyanurates, represented by compound **2**, seem to be a promising flame retardant for PP, but further investigations are required and are currently being performed.

Quantum chemical calculations

Bond dissociation energies were calculated for the compounds **1**, **2** and triphenylthiocyamelurate (**9**) in order to learn more about the bond breaking processes in the compounds under investigation. Three main bond breaking pathways are expected in these compounds (see Scheme 1):

a Formation of a phenyl-S-radical
b Dissociation of the phenyl-carbon sulfur bond
c Formation of a phenyl-S-S-radical from **2**

The enthalpies and Gibbs free energies of these compounds are listed in Table 8. Full details are given in the supporting information. The comparison of the Gibbs free energies shows the following: the breaking of a triazin- or heptazin-carbon-sulfur bond under formation of a phenyl-sulfur-radical needs about 230 kJ/mol to 240 kJ/mol. This energy is lowered by about 100 kJ/mol in case of the 2,4,6-tris(phenyldithio)-1,3,5-triazine (**2**). Cleavage of the sulfur-sulfur bond needs only 133.8 kJ/mol (section **a** in Table 8). This value is comparable to the value of 140.8 kJ/mol for breaking a sulfur-sulfur-bond in bis(benzothiazolyl) disulfide.[5] Formation of a phenyl radical from **1** or **9** needs 277 kJ/mol. The Gibbs free energy for the analogous process in **2** needs only 227.3 kJ/mol (section **b** in Table 8). The formation of a phenyl-S-S radical from **2** needs 199 kJ/mol (section **c** of Table 8). All in all the dithio-derivative **2** has the lowest bond dissociation energies of all three compounds. Compounds **1** and **9** have very similar bond dissociation energies. This can be explained by the identical bonding situation of the peripheral substituents.



Scheme 1. Bonds of compounds **1**, **2**, and **9** for dissociation energy calculation.

Table 8. Computed reaction thermodynamics at 298 K and 1 atm (values in kJ/mol).

Reaction	ΔH	ΔG
a - Formation of a phenyl-S-radical		
(**1**): Triazine(SPh)$_3$ → Triazine(SPh)$_2$ radical + PhS-radical	283.2	231.7
(**2**): Triazine(S-SPh)$_3$ → (Ph-S-S)$_2$Triazine-S radical + PhS-radical	185.5	133.8
(**9**): Heptazine(SPh)$_3$ → Heptazine(SPh)$_2$ radical + PhS-radical	290.6	239.5
b - Dissociation of the phenyl-carbon sulfur bond		
(**1**): Triazine(SPh)$_3$ → (PhS)$_2$Triazine-S radical + Ph-radical	329.8	277.5
(**2**): Triazine(S-SPh)$_3$ → (Ph-S-S)$_2$Triazine-S-S radical + Ph-radical	282.2	227.3
(**9**): Heptazine(SPh)$_3$ → (PhS)$_2$Heptazine-S radical + Ph-radical	329.0	277.1
c - Formation of a phenyl-S-S-radical		
(**2**): Triazine(S-SPh)$_3$ → (Ph-S-S)$_2$Triazine radical + Ph-S-S-radical	254.8	199.0

Conclusions

In this paper, the synthesis and characterization of aliphatic and aromatic thio and dithio s-triazines, and their ability to release thiyl radicals by thermal induction, are reported.

It was found that neither aliphatic nor aromatic thio s-triazines are capable of releasing thiyl radicals from the condensed phase. Thio s-triazines are released into the gaseous phase without previous thermal decomposition. However, thio s-heptazines are thermally decomposed with the release of thiyl radicals. Since quantum chemical calculations of bond dissociation energies show that the thiyl radical formation from thio s-triazines and thio s-heptazines is similar, lower evaporability of thio s-heptazines, resulting from the molar mass, is responsible for this.

However, both aliphatic and aromatic dithio s-triazines are able to release decomposition products due to thermal induction at about 220 °C. The decomposition products, characterised by TG-MS, consist of sulfur species which show flame retardant effects in the LOI test. These flame retardant effects are attributed to the release of thiyl radical species during thermal decomposition of the dithio s-triazines, an effect which is known from organic disulfides[3,5]. Quantum chemical calculations show that the formation of thiyl radicals by disulfide bond cleavage lowers enthalpies and Gibbs free energies by about 100 kJ/mol in comparison to sulfides.

The TG-MS and LOI results show the ability of organic s-triazines to act as thermal thiyl radical generators with a flame retardant effect in PP.

For flame retardant applications, the ability of dithio s-triazines to release thiyl radicals in the gas and condensed phases seems to be promising. A detailed analysis of these phenomena will form part of further investigations.

