4- and 4,5-Substituted *N*-Methoxythiazole-2(3*H*)-thiones – Preparation, UV/Vis Spectra, and Assignment of Electronic Transitions in Comparison to *N*-Methoxypyridine-2(1*H*)-thione Using Time-Dependent Density Functional Theory Calculations

Jens Hartung,*[a] Kristina Špehar,[a] Ingrid Svoboda,[b] Hartmut Fuess,[b] Mario Arnone,[c] and Bernd Engels*[c]

Dedicated to Prof. Dr. Helmut Quast on the occasion of his 70th birthday

Keywords: Alkoxyl radical precursor / Pyridinethione / Thiazolethione/ Thiocarbonyl chromophore/ Time-dependent density functional theory

Experimentally observed absorptions in UV/Vis spectra of *N*-methoxy-4-methylthiazole-2(3*H*)-thione, *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione, *N*-methoxypyridine-2(1*H*)-thione, and selected *N*-hydroxy derivatives thereof have been assigned to π→π*-type transitions as dominating character, using the results from ab initio calculations [time-dependent density functional theory (TD)RI-BLYP/TZVPP]. Theory further predicts that electronic excitations in *N*-methoxythiazole-2(3*H*)-thiones on one side and *N*-methoxypyridine-2(1*H*)-thione on the other side differ significantly with respect to character and statistical weight of contributing transitions. These effects originate predominantly from contributions of the endocyclic sulfur atom onto orbital energies and shapes in thiazole-2(3*H*)-thiones, and may be intensified by substituents such as a *p*-methoxyphenyl group located in position 5. Since the majority of the calculated spectral differences between thiazole- and pyridinethiones refers to excitations of low intensity, the findings from the present study correlate with two important experimental facts: (i) Apart from minor shifts in the exact spectral location of UV/Vis absorptions, electronic spectra of *N*-hydroxy- or *N*-methoxy-substituted pyridine-2(1*H*)-thiones and thiazole-2(3*H*)-thiones are surprisingly similar in shape. (ii) *N*-alkoxypyridine-2(1*H*)-thiones and *N*-alkoxythiazole-2(3*H*)-thiones liberate upon UV/Vis excitation oxygen-centered radicals with a comparable efficiency.

Introduction[1]

UV/Vis photolysis of *N*-alkoxy- and *N*-hydroxythiazole-2(3*H*)-thiones provides oxygen-centered radicals[2] for an application in photobiological,[3,4] mechanistic,[5] and synthetic studies.[6] Since light quanta of comparatively low energy suffice in order to induce N,O homolysis, it is likely that the primary photophysical event upon UV/Vis excitation of *N*-alkoxypyridine-2(1*H*)-thiones[7] and *N*-alkoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thiones,[8] is associated with an excitation of the thiocarbonyl chromophore[9] rather than the olefinic part or the N,O bond itself.[10] According to fundamentals of thiocarbonyl photochemistry[11] and photophysics,[12] the two energetically lowest and hence photochemically relevant electronic excitations between singlet potential energy surfaces in aliphatic and aromatic thiocarbonyl compounds originate from symmetry-forbidden n→π* excitations in the visible to near IR region and symmetry-allowed π→π* transitions in the near UV region.[13] Substituting an amino or a thiyl group for an alkyl substituent in thioketones causes thiocarbonyl π→π* transitions to be red-shifted and C=S n→π* transitions to be blue-shifted.[14] In view of this background, it is surprising to note that a concise assignment of electronic transitions that are associated with the near UV/Vis absorption bands of heterocyclic thiohydroxamic acids and their *O*-alkyl or *O*-acyl derivatives, has so far not been reported.[15,16] Therefore it was the aim of the present investigation, to prepare 4- and 4,5-substituted *N*-methoxythi-

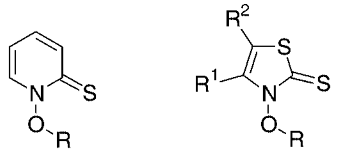
---

[a] Fachbereich Chemie, Technische Universität Kaiserslautern,
Erwin-Schrödinger-Straße, 67663 Kaiserslautern, Germany
Fax: +49-631-205-3921
E-mail: hartung@chemie.uni-kl.de
[b] Institut für Materialwissenschaft, Technische Universität Darmstadt,
Petersenstraße 23, 64287 Darmstadt, Germany
Fax: +49-6151-16-6023
[c] Institut für Organische Chemie, Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany
Fax: +49-931-888-5331
E-mail: engels@chemie.uni-wuerzburg.de

💻 Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejoc.200400674

azole-2(3*H*)-thiones **3b**–**7b** (Figure 1), to record their electronic spectra in order to systematically probe the effect of CH_3 and aryl substituents, and to assign the experimentally observed UV/Vis bands of thiazole-2(3*H*)-thiones **3a**–**b** and **5b** to electronic transitions using results from time-dependent density functional theory (TD-DFT).[14,17,18] *N*-Methoxypyridine-2(1*H*)-thione (**1b**) and *N*-hydroxypyridine-2(1*H*)-thione (**1a**) have been included into the experimental and the theoretical part of the present study, in view of the significance of derivatives thereof in contemporary photochemically induced free radical reactions.[7,19]



