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Homolytic Dissociation of the Vulcanization Accelerator Tetramethylthiuram Disulfide (TMTD) and Structures and Stabilities of the Related Radicals $Me_2NCS_n^•$ ($n = 1-4$)

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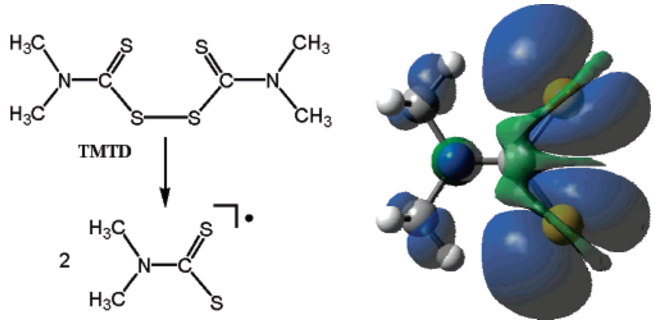
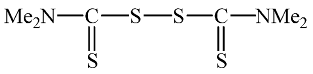
Received June 29, 2006



The homolytic dissociation of the important vulcanization accelerator tetramethylthiuram disulfide (TMTD) has been studied by ab initio calculations according to the G3X(MP2) and G3X(MP2)-RAD theories. Homolytic cleavage of the SS bond requires a low enthalpy of 150.0 kJ mol^{-1}, whereas 268.0 kJ mol^{-1} is needed for the dissociation of one of the C−S single bonds. To cleave one of the SS bonds of the corresponding trisulfide (TMTT) requires 191.1 kJ mol^{-1}. $Me_2NCS_2^•$ is a particularly stable sulfur radical as reflected in the low S−H bond dissociation enthalpy of the corresponding acid $Me_2NC(=S)SH$ (301.7 kJ mol^{-1}). $Me_2NCS_2^•$ ($^2B_2$) is a σ radical characterized by the unpaired spin density shared equally between the two sulfur atoms and by a 4-center (NCS_2) delocalized π system. The ESR g-tensors of the radicals $Me_2NCS_n^•$ ($n = 1-3$) have been calculated. Both TMTD and the mentioned radicals form stable chelate complexes with a Li^+ cation, which here serves as a model for the zinc ions used in accelerated rubber vulcanization. Although the binding energy of the complex $[Li(TMTD)]^+$ is larger than that of the isomeric species $[Li(S_2CNMe_2)_2]^+$ (**12**), the dissociation enthalpy of TMTD as a ligand is smaller (125.5 kJ mol^{-1}) than that of free TMTD. In other words, the homolytic dissociation of the SS bonds of TMTD is facilitated by the presence of Li^+ ions. The sulfurization of TMTD in the presence of Li^+ to give the paramagnetic complex $[Li(S_3CNMe_2)_2]^+$ is strongly exothermic. These results suggest that TMTD reacts with naked zinc ions as well as with the surface atoms of solid zinc oxide particles in an analogous manner producing highly reactive complexes, which probably initiate the crosslinking process during vulcanization reactions of natural or synthetic rubber accelerated by TMTD/ZnO.

Introduction

The global annual production of rubber is approximately 17 million tons. To turn a natural or synthetic polyolefin ("rubber") into a useful elastomer, sulfur vulcanization is usually performed to generate sulfidic and disulfidic cross-links between neighboring macromolecules. Tetramethylthiuram disulfide (TMTD) is one of the most important accelerators for this type of vulcanization:

TMTD:


$$Me_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-NMe_2$$

TMTD is usually applied together with zinc oxide,[1] and the function of the latter in this context has recently been studied

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10.1021/jo061345o CCC: $33.50

extensively.[2] The formation of zinc thiolate complexes has been postulated, which are believed to add more sulfur atoms either from each other by disproportionation or from added elemental sulfur. These polysulfido complexes are assumed to attack the polyolefin of natural or synthetic rubbers, eventually resulting in crosslinking between the polymeric chain molecules.[3]

The thermal behavior of pure TMTD has repeatedly been studied by several groups. Free radicals have been detected by electron spin resonance (ESR) spectroscopy when TMTD was heated to 130−150 °C.[4−6] The intriguing question is which of the covalent bonds of TMTD was broken homolytically. A triplet signal at $g = 2.05$ with a peak separation of ca. 15 G was observed after heating of TMTD followed by cooling to room temperature. This signal was assigned to the thiuram radical $\mathrm{Me_2NCS_2^{\bullet}}$.[4] If TMTD was heated followed by quenching to −56 °C, a singlet was observed at $g = 2.02$ and was assigned to a persulfenyl radical $\mathrm{Me_2NCS_3^{\bullet}}$.[5] In addition, a weak signal at $g = 2.006$ was recorded after heating TMTD for 120 min to 145 °C; this signal was assigned to an unknown carbon radical.[5] However, all of these assignments have so far not been substantiated by any theoretical calculations, and even the structures of the various $\mathrm{Me_2NCS}_n^{\bullet}$ species except for $n = 2$ are unknown. The structure of the radical $\mathrm{Me_2NCS_2^{\bullet}}$ was investigated by “MNDO RHF-CI” calculations reported in 1992. A planar $\mathrm{C_2NCS_2}$ skeleton was predicted with two identical C−S bonds 161 pm in length.[7] By thermolysis of the related tetraisopropyl-thiuramdisulfide, the radical $^{i}\mathrm{Pr_2NCS_2^{\bullet}}$ was generated which was detected by a single line at $g = 2.015$ in the ESR spectrum when the precursor molecule, dissolved in decalin, was heated to temperatures above 45 °C.[8] From the temperature dependence of the ESR signal intensity, the dissociation enthalpy of $(^{i}\mathrm{Pr_2NCS_2})_2$ was calculated as 104 ± 2 kJ mol^{-1}. For the corresponding methyl derivative (TMTD), this entity was roughly estimated (not determined) as 130 kJ mol^{-1}.[8] The radical $^{i}\mathrm{Pr_2NCS_2^{\bullet}}$ was also generated from the corresponding disulfide (dissolved in acetonitrile) by laser flash photolysis, and an absorption band at 580 nm was assigned to it.[7]

Depending on the nature and the concentration of the $\mathrm{Me_2NCS}_n^{\bullet}$ radicals, the vulcanization of rubber accelerated by TMTD may take place by either an anionic or a radical mechanism or by both. Under equilibrium conditions, the concentration of radicals depends on the various dissociation enthalpies of TMTD, which are not known accurately. To address this question, we have calculated the structures of the radicals $\mathrm{Me_2NCS}_n^{\bullet}$ ($n = 1−4$) and studied the various homolytic dissociation reactions of TMTD and of the related trisulfide (tetramethylthiuram trisulfide, TMTT) for the first time by high-level ab initio calculations according to the G3X(MP2) and G3X(MP2)-RAD theories. In addition, the influence of a metal cation on the dissociation was investigated using lithium ions as a probe and as a model ion for the impact of zinc cations during rubber vulcanization accelerated by the TMTD/ZnO system. The zinc ions on the surface of solid ZnO particles have an atomic charge much smaller than +2. Their interaction with TMTD and other substrates can therefore be modeled by a singly charged ion such as Li^{+}.