Experimental Section

Materials

All chemicals were used as received from Sigma Aldrich. Solvents were dried over a molecular sieve. PP Daploy® WB 140 HMS (MFR = 2.1 g/10 min (230 °C/2.16 kg) from BOREALIS was used for the LOI test.

Methods

NMR: Standard ^{1}H and ^{13}C NMR spectra were recorded on an AVANCE DPX 400 NMR spectrometer at 293 K (^{1}H: 400 MHz, ^{13}C: 101 MHz). The chemical shifts are reported relative to tetramethylsilane. **ATR-FTIR:** For the attenuated total reflection (ATR) fourier transform infrared (FTIR) spectroscopy a FTIR spectrometer Nicolet 6700 from Thermo Scientific and a DuraScope diamond ATR unit was used. **Raman:** The Raman spectroscopy was performed with a Bruker RFS 100 Raman spectrometer (Nd:YAG, 1064 nm). **EA:** Elemental analyses were performed with a CHNS-O analyzer Flash EA 1112 from Thermo Fisher. **TGA:** The measurements were performed with a TG 209 F1 Iris ASC from Netzsch in nitrogen with a heating rate of 10 K/min. **TGA-MS:** The measurements were performed with a TG 209 F1 Iris ASC coupled with a QMS 403 C Aeolos from Netzsch in nitrogen with a heating rate of 10 K/min. MS signals in the range of m/z 10 to 120 were observed. **mp:** For the determination of the melting points a melting point apparatus Melting Point B-540 from Büchi was used. **LOI test:** Grounded PP was premixed with the compound **1** or **2** and extruded with a MiniLab form ThermoHaake and granulated. The LOI samples were prepared with a MiniLab extruder from ThermoHaake at 210 °C and a MiniJet II injection molding system from Thermo Scientific, Haake. The sample size is type IV (70 x 6.5 x 3 mm^3). The LOI value was measured by using an oxygen index module from FIRE according to DIN EN ISO 4589-2 standardized procedure. **Molecular structure determination:** Single-crystal X-ray diffraction data were collected on a STOE IPDS-2T image plate diffractometer equipped with a low-temperature device using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Software for data collection: X-AREA, cell refinement: X-AREA and data reduction: X-RED[34]. Preliminary structure models were derived by direct methods[35] and the structures were refined by full-matrix least-squares calculations based on F^2 for all reflections using SHELXL[36]. Hydrogen atoms were included in the models in calculated positions and were refined as constrained to the bonding atoms. Further details regarding crystallographic results are reported in the Supporting Information. CCDC 1832062-1832064 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data _request/cif. **Quantum chemical calculations:** The geometries of the compounds **1**,

2, and **9** were optimized with the density functional method B3LYP[37] and the basis set 6-31G*[38], using the Gaussian 09[39] package. The calculation of Hessian-matrices verified the presence of local minima on the potential energy surface with zero imaginary frequencies. Thermodynamic values have been calculated for isolated molecules in the gas phase at 298 K and 1 atm.

Synthetic procedures

Synthesis of 2,4,6-tris(phenylthio)-1,3,5-triazine (1). The synthesis of compound **1** has been reported in the literature by ANGAMUTHU et al.[14]. However, we used another method. Thiophenol (0.91 g, 8.3 mmol) was added to a solution of sodium (0.21 g, 9.0 mmol) in 16 mL diethyl ether at r.t. and stirred for 9.5 h under reflux. The resulting suspension was treated with a suspension of cyanuric chloride (0.46 g, 2.5 mmol) in 10 mL diethyl ether and stirred for 6.5 h under reflux. After that, the solvent was removed and the crude product washed with 75 mL water and recrystallized in n-heptane. 0.49 g (η = 49 %) of compound **1** was obtained as a white and odourless powder. Mp: 97-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, ^3J = 8.4, 2H), 7.29 (t, ^3J = 7.4, 1H), 7.19 (t, ^3J = 7.4, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.2, 134.8, 129.3, 128.9, 127.0. Anal. calcd (%) for ($C_{21}H_{15}N_3S_3$): C 62.19, H 3.73, N 10.36, S 23.72, found: C 62.0, H 3.7, N 10.1, S 23.5.