1 **2**–**7**

a: R = H
b: R = CH_3

2–7	R^1	R^2
2	H	H
3	CH_3	H
4	CH_3	CH_3
5	CH_3	*p*-$(H_3CO)C_6H_4$
6	CH_3	3,4-$(H_3CO)_2C_6H_3$
7	*p*-ClC_6H_4	H

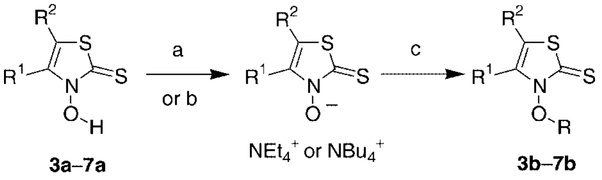
Figure 1. Structures and indexing of pyridine-2(1*H*)-thiones **1** and thiazole-2(3*H*)-thiones **2**–**7**

Results

1. Preparation and UV/Vis Spectra of *N*-Substituted Thiazole-2(3*H*)-thiones and Pyridine-2(1*H*)-thiones

N-hydroxythiazole-2(3*H*)-thiones **3a**–**7a** were prepared in four synthetic steps from the corresponding α-haloketones.[20–23] Neutralization of *N*-hydroxythiazole-2(3*H*)-thiones **3a**–**7a** with tetraethylammonium hydroxide or tetrabutylammonium hydroxide provided the derived tetraalkyl ammonium salts, which were treated with methyl *p*-toluenesulfonate in anhydrous DMF to afford *N*-methoxy-substituted thiones **3b**–**7b** in 62–78% yield (Scheme 1).[20–24]

UV/Vis spectra of *N*-hydroxypyridine-2(1*H*)-thione (**1a**),[26] *N*-hydroxythiazole-2(3*H*)-thiones **3a**–**7a** (R = H), and *N*-methoxy derivatives **1b**, **3b**–**7b** (R = CH_3, Table 1) were recorded in EtOH. The information about the location of electronic transitions in non polar solvents, was restricted to qualitative data for 5-(*p*-methoxyphenyl)-4-methylthiazolethiones **5a** and **5b** (Table 1), since the low solubility of most of the thiazole-2(3*H*)-thiones in *n*-hexane caused a scatter of the experimentally determined lg ε values. In going from polar to nonpolar solvent, a hypsochromic shift of 5 nm for **5a** was observed, whereas no such effect was noted for the *N*-methoxy compound **5b** (Table 1, entry 4, and Figure 2).



compound	R^1	R^2	yield [%]
3	CH_3	H	65
4	CH_3	CH_3	68
5	CH_3	*p*-$(H_3CO)C_6H_4$	64
6	CH_3	3,4-$(H_3CO)_2C_6H_3$	78
7	*p*-ClC_6H_4	H	62

Scheme 1. Preparation of *N*-methoxythiazole-2(3*H*)-thiones; reagents and conditions: (a) NEt_4OH, MeOH, then freeze-drying for **3b**; (b) NBu_4OH, MeOH, then freeze-drying; synthesis of **4b**–**7b**;[25] (c) $TsOCH_3$, DMF, 20 °C

Table 1. UV/Vis spectra of pyridinethiones **1** and thiazolethiones **3**–**7**[a]

Entry	R = H	λ_{max} [nm] (lg ε)	R = CH_3	λ_{max} [nm] (lg ε)
1	**1a**	350 (3.87), 283 (4.37), 218 (4.29)	**1b**	359 (3.54), 288 (3.95)
2	**3a**	315 (3.97), 233 (3.57)	**3b**	320 (4.09)
3	**4a**	317 (4.87)	**4b**	323 (4.12), 244 (3.38)
4	**5a**	334 (4.38), 255 (4.02), 203 (4.67)[b]	**5b**	335 (4.31), 258 (3.78), 228 (4.18)[c]
5	**6a**	336 (4.39), 256 (4.09)	**6b**	335 (4.45), 232 (4.23), 208 (4.69)
6	**7a**	312 (4.21), 241 (4.25)	**7b**	317 (4.40), 232 (4.46)

[a] Spectra were recorded in EtOH. For structures of compounds **1** and **3**–**7** see Figure 1. [b] In *n*-hexane: 329, 295(sh) nm (sh = shoulder). [c] In *n*-hexane: 335 nm.

Upon *O*-methylation a red shift of the energetically lowest transition was noted for thiones **1b** (9 nm), **3b** (5 nm), **4b** (6 nm), and **7b** (5 nm) in comparison to the spectra of the parent *N*-hydroxy compounds (for thiones **7a**–**b** see Figure 3). No significant shift upon *O*-methylation was observed for 5-aryl-4-methyl-substituted thiazolethiones **5a** and **6a** (Table 1, entries 4 and 5, second column).