Computational Methods

The structures and energies of TMTD and its various derivatives were examined using G3X(MP2) theory.[9] This composite method corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy calculations together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2)[10] theory with three important changes: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large basis set for the second-row atoms at the Hartree-Fock level. All three features are particularly important for the proper description of sulfur-containing species. Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real, and transition states, with one imaginary frequency. Selected reactions were also examined by the G3X(MP2)-RAD theory,[11] which was designed to provide a better theoretical treatment for free radicals. RHF was used for closed-shell species, and the UHF formalism was employed for the open-shell systems, except for certain G3X-(MP2)-RAD calculations. For all investigated species, a charge density analysis was performed using the natural bond orbital (NBO)[12] approach based on the B3LYP/6-31G(2df,p) wavefunction. NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[13] Unless otherwise noted, relative energies reported in the text correspond to the G3X(MP2) ΔH°_{298} values. The same holds for the reaction enthalpies and Gibbs energies. All reported structural parameters correspond to the B3LYP/6-31G-(2df,p) level. The electronic transition energies of radical **2** and its isopropyl analogue were calculated using the time-dependent DFT (TD-DFT) method[14] at the B3LYP/6-31G(2df,p) level. The DFT calculations of ESR *g*-tensors based on the gauche-including atomic orbitals (GIAO)[15] approach were carried out using the Amsterdam density functional program package *ADF*.[16] All other calculations were performed using the *GAUSSIAN* 03[17] and *MOLPRO* 2002[18] programs.

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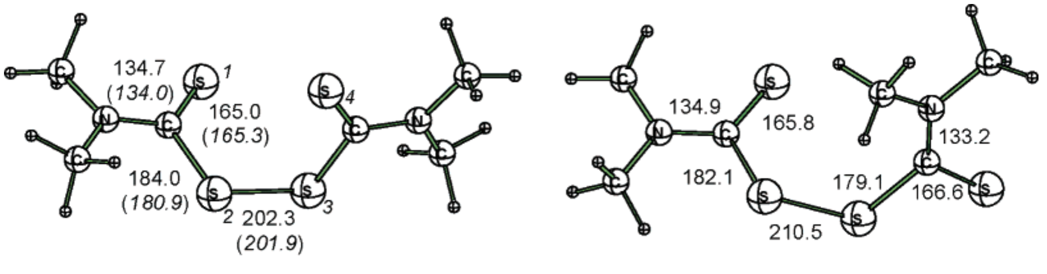
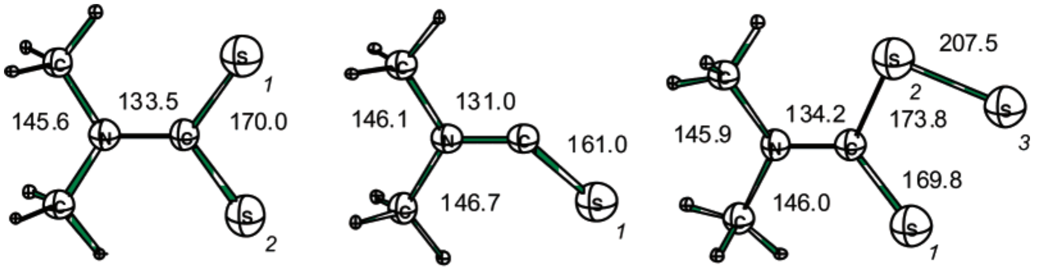


1 (C_2) **1a** (C_1)

FIGURE 1. Optimized geometries [B3LYP/6-31G(2df,p)] of the two conformers of TMTD (bond lengths in picometers). X-ray structural parameters are given in parentheses.



2 (C_{2v}, $^2B_2$) **3** (C_s, $^2A'$) **4** (C_1, ^2A)

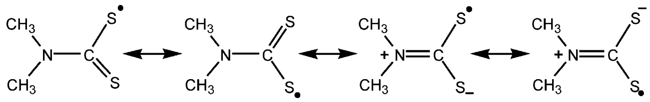
FIGURE 2. Optimized geometries [B3LYP/6-31G(2df,p)] of the radicals $Me_2NCS_n^{\bullet}$ with $n = 1-3$ (bond lengths in picometers). Molecular symmetry and electronic state are given in parentheses.

Results and Discussion

In Figure 1, the calculated structure of the TMTD molecule (**1**) is shown. In addition, the bond lengths determined by X-ray diffraction on single crystals at 138 K are given. Solid TMTD crystallizes as two allotropes: a low-temperature phase of unknown structure below 133 K and a monoclinic high-temperature phase in which the two independent molecules of the asymmetric unit are of C_2 symmetry.[19] The most stable calculated structure is also of C_2 symmetry with bond lengths that agree within 3 pm with the experimental values. However, there exists a rotational isomer of **1** that is less stable by 13.9 kJ mol^{-1} ($\Delta H°_{298}$) (**1a**). The main difference between **1** and **1a** concerns the two torsional angles N−C−S−S, which are −177.3° in **1** compared to 9.5° and 155.0° in **1a**, which is of C_1 symmetry. The torsional angles C−S−S−C are 88.7° in **1** and 78.3° in **1a**. It is worth noting that the CN bonds in **1** and **1a** are relatively short (133.2−134.7 pm) compared to a typical C−N single bond length (146 pm). This indicates the delocalization of the π electrons in the NCS frameworks.

Previous authors have discussed the possibilities that either the S−S bond or one of the C−S single bonds of TMTD breaks on heating, which would give either two $Me_2NCS_2^{\bullet}$ radicals (**2**) or the species $Me_2NCS^{\bullet}$ (**3**) together with $Me_2NCS_3^{\bullet}$ (**4**).[5] The calculated structures of these radicals are shown in Figure 2. It is interesting to note that the structural units C_2NCS_n ($n = 1-3$) of all of these species are either exactly planar (**2**−**4**) or nearly planar (**1**). Expectedly, the most dramatic structural changes on dissociation of TMTD take place at the CS_2 unit and in particular with the bond lengths. Whereas in TMTD there are two regular C═S double bonds (165.0 pm) and two C−S single bonds (184.0 pm), radical **3** has just one very short C═S bond of length 161.0 pm. In addition, the C−N bond length has decreased from 134.7 pm in **1** to 131.0 pm in **3**. Evidently, the π electron system of **3** extends from sulfur to nitrogen. In contrast, radical **2** has two identical C−S bonds (170.0 pm) and a relatively short C−N bond (133.5 pm). Structurally, the persulfenyl radical **4** resembles the parent compound **1**.

As seen in the spin density plots in Figure 3, all three radicals correspond to a σ type of radical. For radical **2** ($^2B_2$ ground state), the unpaired spin density is located almost exclusively in the two sulfur atoms. Essentially, the SOMO is a linear combination of the two sulfur lone pair orbitals. The resonance hybrid of **2** clearly indicates the delocalization of the π orbitals over the 4-center NCS_2 framework as well as the delocalization of the spin density:



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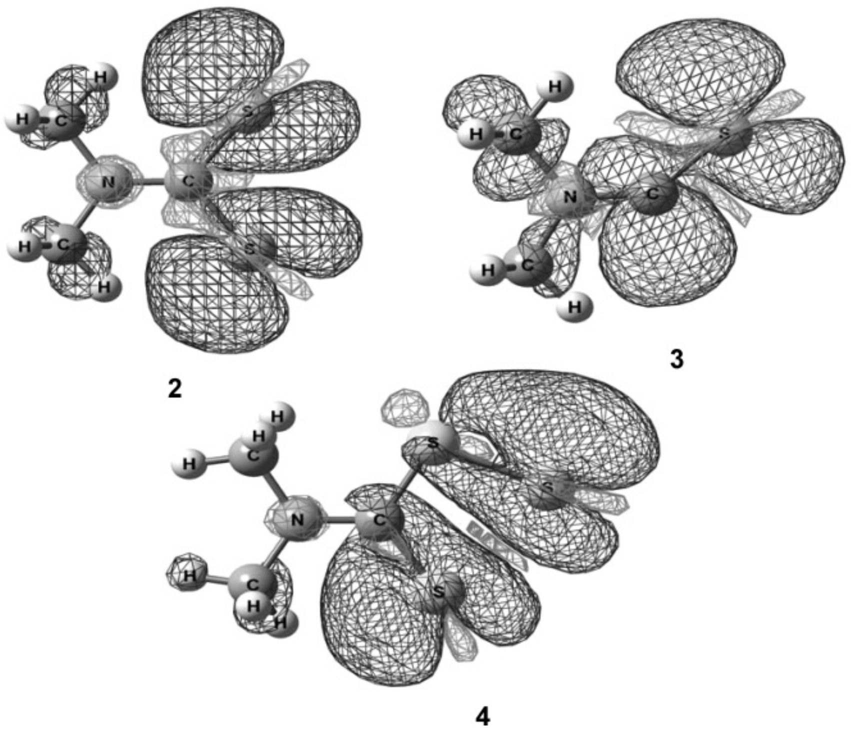

FIGURE 3. Spin density plots [UB3LYP/6-31G(2df,p)] of the $Me_2NCS_n^{\bullet}$ radicals **2**−**4** ($n = 1{-}3$).