Synthesis of 2,4,6-tris(phenyldithio)-1,3,5-triazine (2). Thiophenol (22.4 g, 203 mmol) was added to a solution of sulfuryl chloride (35.0 g, 259 mmol) in 50 mL dichloromethane at 0 °C and stirred for 2 h. The reaction mixture was then stirred for 1 h at r.t.. The resulting red solution was vacuum distilled (around 24.75 g, 171 mmol phenylsulfenyl chloride) and immediately added dropwise to a suspension of sodium thiocyanurate (12.9 g, 53 mmol) in 100 mL toluene and stirred at r.t.. After 17 h, the suspension was diluted with 100 mL dichloromethane and stirred for 3 h. After that, the resulting suspension was filtrated, the filtrate extracted with water (3 x 100 mL, pH = basic by potassium carbonate), dried over magnesium sulfate and the solvent was evaporated. After solidification, the crude product was washed with diethyl ether and recrystallized from n-heptane. 11.0 g (η = 41 %) of **2** were obtained as a white and odourless powder. Mp: 93-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, ^3J = 7.7, 2H), 7.22-7.11 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.1, 135.3, 131.0, 129.1, 128.6. Anal. calcd (%) for ($C_{21}H_{15}N_3S_6$): C 50.27, H 3.01, N 8.38, S 38.34, found: C 50.6, H 2.7, N 8.6, S 38.3.

Synthesis of 2,4,6-tris(p-tolylthio)-1,3,5-triazine (3). This compound has been reported in the literature by ANGAMUTHU et al.[14] and MOHAMMADPOOR-BALTORK and MIRKHANI et al.[16] with synthesis methods different from our approach. 4-Methylthiophenol (2.70 g, 21.8 mmol) solved in 10 mL diethyl ether was added to a solution of sodium (0.50 g, 21.8 mmol) in 20 mL diethyl ether at r.t.. The suspension was stirred under reflux until all sodium was consumed. The resulting suspension was treated with a suspension of cyanuric chloride (1.16 g, 6.3 mmol) in 10 mL diethyl ether and stirred for 6.5 h under reflux. The suspension was then filtrated and the solvent evaporated from the filtrate. The crude product obtained was resolved in 100 mL dichloromethane, extracted with water (3 x 20 mL), dried over magnesium sulfate, the solvent removed and dried under high vacuum. 2.23 g (η = 79 %) of compound **3** were obtained as a white and odourless powder. Mp: 116-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, ^3J = 8.0, 2H), 6.96 (d, ^3J = 8.0, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 139.2, 134.8, 129.6, 123.7, 21.4. Anal. calcd (%) for ($C_{24}H_{21}N_3S_3$): C 64.39, H 4.73, N 9.39, S 21.49, found: C 64.3, H 4.4, N 9.1, S 21.5.

Synthesis of 2,4,6-tris(p-tolyldithio)-1,3,5-triazine (4). Sulfuryl chloride (5.72 g, 41 mmol) was added to a solution of 4-methylthiophenol (4.0 g, 32 mmol) in 30 mL dichloromethane at 0 °C. The reaction mixture was then stirred for 67 h at r.t.. The resulting red solution was vacuum distilled (around 4.0 g, 25 mmol p-tolylsulfenyl chloride) and immediately added dropwise to a suspension of sodium thiocyanurate (1.84 g, 7.6 mmol) in 50 mL toluene and stirred for 22 h at r.t.. After that, the suspension was extracted with water (3 x 25 mL), dried over magnesium sulfate and the solvent was evaporated. The crude product was finally purified by flash chromatography (cyclohexane with dichloromethane gradient). 1.8 g (η = 44 %) of compound **4** were obtained as a white and odourless powder. Mp: 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, ^3J = 8.0, 2H), 7.05 (d, ^3J = 7.9, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.2, 139.2, 131.9, 131.8, 129.9, 21.2. Anal. calcd (%) for ($C_{24}H_{21}N_3S_6$): C 53.00, H 3.89, N 7.73, S 35.38, found: C 52.8, H 3.6, N 7.6, S 35.0.

Synthesis of 2,4,6-tris(ethylthio)-1,3,5-triazine (5). Ethanethiol (1.35 g, 21.8 mmol) was added to a suspension of sodium (0.50 g, 21.8 mmol) in 20 mL diethyl ether at r.t.. The suspension was stirred under reflux until all sodium was consumed. The resulting suspension was treated with a suspension of cyanuric chloride (1.20 g, 6.5 mmol) in 30 mL diethyl ether and stirred for 20.5 h under reflux. Then the mixture was filtrated and the solvent evaporated from the filtrate. The obtained crude product was dissolved in 100 mL dichloromethane, extracted with water (3 x 20 mL), dried over magnesium sulfate, the solvent removed and dried under high vacuum. 1.17 g (η = 67 %) of compound **5** were obtained as a slightly yellow and odourless liquid, which solidified at 23-25°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (q, ^3J = 7.4, 2H), 1.38 (t, ^3J = 7.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 24.6, 14.3. Anal. calcd (%) for ($C_9H_{15}N_3S_3$): C 41.35, H 5.78, N 16.07, S 36.80, found: C 41.2, H 5.5, N 15.8, S 36.3.