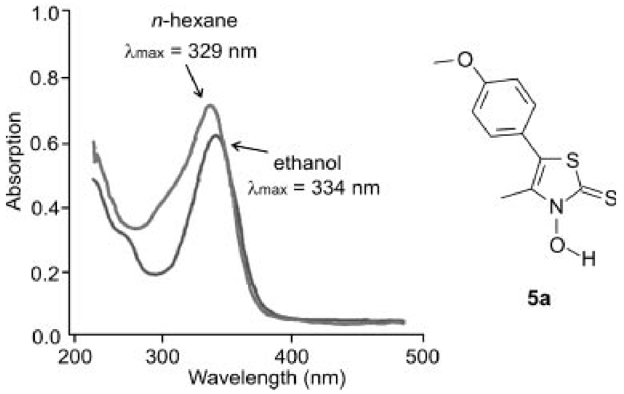


Figure 2. UV/Vis spectra of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) in EtOH and in *n*-hexane; the peak height of the spectrum recorded in *n*-hexane (qualitative spectrum) has been adapted for presentation purposes to the band observed for **5a** in EtOH

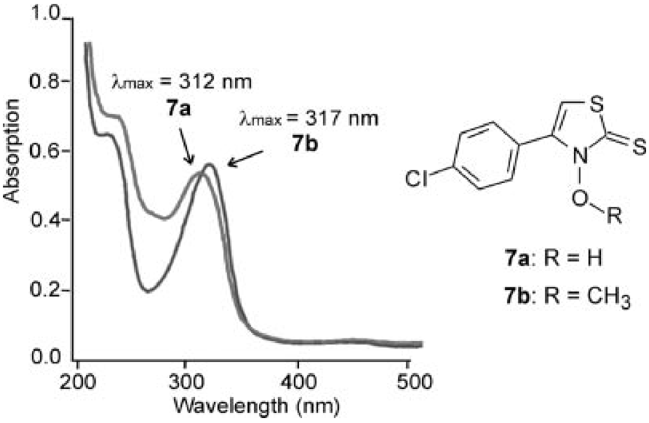
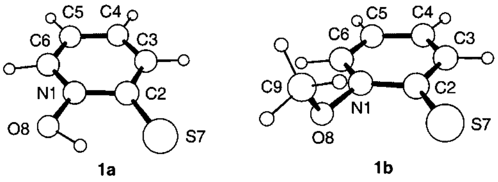


Figure 3. UV/Vis spectra of *N*-hydroxy-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione (**7a**) and *N*-methoxy derivative **7b** in EtOH

2. Equilibrium Geometries and Electronic Spectra of *N*-Hydroxypyridine-2(1*H*)-thione (1a) and *N*-Methoxypyridine-2(1*H*)-thione (1b)

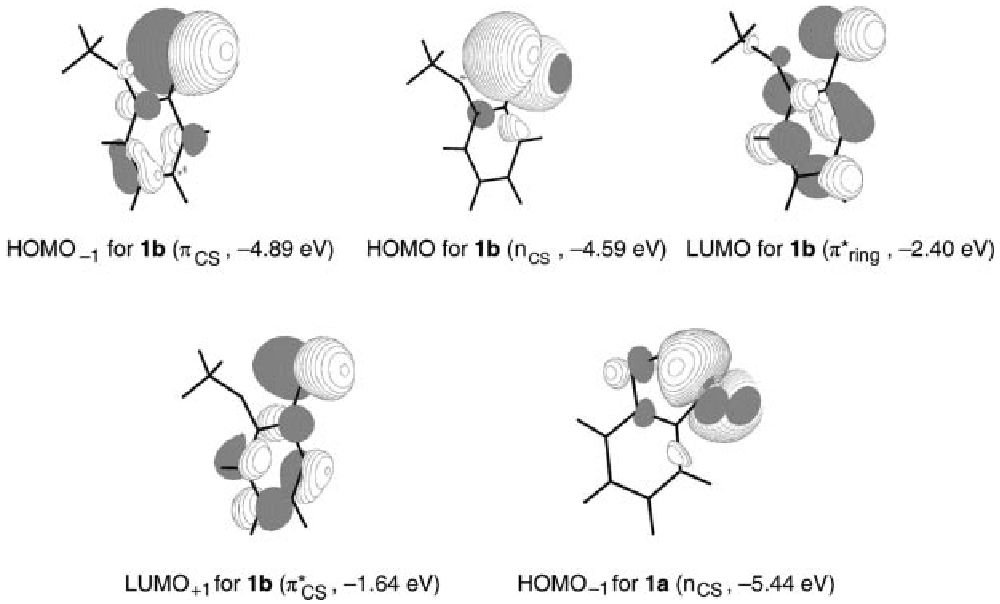
The equilibrium geometry of *N*-hydroxypyridine-2(1*H*)-thione (**1a**) and *N*-methoxypyridinethione **1b** were optimized using the BLYP[27] density functional in combination with the Resolution of Identity approximation and the single valance basis set including polarization functions (RI-BLYP/SVP, Table 2, see also Computational Details).[28] Thione **1a** exhibits a planar arrangement of atoms with the heterocyclic core distorted from a regular hexagon. The sequence of shorter and longer bonds, as well as the bond lengths within the thiohydroxamate functional group (Table 2), are in reasonable agreement with the values obtained from an X-ray crystallographic analysis.[29] Similar to the situation in the solid state, $(\mathrm{N1{-}C2{-}C3})_{\mathrm{calc}} = 114.0°$ is the smallest and $(\mathrm{C2{-}N1{-}C6})_{\mathrm{calc}} = 125.2°$ the largest angle of the heterocyclic core in thione **1a**. Theory predicts the formation of an intramolecular hydrogen bond between the OH group and the thiocarbonyl sulfur atom, which is also present in the solid-state structure of **1a**. The computed structure of *N*-methoxypyridine-2(1*H*)-thione (**1b**), a labile compound that has so far not been crystallized, was compared to the corresponding subunit in *N*-[*trans*-(*tert*-butylcyclohexyl)-4-oxy]pyridine-2(1*H*)-thione, which points to a similar correlation between theory and experiment as outlined for the acid **1a**.[16,30]