Species **2** has a large dipole moment of 4.92 D as expected from the contributing dipolar resonance forms. For comparison, the parent radical $HCS_2^{\bullet}$ has a smaller dipole moment of 1.49 D at the same level of theory. Note that the π-type radical ($^2A_2$) corresponds to an excited state with a relative enthalpy of 71.3 kJ mol^{-1}. The stability of this radical is readily reflected in the S−H bond dissociation enthalpy of the corresponding acid $Me_2NC({=}S)SH$. The calculated value of 301.7 kJ mol^{-1} is the lowest among various known sulfur-containing compounds as the following examples demonstrate: 381.6 (H_2S), 365.7 (CH_3SH), 349.4 (C_6H_5SH), 330.5 (HOSH), and 318.0 (HSSH) kJ mol^{-1}.[20] The stabilizing effect of the dimethylamino group in radical **2** can be estimated by the following isodesmic reaction:

$$Me_3N + HCS_2^{\bullet} \rightarrow Me_2NCS_2^{\bullet} + CH_4 \qquad \Delta H^{\circ}_{298} = -159.0\ \text{kJ mol}^{-1} \quad (1)$$

This computed radical stabilization energy is substantially larger than those calculated for carbon radicals ($XCH_2^{\bullet}$).[21] As in the case of **2**, the spin density of radical **4** resides mainly in the two terminal sulfur atoms. On the other hand, the unpaired electron spin in **3** is located in both the carbon and sulfur atoms (Figure 3).

The ESR *g*-tensors of radicals **2**−**4** were investigated by the DFT-GIAO method at the BLYP/TZ2P level. The calculated isotropic *g*-values are 2.017, 2.001, and 2.017 for $Me_2NCS_2^{\bullet}$, $Me_2NCS^{\bullet}$, and $Me_2NCS_3^{\bullet}$, respectively. Both radicals **2** and **4** are predicted to have similar *g*-tensor values. However, based on the molecular symmetry and the fact that the spin density is equally shared between the two sulfur atoms, we can safely assign the observed triplet signal[4] to $Me_2NCS_2^{\bullet}$ (**2**). On the other hand, the calculated *g*-tensor of **3** appears to match well with the ESR signal previously assigned to an "unknown carbon radical"[5] (see Introduction). We have computed also the *g*-tensor of radical $^{i}Pr_2NCS_2^{\bullet}$, which has a definitive ESR spectrum.[8] In this case, the calculated value of $g = 2.015$ is in perfect agreement with the observed value ($g = 2.015$). The magnitude of the computed *g*-value is very close to that calculated for the methyl analogue **2** ($g = 2.017$). This is not unexpected as both radicals have similar electronic structures. It thus appears that the experimental *g*-value of $Me_2NCS_2^{\bullet}$ (2.02) is somewhat high and may require re-examination.

The homolytic dissociation energies of the S−S bond and of one of the C−S single bonds of **1** differ considerably, and the former process is clearly favored:

$$(Me_2NCS_2)_2\ (\mathbf{1}) \rightarrow 2Me_2NCS_2^{\bullet}\ (\mathbf{2}) \qquad (2)$$

$$\Delta H^{\circ}_{298} = 155.1\ \text{kJ mol}^{-1} \qquad \Delta G^{\circ}_{298} = 100.3\ \text{kJ mol}^{-1}$$

$$(Me_2NCS_2)_2\ (\mathbf{1}) \rightarrow Me_2NCS^{\bullet}\ (\mathbf{3}) + Me_2NCS_3^{\bullet}\ (\mathbf{4}) \qquad (3)$$

$$\Delta H^{\circ}_{298} = 266.4\ \text{kJ mol}^{-1} \qquad \Delta G^{\circ}_{298} = 206.3\ \text{kJ mol}^{-1}$$

The low S−S bond dissociation enthalpy is attributed to the remarkable stability of the $Me_2NCS_2^{\bullet}$ radical. To provide more definitive estimates of the various bond dissociation enthalpies of **1**, the structures and energies of species **1**−**5** were also examined by the G3X(MP2)-RAD method, which yields more reliable predictions of thermochemical data of free radicals.[22] As can be seen from the data in Table 1, the computed

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TABLE 1. Calculated Reaction Enthalpies (ΔH_{298}, kJ mol^{-1}) Using the G3X(MP2) and G3X(MP2)-RAD Methods

reaction in equation	G3X(MP2)	G3X(MP2)-RAD
2	155.1	150.0
3	266.4	268.0
4	111.3	117.8
6	267.0	265.2
7	111.9	115.3

dissociation enthalpies obtained by both methods agree within 5 kJ mol^{-1}. This result is perhaps not surprising as all radicals **2**−**4** do not have a significant spin contamination in their UHF-based wavefunctions ($\langle S^2 \rangle = 0.77$ in all cases). Hence, our best theoretical estimate of the lowest dissociation enthalpy of TMTD is 150.0 kJ mol^{-1}, in perfect agreement with the value of 151 kJ mol^{-1} reported by Blokh[23] who investigated the isotopic exchange between TMTD and S_8 using radioactive ^{35}S. In this context, it is interesting to note that TMTD triggers radical polymerization reactions of styrene and of methyl 2-methylacrylate already at 70 °C.[24]

The calculated dissociation enthalpies of **1** are in agreement with literature data on the homolytic dissociation of similar compounds.[25] We have also investigated the homolytic dissociation of related tetra-isopropylthiuram disulfide at the B3LYP/6-31G(d) level. The calculated bond dissociation enthalpy to form two $^i\mathrm{Pr_2NCS_2}^\bullet$ radicals is 40 kJ mol^{-1} smaller than the corresponding value of TMTD. On the basis of this difference and the G3X(MP2)-RAD value of TMTD, we estimate the dissociation enthalpy of $(^i\mathrm{Pr_2NCS_2})_2$ to be 110 kJ mol^{-1}, in excellent accord with the experimental value of 104 ± 2 kJ mol^{-1}. This lends further support to the assignment of the ESR spectrum of a sulfur radical with $g = 2.015$[8] to the thiuram radical $^i\mathrm{Pr_2NCS_2}^\bullet$. The lower S−S bond dissociation enthalpy suggests that $^i\mathrm{Pr_2NCS_2}^\bullet$ is significantly more stable than the methyl analogue **2**. We have also examined the electronic spectrum of $^i\mathrm{Pr_2NCS_2}^\bullet$. A strong absorption at 545 nm is calculated, in good accord with the experimental value of 580 nm.[7] A similar excitation energy of 550 nm is predicted for radical **2**.