Synthesis of 2,4,6-tris(ethyldithio)-1,3,5-triazine (6). Sulfuryl chloride (4.5 g, 32 mmol) was added to a solution of ethanethiol (2.0 g, 32 mmol) in 24 mL dichloromethane at r.t.. The reaction mixture was then stirred for 19.5 h at r.t.. The solvent was removed by vacuum from the resulting orange solution. The product was immediately added dropwise to a suspension of sodium thiocyanurate (2.3 g, 10 mmol) in 10 mL toluene. After 1.5 h, 30 mL dichloromethane were added and the dispersion was stirred for a further 1.5 h at r.t.. The suspension was then extracted with water (3 x 40 mL), dried over magnesium sulfate and the solvent was evaporated. The crude product was finally purified by flash chromatography (cyclohexane with dichloromethane gradient). 0.95 g (η = 28 %) of compound **6** were obtained as a slightly yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (q, ^3J = 7.4, 2H), 1.29 (t, ^3J = 7.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.3, 32.1, 13.9. Anal. calcd (%) for ($C_9H_{15}N_3S_6$): C 30.23, H 4.23, N 11.75, S 53.80, found: C 29.5, H 4.0, N 11.2, S 53.2.

Synthesis of 2,4,6-tris(tert-butylthio)-1,3,5-triazine (7). 2-Methylpropane-2-thiol (1.96 g, 21.8 mmol) was added to a suspension of sodium (0.50 g, 21.8 mmol) in 10 mL diethyl ether at r.t.. The suspension was stirred under reflux until all sodium was consumed. The resulting mixture was treated with a suspension of cyanuric chloride (1.16 g, 6.3 mmol) in 10 mL diethyl ether and stirred for 6 h under reflux. The suspension was then filtrated and the solvent evaporated from the filtrate. The obtained crude product was dissolved in 100 mL dichloromethane, extracted with water (3 x 20 mL), dried over magnesium sulfate, the solvent removed and dried under high vacuum. 1.4 g (η = 64 %) of compound **7** were obtained as a white and odourless powder. Mp: 147 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 47.7, 29.9. Anal. calcd (%) for ($C_{15}H_{27}N_3S_3$): C 52.13, H 7.87, N 12.16, S 27.84, found: C 52.2, H 7.7, N 12.0, S 27.6.

Synthesis of 2,4,6-tris(tert-butyldithio)-1,3,5-triazine (8). Sulfuryl chloride (2.4 g, 18 mmol) was added to a solution of tert-butylthiol (1.6 g, 18 mmol) in 5 mL dichloromethane at r.t.. The reaction mixture was then stirred for 4.5 h at r.t.. The solvent was removed by vacuum from the resulting orange solution. The product was immediately added dropwise to a suspension of sodium thiocyanurate (1.1 g, 9 mmol) in 19 mL toluene and stirred for 2 h. 50 mL dichloromethane were then added and the dispersion stirred for a further 15.5 h at r.t.. After that, the suspension was extracted with water (3 x 50 mL), dried over magnesium sulfate and the solvent was evaporated. 1.05 g (η = 53 %) of the crude product was obtained as a slightly yellow liquid. Purification by flash chromatography (cyclohexane with dichloromethane gradient) gave a colourless liquid. Impurities were observed by NMR and EA: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6, 49.5, 29.7. Anal. calcd (%) for ($C_{15}H_{27}N_3S_6$): C 40.8, H 6.2, N 9.5, S 43.5, found: C 35.7, H 5.0, N 6.9, S 48.3.

Acknowledgements

U.B. thanks the computing centre of the TU Bergakademie Freiberg for computing time at the High Performance Compute Cluster. C.-C.H. thanks his colleagues from Fraunhofer ICT, Pfinztal Wenka Schweikert, Stefan Müller, Manuela Dörich, Beatrice Tübke, Yvonne Galus, Ilona Schmelcher, Kristin Schäfer, Sonja Lauinger, Matthias Stricker and Carolyn Fisher, and also the group of E. Kroke, TU Bergakademie Freiberg, for the analytical support. Financial support was provided by Fraunhofer ICT and TU Bergakademie Freiberg.

Keywords: s-triazine • heterocycles • sulfur • thermal radical generators • TGA-MS

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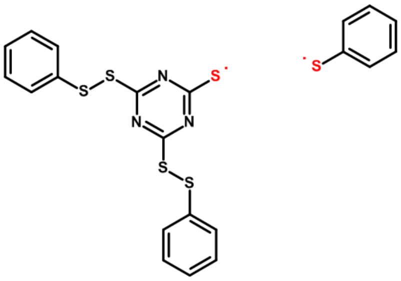
FULL PAPER

Thermal thiyl radical generators: Sulfides and disulfides of s-triazine are synthesised and their thermal degradation is studied. The s-triazine disulfids show significant potential as thermal thiyl radical generators.



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