Table 2. RI-BLYP/SVP-calculated energy and equilibrium geometry of *N*-hydroxypyridine-2(1*H*)-thione (**1a**) and *N*-methoxypyridine-2(1*H*)-thione (**1b**)



Parameter	1a	1b
E [a.u.]	–721.698422	–760.972371
N1–C2 [Å]	1.451	1.421
C2–C3 [Å]	1.433	1.450
C3–C4 [Å]	1.392	1.389
C4–C5 [Å]	1.422	1.431
C5–C6 [Å]	1.389	1.380
C6–N1 [Å]	1.363	1.375
C2–S7 [Å]	1.701	1.681
N1–O8 [Å]	1.371	1.400
O8–R [Å]	1.037 (R = H)	1.451 [R = C(9)]
C2–N1–C6 [°]	125.2	125.4
N1–C2–C3 [°]	114.0	112.2
C2–C3–C4 [°]	122.0	123.3
C3–C4–C5 [°]	120.4	120.4
N1–O8–R [°]	99.5 (R = H)	112.1 [R = C(9)]
S7–C2–N1–O8 [°]	0.0	–5.1
C2–N1–O8–R [°]	0.0 (R = H)	82.3 [R = C(9)]
N1–C2–C3–S7 [°]	0.0	0.0

Electronic excitations in pyridinethiones **1a** and **1b** in the spectral region of $\lambda > 280$ nm were calculated using the time dependent (TD)RI-BLYP functional[31] in combination with the TZVPP basis set (Table 3), and were supplemented by data from (TD)RI-B3LYP/TZVP calculations (Supporting Information).[32] The results from (TD)RI-BLYP computations predict that the UV/Vis spectrum of *N*-hydroxypyridine-2(1*H*)-thione (**1a**) consists of two major absorption bands. A weak band with an oscillator strength of $f = 0.018$ is located at 406 nm and a stronger one at 295 nm ($f = 0.194$). Two additional bands with $f < 10^{-3}$ are present at 411 nm and at 335 nm. The calculated UV/Vis spectrum of *N*-methoxypyridinethione **1b** exhibits two stronger [422 nm ($f = 0.024$), 297 nm ($f = 0.229$)] and two very weak bands (553 nm, 409 nm, both $f < 10^{-3}$, Table 3). The computed characters of these states are governed by one dominating configuration with weights that range between 0.997 and 0.796 (Table 3). A noteworthy blue shift of 142 nm has been calculated for the lowest energy transition in the spectrum of acid **1a**, in comparison to the corresponding band in *N*-methoxypyridinethione **1b**. The orbitals required for an assignment of the calculated transitions in thiones **1a** and **1b** are depicted in Figure 4.



HOMO$_{-1}$ for **1b** (π_{CS}, –4.89 eV) HOMO for **1b** (n_{CS}, –4.59 eV) LUMO for **1b** (π^*_{ring}, –2.40 eV)

LUMO$_{+1}$ for **1b** (π^*_{CS}, –1.64 eV) HOMO$_{-1}$ for **1a** (n_{CS}, –5.44 eV)

Figure 4.[1] Visualization of relevant orbitals for an assignment of electronic spectra of pyridine-2(1*H*)-thiones **1a** and **1b** (BLYP). Except of n_{CS}, the shapes of orbitals π_{CS}, LUMO (π^*_{ring}), and LUMO$_{+1}$ (π^*_{CS}) in thiones **1a** and **1b** are similar. Calculated orbital energies [eV] for **1a**: –5.44 (HOMO$_{-1}$, n_{CS}), –5.11 (HOMO, π_{CS}), –2.46 (LUMO, π^*_{ring}), –1.80 (LUMO$_{+1}$, π^*_{CS})

Table 3.[1] Assignment of electronic transitions in the equilibrium structure of *N*-hydroxypyridine-2(1*H*)-thione (**1a**) and *N*-methoxypyridine-2(1*H*)-thione (**1b**) [(TD)RI-BLYP/TZVPP, $\lambda > 280$ nm, equilibrium geometry][a]