From the above data, it follows that the disproportionation or "self-sulfuration" of radical **2** is thermodynamically unfavorable:

$$2\mathrm{Me_2NCS_2}^\bullet\ (\mathbf{2}) \rightarrow \mathrm{Me_2NCS}^\bullet\ (\mathbf{3}) + \mathrm{Me_2NCS_3}^\bullet\ (\mathbf{4}) \qquad (4)$$

$$\Delta H^\circ_{298} = 111.3\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = 120.5\ \mathrm{kJ\ mol^{-1}}$$

The dissociation of one of the C−N bonds of **1** with formation of another radical (**6**) has also been discussed in the literature:

$$(\mathrm{Me_2NCS_2})_2\ (\mathbf{1}) \rightarrow \mathrm{Me_2N}^\bullet\ (\mathbf{5}) + \mathrm{Me_2NC_2S_4}^\bullet\ (\mathbf{6}) \qquad (5)$$

However, radical **6** is not a stable equilibrium structure. Upon geometry optimization, it spontaneously dissociates into CS_2 and $\mathrm{Me_2NCS_2}^\bullet$. The overall reaction is therefore as follows and no carbon radical is formed:

$$(\mathrm{Me_2NCS_2})_2\ (\mathbf{1}) \rightarrow \mathrm{Me_2N}^\bullet\ (\mathbf{5}) + \mathrm{CS_2} + \mathrm{Me_2NCS_2}^\bullet\ (\mathbf{2}) \qquad (6)$$

$$\Delta H^\circ_{298} = 267.0\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = 173.4\ \mathrm{kJ\ mol^{-1}}$$

On the basis of our calculated energies, the reported formation of a carbon radical by thermal dissociation of TMTD at 145 °C is unlikely.

The homolytic dissociation of radical **2** is less endothermic than the homolysis of the SS bond of TMTD:

$$\mathrm{Me_2NCS_2}^\bullet\ (\mathbf{2}) \rightarrow \mathrm{Me_2N}^\bullet\ (\mathbf{5}) + \mathrm{CS_2} \qquad (7)$$

$$\Delta H^\circ_{298} = 111.9\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = 73.2\ \mathrm{kJ\ mol^{-1}}$$

Therefore, at temperatures high enough to initiate the reaction in eq 2, the latter reaction will also take place. However, since the concentration of radical **2** will always be very small, the concentration of $\mathrm{Me_2N}^\bullet$ will be even smaller unless the CS_2 is allowed to escape, in which case $\mathrm{Me_2N}^\bullet$ is continuously produced.

The thermal decomposition of **1** has been reported to yield eventually CS_2, tetramethylthiurea (TMTU), and elemental sulfur.[5] This reaction is predicted to be slightly endothermic but exergonic if all species are gaseous:

$$(\mathrm{Me_2NCS_2})_2\ (\mathbf{1}) \rightarrow \mathrm{CS_2} + (\mathrm{Me_2N})_2\mathrm{CS} + {}^1/_8\mathrm{S_8} \qquad (8)$$

$$\Delta H^\circ_{298} = 2.7\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = -35.2\ \mathrm{kJ\ mol^{-1}}$$

However, other studies did not demonstrate TMTU as a product of the thermal TMTD decomposition, but instead the formation of tetramethylthiuram monosulfide $(\mathrm{Me_2NCS})_2\mathrm{S}$ (TMTM) was observed.[26] The radicals $\mathrm{Me_2N}^\bullet$, **2**, and **4** as well as tetramethylthiuram polysulfides are believed to be intermediates in these reactions. In this context we have calculated the hitherto unknown structure of $\mathrm{Me_2NCS_4}^\bullet$ to find out whether it is a cyclic or a chain-like species. The results are shown in Figure 4. Three isomers were obtained (**7**, **7a**, and **7b**). The two conformers **7** and **7a** differ mainly by their torsional angles. The global minimum structure **7** has all non-hydrogen atoms practically in one plane. Dipole moment and NBO atomic charges are given in Table 2. The relative enthalpy of **7a** is 11.3 kJ mol^{-1}. In this conformer, the sulfur atoms S3 and S4 are out of the plane defined by the NCS_2 group (torsion angles: N−C−S−S −32.3°, S−C−S−S 149.9°, C−S−S−S −59.1°). The third isomer (**7b**) was obtained when we tried to construct a cyclic structure with a five-membered CS_4 heterocycle. This species with a relative enthalpy of 62.6 kJ mol^{-1} is of C_2 symmetry with one rather long SS bond of 270.0 pm connecting the two disulfide groups. Therefore, radical **7b** may be denoted as $\mathrm{Me_2NC(S_2)_2}^\bullet$. The spin density plots of the three isomers are shown in Figure 5. Essentially, **7** and **7a** are π radicals with unpaired spin densities located in the terminal SS moiety. On the other hand, **7b** is better described as a σ radical. The predicted isotropic g-tensor values of **7**, **7a**, and **7b** are 2.024, 2.029, and 2.011, respectively. These ESR g-values may be used to differentiate these species from the related radicals **2**−**4**.

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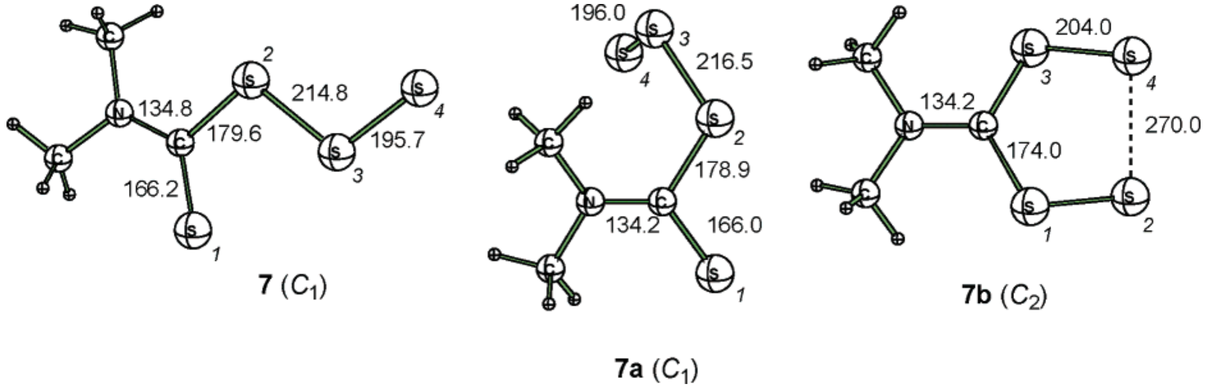

FIGURE 4. Optimized geometries [B3LYP/6-31G(2df,p)] of the isomeric $Me_2NCS_4^{\bullet}$ radicals **7**, **7a**, and **7b** (bond lengths in picometers) and numbering of sulfur atoms.

TABLE 2. Atomic Charges (NBO) of the Donor Atoms and Dipole Moments μ (in Debye) of Species 1−4, 7, 7a, and 7b[a]

species	N	S1	S2	S3	S4	μ
TMTD (**1**)	−0.44	−0.12	+0.17	+0.17	−0.12	0.95
$Me_2NCS^{\bullet}$ (**3**)	−0.45	−0.02				4.44
$Me_2NCS_2^{\bullet}$(**2**)	−0.42	−0.04	−0.04			4.92
$Me_2NCS_3^{\bullet}$(**4**)	−0.43	+0.06	+0.24	−0.21		6.03
$Me_2NCS_4^{\bullet}$ (**7**)	−0.43	−0.12	+0.15	+0.20	−0.16	5.28
$Me_2NCS_4^{\bullet}$ (**7a**)	−0.43	+0.06	+0.16	+0.09	−0.13	4.51
$Me_2NC(S_2)_2^{\bullet}$ (**7b**)	−0.41	+0.26	−0.23	+0.26	−0.23	7.73

[a] B3LYP/6-31G(2df,p) level. [b] For atom labeling, see Figures 1, 2, and 4.