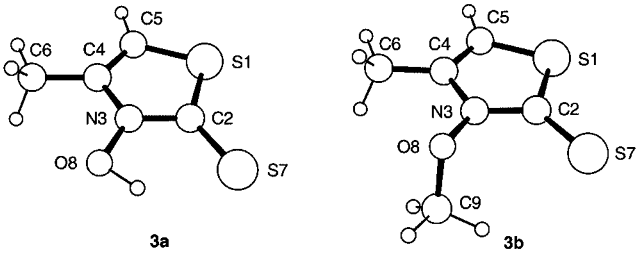
Character	**1a**			**1b**		
	ΔE [nm]	f	Weight	ΔE [nm]	f	Weight
$n_{CS}\rightarrow\pi^*_{ring}$	411	$< 10^{-3}$	0.997	553	$< 10^{-3}$	0.996
$\pi_{CS}\rightarrow\pi^*_{ring}$	406	0.018	0.894	422	0.024	0.859
$n_{CS}\rightarrow\pi^*_{CS}$	335	$< 10^{-3}$	0.984	409	$< 10^{-3}$	0.984
$\pi_{CS}\rightarrow\pi^*_{CS}$	295	0.194	0.796	297	0.229	0.796

[a] Configurations with weights below 0.10 have, for the sake of clarity, not been considered.

3. Structures of 4-Methylthiazole-2(3*H*)-thiones 3a–b and UV/Vis Spectra of *N*-Substituted Thiazole-2(3*H*)-thiones 2–3

N-Hydroxythiazole-2(3*H*)-thione (**2a**) has hitherto not been prepared. Therefore, *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**) has been selected for a comparison of the RI-BLYP/SVP-calculated geometry to results from X-ray diffraction experiments (Table 4). The match between computed bond lengths and angles within the thiohydroxamate entity and the heterocyclic ring (Table 4) agree reasonably with the geometrical parameter obtained from an X-ray analysis of **3a**.[33,34] The OH group forms an intramolecular hydrogen bond in the computed structure, whereas hydrogen-bonded dimers, similar to the arrangement observed in the crystal structure of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5a** (see Figure 6), have been found for thione **3a** in the solid state.[34] A comparison between the computed equilibrium geometry of *N*-methoxy-substituted thiazolethione **3b** to the solid-state structure of 2-(4-methyl-2-thioxo-2,3-dihydrothiazol-3-yloxy)propanoate points to a satisfactory agreement between theory and experiment.[35,36]

Table 4. RI-BLYP/SVP-calculated energy and equilibrium structure of *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**) and *N*-methoxy-4-methylthiazole-2(3*H*)-thione (**3b**)



3a **3b**

Parameter	**3a**	**3b**
E [a.u.]	–1081.793419	–1121.074379
S1–C2 [Å]	1.782	1.772
C2–N3 [Å]	1.379	1.375
N3–C4 [Å]	1.396	1.400
C4-C5 [Å]	1.372	1.352
C5–S1 [Å]	1.767	1.754
C2–S7 [Å]	1.680	1.659
N3–O8 [Å]	1.382	1.392
C4–C6 [Å]	1.501	1.495
O8–R [Å]	1.014 (R = H)	1.447 [R = C(9)]
C2–N3–C4 [°]	119.3	118.8
S1–C2–N3 [°]	106.4	105.9
C5–S1–C2 [°]	91.9	92.5
N3–C4–C5 [°]	112.8	110.9
N3–O8–R [°]	100.0 (R = H)	111.7 [R = C(9)]
S7–C2–N3–O8 [°]	0.0	–6.8
C2–N3–O8–R [°]	0.1 (R = H)	83.3 [R = C(9)]

The (TD)RI-BLYP/TZVPP-computed spectrum of *N*-hydroxythiazole-2(3*H*)-thione (**2a**)shows two stronger transitions [323 nm (f = 0.104), 266 nm (f = 0.095), Table 5] and four bands with very small oscillator strengths [337, 313, 267 nm ($f < 10^{-3}$ each), and 277 nm ($f = 6{\cdot}10^{-3}$); for

B3LYP-calculated transitions see Supporting Information]. For *N*-methoxythiazolethione **2b**, four bands of significant intensity [325 nm (f = 0.052), 306 nm (f = 0.017), 298 nm (f = 0.025), and 277 nm (f = 0.086)] and two with oscillator strengths below $< 10^{-3}$ (383 and 314 nm) are predicted. The energetically lowest transition in *N*-hydroxythiazolethione **2a** exhibits a blue shift of 46 nm in comparison to the similar excitation in the *N*-methoxy compound **2b** (Table 6). The relevant orbitals for an assignment of BLYP-computed UV/Vis spectra of thiones **2a** and **2b** are shown in Figure 5.

BLYP-calculated electronic transitions in *N*-hydroxy-4-methylthiazolethione **3a** and *N*-methoxy-4-methylthiazolethione **3b** are shown in Tables 7 and 8.

Table 5.[1] Excitation energies ΔE and assignment of UV/Vis transitions in *N*-hydroxythiazole-2(3*H*)-thione (**2a**) [(TD)RI-BLYP/TZVPP, $\lambda > 250$ nm, equilibrium geometry]

Transition	ΔE [nm]	f	Character	Weight
1	337	$< 10^{-3}$	$n_{CS}\rightarrow\pi^*_{SCS}$	0.997
2	323	0.104	$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.821
3	313	$< 10^{-3}$	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+1}$	0.997
4	277	$6\cdot10^{-3}$	$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.490
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.409
5	267	$< 10^{-3}$	$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.998
6	266	0.095	$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.457
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.358
			$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.109

Table 6.[1] Excitation energies ΔE and assignment of UV/Vis transitions in *N*-methoxythiazole-2(3*H*)-thione (**2b**) [(TD)RI-BLYP/TZVPP, $\lambda > 250$ nm, equilibrium geometry]

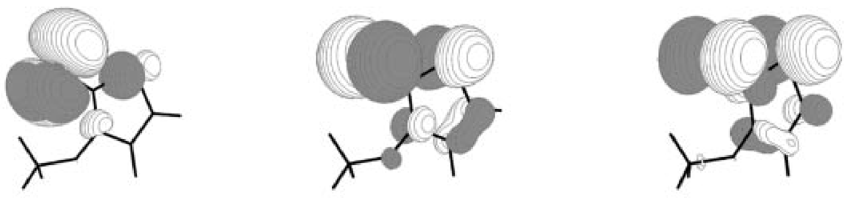
Transition	ΔE [nm]	f	Character	Weight
1	383	$< 10^{-3}$	$n_{CS}\rightarrow\pi^*_{SCS}$	0.997
2	325	0.052	$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.611
			$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.280
3	314	$< 10^{-3}$	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+1}$	0.886
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.110
4	306	0.017	$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.518
			$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.360
5	298	0.025	$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.565
			$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.165
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.138
6	277	0.086	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.612
			$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.140

Table 7.[1] Excitation energies ΔE and assignment of UV/Vis transitions in *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**) [(TD)RI-BLYP/TZVPP, $\lambda > 250$ nm, equilibrium geometry]

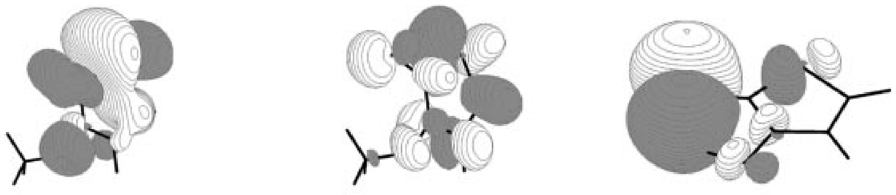
Transition	ΔE [nm]	f	Character	Weight
1	330	$< 10^{-3}$	$n_{CS}\rightarrow\pi^*_{SCS}$	0.997
2	316	0.123	$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.852
3	310	$< 10^{-3}$	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+1}$	0.997
4	275	0.015	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.596
			$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.221
5	265	0.061	$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.724
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.156
6	260	$< 10^{-3}$	$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.998

Table 8.[1] Excitation energies ΔE and assignment of UV/Vis transitions in *N*-methoxy-4-methylthiazole-2(3*H*)-thione (**3b**) [(TD)RI-BLYP/TZVPP, $\lambda > 250$ nm, equilibrium geometry]

Transition	ΔE [nm]	f	Character	Weight
1	377	$< 10^{-3}$	$n_{CS}\rightarrow\pi^*_{SCS}$	0.997
2	315	0.075	$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.688
			$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.174
3	313	$< 10^{-3}$	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+1}$	0.737
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.260
4	300	0.010	$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.686
			$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.238
5	291	0.027	$n_{CS}\rightarrow\mathrm{LUMO}_{+2}$	0.672
			$n_{CS}\rightarrow\mathrm{LUMO}_{+1}$	0.116
6	280	0.086	$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+2}$	0.558
			$\pi_{SCS}\rightarrow\mathrm{LUMO}_{+1}$	0.183



HOMO_{-1} for **2b** (n_{CS}, –5.03 eV) HOMO for **2b** (π_{SCS}, –4.96 eV) LUMO for **2b** (π^*_{SCS}, –1.88 eV)



LUMO_{+1} for **2b** (–1.09 eV) LUMO_{+2} for **2b** (–0.95 eV) HOMO_{-1} for **2a** (n_{CS}, –5.54 eV)

Figure 5.[1] Visualization of and notation for orbitals required for an assignment of electronic spectra of thiazole-2(3*H*)-thiones **2a** and **2b**. Except for n_{CS}, the shapes of the HOMO (π_{SCS}), LUMO (π^*_{SCS}), LUMO_{+1}, and LUMO_{+2} in **2a** and **2b** are similar. Calculated orbital energies [eV] for **2a**: –5.54 (HOMO_{-1}, n_{CS}), –5.09 (HOMO, π_{SCS}), –2.03 (LUMO, π^*_{SCS}), –1.17 (LUMO_{+1}), –1.03 (LUMO_{+2}).