The formation of **4** and **7** by sulfuration of **2** with elemental sulfur is slightly endothermic and endergonic, and the corresponding equilibria are on the left side at moderate temperatures:

$$Me_2NCS_2^{\bullet}\ (\mathbf{2}) + {}^1/_8S_8 \rightarrow Me_2NCS_3^{\bullet}\ (\mathbf{4}) \tag{9}$$

$$\Delta H^{\circ}_{298} = 41.6\ \text{kJ mol}^{-1} \quad \Delta G^{\circ}_{298} = 40.1\ \text{kJ mol}^{-1}$$

$$Me_2NCS_2^{\bullet}\ (\mathbf{2}) + {}^1/_4S_8 \rightarrow Me_2NCS_4^{\bullet}\ (\mathbf{7}) \tag{10}$$

$$\Delta H^{\circ}_{298} = 9.3\ \text{kJ mol}^{-1} \quad \Delta G^{\circ}_{298} = 16.8\ \text{kJ mol}^{-1}$$

By recombination reactions between radicals **2**, **4**, and **7**, various tetramethylthiuram polysulfides (TMTP) can be formed. Thus, one possible reaction sequence for the formation of TMTP on heating of TMTD is **1** → **2** → **4** → **7** → TMTP. However, the disproportionation of the disulfide TMTD into the monosulfide (TMTM) and the trisulfide (TMTT) has also been discussed in the literature:[27]

$$2R_2S_2\ (\text{TMTD}) \rightarrow R_2S\ (\text{TMTM}) + R_2S_3\ (\text{TMTT});\ R = Me_2NC({=}S) \tag{11}$$

$$\Delta H^{\circ}_{298} = 6.5\ \text{kJ mol}^{-1} \quad \Delta G^{\circ}_{298} = 9.5\ \text{kJ mol}^{-1}$$

$$\text{TMTD}\ (\mathbf{1}) + Me_2NCS_2^{\bullet}\ (\mathbf{2}) \rightarrow \text{TMTM} + Me_2NCS_3^{\bullet}\ (\mathbf{4}) \tag{12}$$

$$\Delta H^{\circ}_{298} = 47.3\ \text{kJ mol}^{-1} \quad \Delta G^{\circ}_{298} = 45.1\ \text{kJ mol}^{-1}$$

The trisulfide molecule TMTT is of C_2 symmetry with normal geometrical parameters ($d_{SS} = 205.3$ pm, $\tau_{CSSS} = 85.4°$). The substituents $Me_2NC({=}S)$ are *trans* to each other. It is not known whether the reaction in eq 11 proceeds via the intermediate formation of radicals, e.g., as in eqs 2, 12, and 13:

$$Me_2NCS_2^{\bullet}\ (\mathbf{2}) + Me_2NCS_3^{\bullet}\ (\mathbf{4}) \rightarrow \text{TMTT} \tag{13}$$

$$\Delta H^{\circ}_{298} = -195.9\ \text{kJ mol}^{-1} \quad \Delta G^{\circ}_{298} = -135.9\ \text{kJ mol}^{-1}$$

It is remarkable that the S−S bond dissociation enthalpy of TMTT (195.9 kJ mol^{-1}) is *larger* than that of TMTD (150.0 kJ mol^{-1}), whereas normally disulfide bonds are thermally more stable than the tri- and tetrasulfide chains of organic polysulfides.[25,28]

Impact of Metal Cations on the Dissociation of TMTD and TMTT. The various radicals as well as TMTD itself contain several donor atoms with lone electron pairs, and these are expected to interact with the positively charged metal atoms of zinc oxide or zinc complexes added to a rubber vulcanization mixture as essential ingredients ("activators"). The NBO atomic charges of **1**−**4** (Table 2) together with the well-known polarizability values indicate that the terminal sulfur atoms are likely to be the preferred sites for any cation coordination, while the planar coordinated nitrogen atoms are of lower Lewis basicity despite their higher negative charge. In fact, for initial structures with a Li^+ ion directly linked to the nitrogen atoms of radicals **2** and **4**, the Li^+ ion moved to the sulfur atoms on geometry optimization. This finding is in line with the structures of several metal complexes containing TMTD as a bidentate chelate ligand linked to a metal atom by the thione sulfur atoms,[29] e.g., in $[ZnI_2(TMTD)]$[30] and $[HgI_2(TMTD)]$.[31] On the other hand, certain organometallic complexes react with TMTD or the corresponding ethyl derivative at 20 °C with cleavage of the S−S bond and oxidative addition of the thiocarbamato units to the metal atoms. This holds true for $[MeAuPPh_3]$ yielding $[MeAu(S_2CNMe_2)_2]$[32] and for $[\{CpCr(CO)_3\}_2]$ yielding $[CpCr(CO)_2(S_2CNEt_2)]$.[33]

To study the influence of a metal cation on the SS bond dissociation energy of TMTD, we have used the smaller lithium

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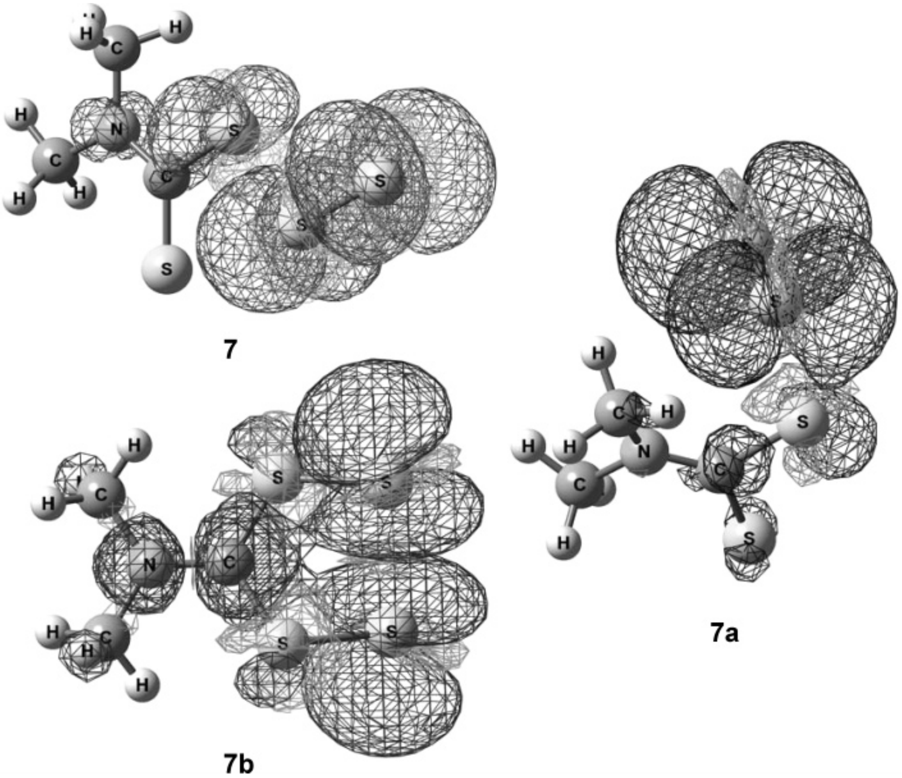

FIGURE 5. Spin density plots [UB3LYP/6-31G(2df,p)] of the isomeric $Me_2NCS_4^{\bullet}$ radicals **7**−**7b**.