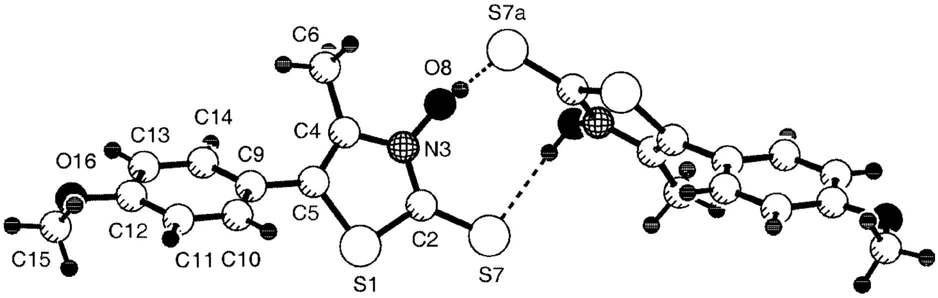
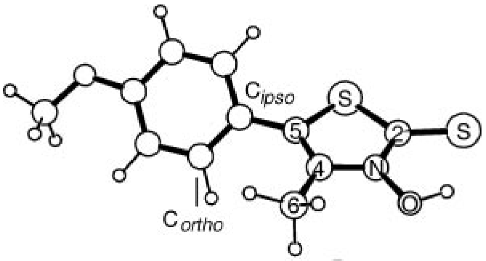


Figure 6. PLATON-Graphic[37] of the solid state geometry of a hydrogen bonded dimer of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) (X-ray diffraction analysis)

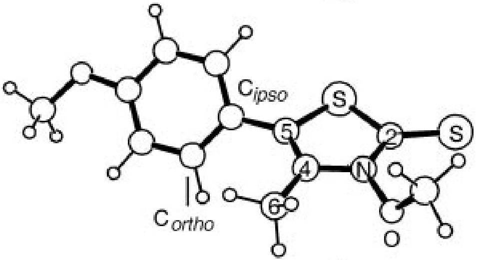
4. Geometry and UV/Vis Spectra of *N*-Substituted 5-(*p*-Methoxyphenyl)-4-methylthiazole-2(3*H*)-thiones 5a–b

In order to reference the computed equilibrium geometry versus information from a solid-state structure, suitable crystals of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) were grown and investigated by X-ray diffraction analysis (Figure 6, and Supporting Information). Thione **5a** crystallizes in monoclinic space group *P*2/c and forms hydrogen bonded dimers [O8–H = 0.83(3) Å, H···S7*a* = 2.26(3) Å, O8···S7*a* = 3.087(2) Å, O8–H···S7a = 175(3)°]. The planar thiazolethione subunit [N3–C2–S1–C5 = 1.2(2) Å, S1–C2–N3–C4 = –1.8(3)°, C5–C4–N3–C2 = 1.5(3)°] is tilted by C4–C5–C9–C14 = –51.8(4)°

Table 9.[1] RI-BLYP/SVP-calculated energy and equilibrium geometry of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) and its *N*-methoxy derivative **5b**



5a



5b

Parameter	**5a**	**5b**
Energy [a.u.]	–1427.372763	–1466.652950
S1–C2 [Å]	1.775	1.794
C2–N3 [Å]	1.377	1.390
N3–C4 [Å]	1.396	1.410
C4–C5 [Å]	1.384	1.379
C5–S1 [Å]	1.794	1.793
C2–S7 [Å]	1.682	1.663
N3–O8 [Å]	1.382	1.395
C4–C6 [Å]	1.504	1.505
O8–R [Å]	1.015 (R = H)	1.452 [R = C(9)]
C2–N3–C4 [°]	119.7	119.5
S1–C2–N3 [°]	106.4	105.3
C5–S1–C2 [°]	92.6	93.4
N3–C4–C5 [°]	112.8	111.9
N3–O8–R [°]	99.8 (R = H)	112.3 [R = C(9)]
S7–C2–N3–O8 [°]	0.5	–6.9
C2–N3–O8–R [°]	0.2 (R = H)	79.6 [R = C(9)]
C4–C5–C*ipso*–C*ortho*	41.8	43.2

Table 10.[1] Excitation energies and an assignment of calculated electronic transitions ($\lambda > 250$ nm) for the *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (equilibrium geometry, $E = -1427.372763$ a.u., φ = C4–C5–C*ipso*–C*ortho* = 41.3°)