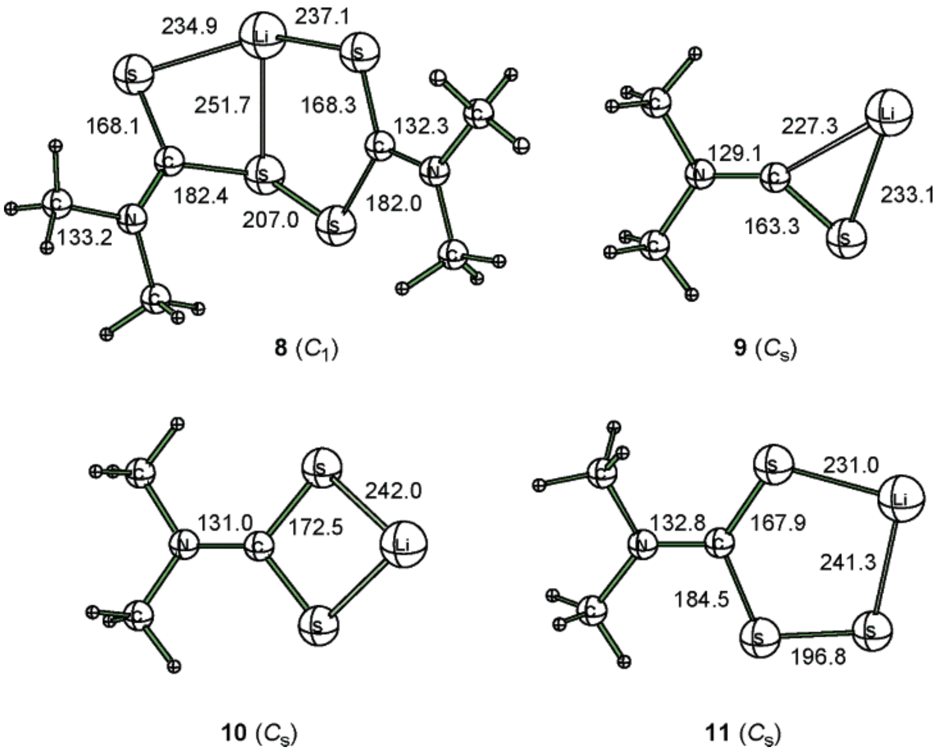

FIGURE 6. Optimized geometries [B3LYP/6-31G(2df,p)] of the cationic lithium complexes [Li(TMTD)]$^+$ (**8**), [Li(SCNMe$_2$)]$^{\bullet+}$ (**9**), [Li(S$_2$CNMe$_2$)]$^{\bullet+}$ (**10**), and [Li(S$_3$CNMe$_2$)]$^{\bullet+}$ (**11**) (bond lengths in picometers).

cation as a probe to save computational time and to allow for a high level of theory for theoretical investigation. All species **1**−**4** form stable chelate complexes with a Li$^+$ ion, which becomes two- or three-coordinated. The optimized structures of these lithium complexes are shown in Figure 6.

The structure of [Li(TMTD)]$^+$ (**8**) is of C_1 symmetry and

TABLE 3. Binding Energies[a] ($kJ\ mol^{-1}$) and Dipole Moments μ[b] (Debye) of the Lithium Complexes 8−12, 14, and 15

complex	$\Delta H°_{298}$	$\Delta G°_{298}$	μ
$[Li(TMTD)]^{+\bullet}$ (**8**)	−284.6	−243.6	3.01
$[Li(SCNMe_2)^{+\bullet}$ (**9**)	−166.1	−137.2	6.16
$[Li(S_2CNMe_2)]^{+\bullet}$ (**10**)	−182.2	−150.1	4.69
$[Li(S_3CNMe_2)]^{+\bullet}$ (**11**)	−253.6	−203.9	2.46
$[Li(S_2CNMe_2)_2]^{+\bullet}$ (**12**)	−314.3	−235.2	4.74
$[Li(TMTT)]^{+}$ (**14**)	−291.5	−254.9	3.17
$[Li(S_3CNMe_2)_2]^{+\bullet}$ (**15**)	−409.2	−326.0	1.42

[a] G3X(MP2) values. [b] B3LYP/6-3G(2df,p) level.

characterized by a seven-membered ring since the metal ion forms a bridge between the two thione sulfur atoms of **1**. The Li−S bond lengths of 234.9 and 237.1 pm are in line with the data of other lithiated sulfur-rich compounds.[34] However, there is an additional Li···S contact of 251.7 pm to one of the disulfide sulfur atoms, and the metal atom may be considered as three-coordinated. The structural parameters of the TMTD ligand changed only slightly from those of the free molecule except for the two torsion angles S−S−C═S (134.3°) and S−S−C−N (−50.5°) on the left side of the molecule **8** in Figure 6. A structure of C_2 symmetry with two-coordinated Li^+ is also a minimum on the potential energy hypersurface of $[Li(TMTD)]^+$, but this isomer (**8a**) is by 10.7 $kJ\ mol^{-1}$ less stable than **8**.

The small $Me_2NCS^\bullet$ radical coordinates to a lithium cation both via the sulfur and the carbon atom resulting in a three-membered ring. All non-hydrogen atoms of $[Li(SCNMe_2)]^+$ (**9**) are coplanar, and the molecular symmetry is C_s (Figure 6). The shortest S···H contact is 284.0 pm. The structure of $[Li(S_2CNMe_2)]^{\bullet+}$ (**10**) is also of C_s symmetry and characterized by a nonplanar four-membered CS_2Li heterocycle. The metal ion is not in the plane of the C_2NCS_2 skeleton; the mirror plane is bisecting the angles C_2N and CS_2. This structure is obviously a compromise between the ion-dipole attraction, which would be maximum if Li^+ were in the C_2NCS_2 plane and located on the dipole vector that is identical to the direction of the N−C(sp^2) bond, and a covalent bond between Li^+ and the sulfur 3*p* lone pairs, which are perpendicular to the C_2NCS_2 plane and which are part of the four-center π electron system of the radical. The torsion angles S−C−S−Li are ± 37.9°. The sulfur-rich radical cation $[Li(S_3CNMe_2)]^{\bullet+}$ (**11**) is also of C_s symmetry with all non-hydrogen atoms in one plane. Both the C═S and S−S bonds contract on Li^+ coordination while the C−S bond considerably expands (by 10.7 pm). Interestingly, the C−N bonds of **1**−**4** become shorter upon complexation with Li^+ (Figures 1, 2, and 6). In general, the geometrical features of the $S\cdots Li^+$ coordination in **8**−**11** are similar to those calculated for the lithium complexes of sulfur clusters.[34]

The binding energies of the four complexes **8**−**11**, i.e. the energy differences between a lithium cation and the free ligand on one side and the complex on the other side, are listed in Table 3. These data demonstrate that the binding energies of the two-coordinated species $[Li(S_nCNMe_2)]^{\bullet+}$ are smaller than that of $[Li(TMTD)]^+$, but these energies increase with the sulfur content of the ligand and reach a maximum for $n = 3$. In the latter case, the radical cation complex contains a five-membered metallacycle. As a consequence of the increase in binding energy with the sulfur content, the sulfurization of **10** by elemental sulfur to produce the trithiolane derivative **11** is exothermic and exergonic:

$$[Li(S_2CNMe_2)]^{\bullet+}\ (\mathbf{10}) + {}^1/{}_8S_8 \rightarrow [Li(S_3CNMe_2)]^{\bullet+}\ (\mathbf{11}) \quad (14)$$

$$\Delta H°_{298} = -19.9\ kJ\ mol^{-1} \quad \Delta G°_{298} = -13.7\ kJ\ mol^{-1}$$

This finding is important since only the polysulfidic complexes are assumed to abstract allylic hydrogen atoms from rubber molecules with the formation of H_2S. Evidently, the polysulfido complexes are formed spontaneously if elemental sulfur is added, in contrast to the *endothermic* sulfuration reactions of the free radical **2**; see eq 9. Using the more reactive (metastable) polymeric sulfur “Crystex”,[35] the equilibrium of the reaction in eq 14 will be even more on the right side.

Because of the high stability of the complex $[Li(TMTD)]^+$, the homolytic dissociation energies of the TMTD ligand with formation of one free radical and one ligand stabilized radical are drastically different from those of free TMTD (**1**):

$$[Li(TMTD)]^+\ (\mathbf{8}) \rightarrow [Li(S_2CNMe_2)]^{\bullet+}\ (\mathbf{10}) + Me_2NCS_2^{\bullet}\ (\mathbf{2}) \quad (15)$$

$$\Delta H°_{298} = 257.6\ kJ\ mol^{-1} \quad \Delta G°_{298} = 193.7\ kJ\ mol^{-1}$$

$$[Li(TMTD)]^+\ (\mathbf{8}) \rightarrow [Li(S_3CNMe_2)]^{\bullet+}\ (\mathbf{11}) + Me_2NCS^{\bullet}\ (\mathbf{3}) \quad (16)$$

$$\Delta H°_{298} = 307.4\ kJ\ mol^{-1} \quad \Delta G°_{298} = 245.9\ kJ\ mol^{-1}$$

$$[Li(TMTD)]^+\ (\mathbf{8}) \rightarrow [Li(SCNMe_2)]^{\bullet+}\ (\mathbf{9}) + Me_2NCS_3^{\bullet}\ (\mathbf{4}) \quad (17)$$

$$\Delta H°_{298} = 384.9\ kJ\ mol^{-1} \quad \Delta G°_{298} = 312.7\ kJ\ mol^{-1}$$

However, a more likely thermal reaction of **8** is the isomerization to the bis-chelate complex **12** with a four-coordinated lithium atom and the TMTD ligand dissociated into two equal fragments:

$$[Li(TMTD)]^+\ (\mathbf{8}) \rightarrow [Li(S_2CNMe_2)_2]^+\ (\mathbf{12}) \quad (18)$$

$$\Delta H°_{298} = 125.5\ kJ\ mol^{-1} \quad \Delta G°_{298} = 108.6\ kJ\ mol^{-1}$$

The complex $[Li(S_2CNMe_2)_2]^+$ can exist as a triplet (**12**) or as a singlet state (**12a**). At the G3X(MP2) level, **12a** is 14.0 $kJ\ mol^{-1}$ less stable than the triplet ground state. Consequently, the enthalpy data in eq 18 apply to the triplet species **12**. The geometry of **12** is shown in Figure 7. Interestingly, the Li and the four S atoms are coplanar in **12**. The fact that the dissociation of the TMTD ligand in **8** to give the dissociated ligands present in **12** requires only 125.5 $kJ\ mol^{-1}$, compared to 155.1 $kJ\ mol^{-1}$ for the dissociation of the free ligand at the G3X(MP2) level, shows that the lithium cation facilitates the dissociation of TMTD at the sulfur−sulfur bond.

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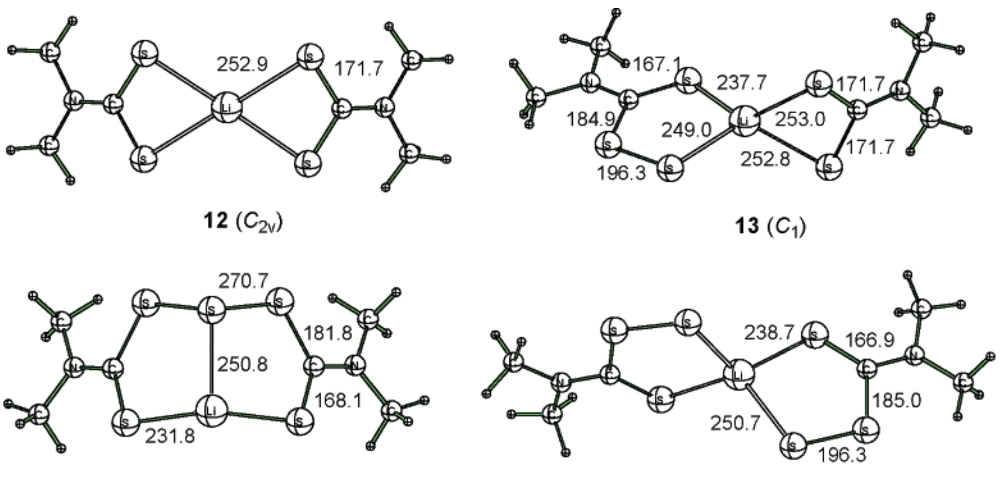

12 (C_{2v})

13 (C_1)

14 (C_s)

15 (C_2)

FIGURE 7. Optimized geometries [B3LYP/6-31G(2df,p)] of the triplet lithium complexes $[Li(S_2CNMe_2)_2]^+$ (**12**), $[Li(S_2CNMe_2)(S_3CNMe_2)]^+$ (**13**), and $[Li(S_3CNMe_2)_2]^+$ (**15**) as well as of the singlet species $[Li(TMTT)]^+$ (**14**) (bond lengths in picometers).

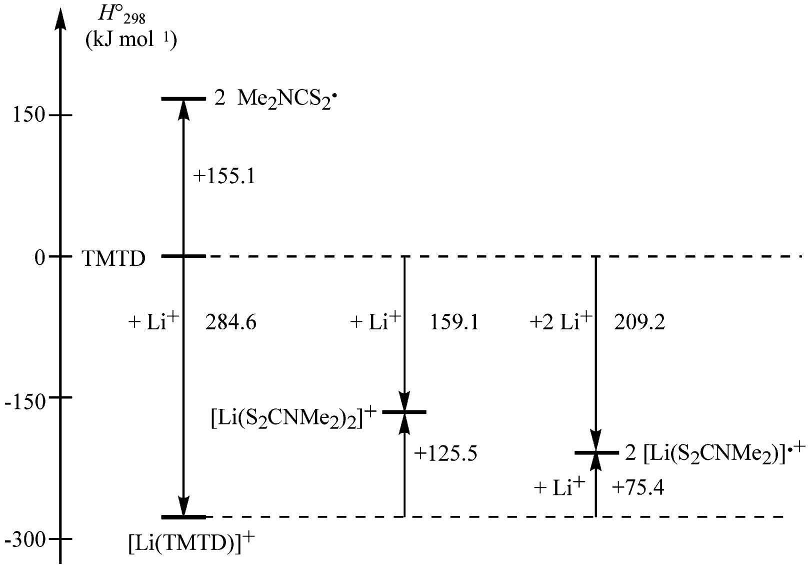

FIGURE 8. Energy level diagram for the homolytic dissociation and complex formation reactions of TMTD with and without Li^+ cations, based on G3X(MP2) computed reaction enthalpies.

If additional lithium cations are available, complex **8** may be cleaved into two identical complexes **10**:

$$[Li(TMTD)]^+ \ (\mathbf{8}) + Li^+ \rightarrow 2\ [Li(S_2CNMe_2)]^{\bullet +} \ (\mathbf{10}) \qquad (19)$$

$$\Delta H°_{298} = 75.4 \text{ kJ mol}^{-1} \qquad \Delta G°_{298} = 43.6 \text{ kJ mol}^{-1}$$

Thus, the overall reaction of TMTD with an excess of Li^+ is strongly exothermic:

$$\text{TMTD } (\mathbf{1}) + 2Li^+ \rightarrow 2[Li(S_2CNMe_2)]^{\bullet +} \ (\mathbf{10}) \qquad (20)$$

$$\Delta H°_{298} = -209.2 \text{ kJ mol}^{-1} \qquad \Delta G°_{298} = -200.0 \text{ kJ mol}^{-1}$$

In Figure 8, the various dissociation reactions of TMTD are shown schematically.

The reaction of **12** with S_8 to the mixed ligand complex $[Li(S_2CNMe_2)(S_3CNMe_2)]^+$ (**13**) in its triplet state is slightly endothermic:

$$[Li(S_2CNMe_2)_2]^+ \ (\mathbf{12}) + {}^1/_8S_8 \rightarrow [Li(S_2CNMe_2)(S_3CNMe_2)]^+ \ (\mathbf{13}) \qquad (21)$$

$$\Delta H°_{298} = 1.5 \text{ kJ mol}^{-1} \qquad \Delta G°_{298} = 5.2 \text{ kJ mol}^{-1}$$

Attempts to optimize the structure of $[Li(S_2CNMe_2)(S_3CNMe_2)]^+$ as a singlet resulted in the novel species $[Li(TMTT)]^+$ (**14**) in which the trisulfide ligand TMTT forms three Li−S bonds to the metal cation (Figure 7). This complex is by 133.1 kJ mol^{-1} more stable than the triplet isomer **13**:

$$\text{TMTT} + Li^+ \rightarrow [Li(TMTT)]^+ \ (\mathbf{14}) \qquad (22)$$

$$\Delta H°_{298} = -291.5 \text{ kJ mol}^{-1} \qquad \Delta G°_{298} = -254.9 \text{ kJ mol}^{-1}$$

As a consequence of the high stability of **14**, the following sulfurization reaction with spin-crossover is exothermic:

$$[\mathrm{Li(S_2CNMe_2)_2}]^+\ (\mathbf{12}) + {}^1/_8\ \mathrm{S_8} \rightarrow [\mathrm{Li(TMTT)}]^+\ (\mathbf{14}) \qquad (23)$$

$$\Delta H^\circ_{298} = -131.6\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = -115.4\ \mathrm{kJ\ mol^{-1}}$$

The geometries of **13** and **14** are shown in Figure 7. These structures are similar to those of the related complexes **10** and **11** depicted in Figure 6. Complex **14** is of C_s symmetry.

Dissociation of the trisulfide TMTT in the presence of 2 equiv of Li^+ is also an exothermic process:

$$\mathrm{TMTT} + 2\mathrm{Li}^+ \rightarrow [\mathrm{Li(S_2CNMe_2)}]^{\bullet +}\ (\mathbf{10}) + [\mathrm{Li(S_3CNMe_2)}]^{\bullet +}\ (\mathbf{11}) \qquad (24)$$

$$\Delta H^\circ_{298} = -229.9\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = -218.2\ \mathrm{kJ\ mol^{-1}}$$

The formation of the paramagnetic lithium complex $[\mathrm{Li(S_3CNMe_2)_2}]^+$ (**15)**, as shown in eq 25, is a thermodynamically favorable process. Interestingly, the Li^+ ions of **13** and **15** are coordinated to four sulfur atoms in a tetrahedral manner (Figure 7).

$$\mathrm{TMTD}\ (\mathbf{1}) + \mathrm{Li}^+ + {}^1/_4\mathrm{S_8} \rightarrow [\mathrm{Li(S_3CNMe_2)_2}]^+\ (\mathbf{15}) \qquad (25)$$

$$\Delta H^\circ_{298} = -187.1\ \mathrm{kJ\ mol^{-1}} \qquad \Delta G^\circ_{298} = -158.5\ \mathrm{kJ\ mol^{-1}}$$

In other words, in the presence of free metal cations and elemental sulfur, TMTD and the corresponding polysulfides TMTP are predicted to spontaneously dissociate with the formation of chelate complexes provided the activation energy is available. This activation energy is expected to be very low since the interaction of TMTD and TMTT with a cation starts with the exothermic coordination to the thione sulfur atoms.

Zinc chloride and tetramethylthiourea form a complex of composition $[\mathrm{ZnCl_2(TMTU)_2}]$ in which the metal atom is approximately tetrahedrally coordinated by two chloride anions and the thione sulfur atoms of two TMTU molecules.[36] In addition, tetracoordinated zinc complexes with the related anions $\mathrm{RCS_2}^-$ [37] and $\mathrm{RCS_3}^-$ [38] have been prepared, and tetra- and hexacoordinated zinc complexes with the thiocarbamato anions $\mathrm{Me_2NCS_2}^-$ [39] and $\mathrm{Me_2NCS_3}^-$ [3] are well-known. It can reasonably be assumed that the radicals **2**−**4** can function as ligands in such complexes also. Our preliminary DFT investigations using zinc ions as a probe support this view.

We, therefore, expect that the three-coordinated zinc ions on the surface of bulk ZnO particles facilitate the formation of radicals from TMTD during the vulcanization of rubber with this accelerator system in a similar fashion as the reaction in eq 20. Since ca. 95% of a typical vulcanization mixture consist of rather unpolar materials such as polyolefins and carbon black, there should be no strong solvent effects. Radical reactions may then play a major role during the vulcanization of rubber with this particular accelerator system. The predicted paramagnetic thiocarbamato zinc complex $[\mathrm{Zn(S_2CNMe_2)}]^{2+}$ is expected to be sulfurized by elemental sulfur with formation of the analogous polysulfidic trithiolane species, which then can react with the polyolefins with crosslinking. These reactions on the surface of ZnO particles are now under investigation and the results will be reported elsewhere. At higher temperatures, additional redox reactions take place between ZnO and TMTD yielding zinc dithiocarbamate, TMTU, elemental sulfur, $\mathrm{CS_2}$, and zinc sulfate.[40] Possible intermediates of this reaction have recently been characterized.[41]

Conclusions

Tetramethylthiuram disulfide (TMTD) and the corresponding trisulfide TMTT are predicted to dissociate on heating preferentially with homolytic dissociation of the SS bonds to give radicals the *g*-tensors of which match some of the reported *g*-values obtained from ESR spectra. The formed radicals $\mathrm{Me_2NCS}_n^\bullet$ ($n = 1-4$) are stabilized by electron delocalization. Interestingly, the dissociation enthalpy of TMTD is considerably smaller than that of TMTT, which is rather uncommon in organosulfur chemistry. The low S−S bond dissociation enthalpy of TMTD (150.0 kJ $\mathrm{mol^{-1}}$) is attributed to the remarkable stability of $\mathrm{Me_2NCS_2}^\bullet$, a σ radical with the unpaired spin density shared equally between the two sulfur atoms and a four-centered delocalized π system. Both the experimental dissociation enthalpy and the ESR *g*-tensor value of tetra-isopropyl-thiuram-disulfide are reproduced well by our calculations. TMTD, TMTT, and the radicals $\mathrm{Me_2NCS}_n^\bullet$ ($n = 1-3$) are excellent ligands toward metal cations. The high binding energies of the complexes $[\mathrm{Li(S}_n\mathrm{CNMe_2)_2}]^+$ ($n = 2, 3$) are responsible for the unexpected finding that the homolytic dissociation of the SS bonds of both TMTD and TMTT are facilitated by lithium cations, especially in the presence of elemental sulfur. Therefore, we expect spontaneous dissociation of these vulcanization accelerators also in the presence of zinc ions and, consequently, also in a rubber vulcanization mixture containing TMTD as an accelerator and zinc oxide as an activator.

Acknowledgment. We are grateful to P. Nieuwenhuizen for a copy of his doctoral dissertation. This work has been supported by the Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen (HLRN), by Grillo AG, and by the National University of Singapore.

Supporting Information Available: Table S1, Cartesian coordinates and absolute energies of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061345O

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