Transition	ΔE [nm]	f	Character	Weight
1	409	$3 \cdot 10^{-3}$	$n_{CS}\rightarrow\pi^*_{SCS}$	0.977
2	392	0.015	$\pi_{SCS}\rightarrow\pi^*_{sub}$	0.910
3	385	0.176	$\pi_{SCS}\rightarrow\pi^*_{SCS}$	0.663
			$\pi_{SCS}\rightarrow LUMO_{+2}$	0.115
4	372	0.034	$n_{CS}\rightarrow\pi^*_{sub}$	0.883
5	350	$2 \cdot 10^{-3}$	$n_{CS}\rightarrow LUMO_{+2}$	0.703
			$\pi_{SCS}\rightarrow LUMO_{+2}$	0.237
6	334	0.113	$\pi_{SCS}\rightarrow LUMO_{+2}$	0.303
			$HOMO_{-2}\rightarrow\pi^*_{SCS}$	0.271
			$n_{CS}\rightarrow LUMO_{+2}$	0.243
7	312	0.005	$\pi_{SCS}\rightarrow LUMO_{+3}$	0.972
8	300	0.006	$n_{CS}\rightarrow LUMO_{+3}$	0.693
			$HOMO_{-2}\rightarrow\pi^*_{SCS}$	0.180
9	288	0.016	$HOMO_{-2}\rightarrow\pi^*_{SCS}$	0.282
			$n_{CS}\rightarrow LUMO_{+3}$	0.264
			$\pi_{SCS}\rightarrow LUMO_{+2}$	0.138
10	284	$9 \cdot 10^{-3}$	$HOMO_{-2}\rightarrow\pi^*_{sub}$	0.722
			$HOMO_{-3}\rightarrow\pi^*_{SCS}$	0.157
11	275	0.042	$\pi_{SCS}\rightarrow LUMO_{+5}$	0.351
			$\pi_{SCS}\rightarrow LUMO_{+4}$	0.291
			$HOMO_{-2}\rightarrow LUMO_{+2}$	0.233
12	272	0.033	$\pi_{SCS}\rightarrow LUMO_{+5}$	0.546
			$\pi_{SCS}\rightarrow LUMO_{+4}$	0.165
			$HOMO_{-2}\rightarrow LUMO_{+2}$	0.109
13	266	0.103	$\pi_{SCS}\rightarrow LUMO_{+4}$	0.382
			$HOMO_{-2}\rightarrow LUMO_{+2}$	0.231
			$n_{CS}\rightarrow LUMO_{+4}$	0.172
14	265	0.179	$n_{CS}\rightarrow LUMO_{+4}$	0.626
			$HOMO_{-2}\rightarrow LUMO_{+2}$	0.180
15	262	0.020	$n_{CS}\rightarrow LUMO_{+5}$	0.897
16	259	0.010	$HOMO_{-3}\rightarrow\pi^*_{SCS}$	0.644
			$HOMO_{-3}\rightarrow LUMO_{+2}$	0.153
			$HOMO_{-2}\rightarrow LUMO_{+3}$	0.103
17	255	$3 \cdot 10^{-3}$	$\pi_{SCS}\rightarrow LUMO_{+6}$	0.977
18	250	$3 \cdot 10^{-3}$	$HOMO_{-2}\rightarrow LUMO_{+3}$	0.843

with respect to the *p*-methoxyphenyl group. The bond lengths N3–O8 = 1.373(3) Å, N3–C2 = 1.349(3) Å, C2–S7 = 1.676(3) Å, N3–C4 = 1.387(3) Å, C4–C5 = 1.349(4) Å, and C5–S1 = 1.747(2) Å agree with previously reported values for *N*-alkoxy- or *N*-hydroxy-substituted thiazole-2(3*H*)-thiones.[22,23] The heterocyclic core of **5a** is distorted from a regular pentagon since the angle C5–S1–C2 = 93.3(1)° is considerably smaller than the angles S1–C2–N3 = 107.1(2)°, C2–N3–C4 = 118.1(2)°, N3–C4–C5 = 111.7(9)°, and C4–C5–S1 = 109.8(2)°.

Bond lengths and angles of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**), in particular those referring to the thiohydroxamate functionality and the tilt angle between the heterocyclic core and the *p*-methoxyphenyl group, are satisfactorily reproduced by RI-BLYP/SVP calculations (Table 9). The OH group forms an intramolecular hydrogen bond in the computed structure, whereas hydrogen-bonded dimers of **5a** are observed in the crystal structure (Figure 6).

The *p*-methoxyphenyl substituent located at position 5 causes a bathochromic shift of 19 nm of the energetically lowest absorption in the experimental spectrum of acid **5a** and 15 nm for *N*-methoxy-substituted heterocycle **5b**, in comparison to the corresponding bands in 4-methylthiazolethiones **3a** and **3b** (Table 1). In view of the significance of *O*-alkyl derivatives of **5a** as sources of oxygen-centered radicals in visible light induced transformations, the UV/Vis spectrum of *N*-methoxy-4-methyl-5-(methoxyphenyl)-thiazole-2(3*H*)-thione (**5b**) was investigated in detail.[8] The spectral information and orbitals, relevant for an assignment of major transitions referring to the equilibrium structure, are provided in Table 10 and Figure 7. The BLYP-computed barrier to rotation about the C5–C_{ipso} bond is 8.0 kJ·mol^{-1}, which points to a significant population of other rotamers than the equilibrium structure at 25 °C.[38] This issue has been addressed in the present study by computing electronic spectra of the structures with a planar (φ = 0°) and with an orthogonal arrangement (φ = 90°) between the two cyclic subunits in thione **5b** (see Figure 8 and Supporting Information).

Discussion

1. Evaluation of the Computational Method

Previous work has documented that time dependent density functional theory (TD-DFT) is suited to reproduce UV/Vis spectral characteristics of thiocarbonyl compounds.[14] The results from the present study show that (TD)RI-BLYP calculations predict the position of experimentally observed energetically lowest transitions in *N*-hydroxy- and *N*-methoxythiazole-2(3*H*)-thiones, i.e. a type of thiocarbonyl compound that has hitherto not been explored using TD-DFT, with a precision of 1–5 nm.[39] The agreement between theory and experiment for the higher energy transitions is less. On the other hand, results from

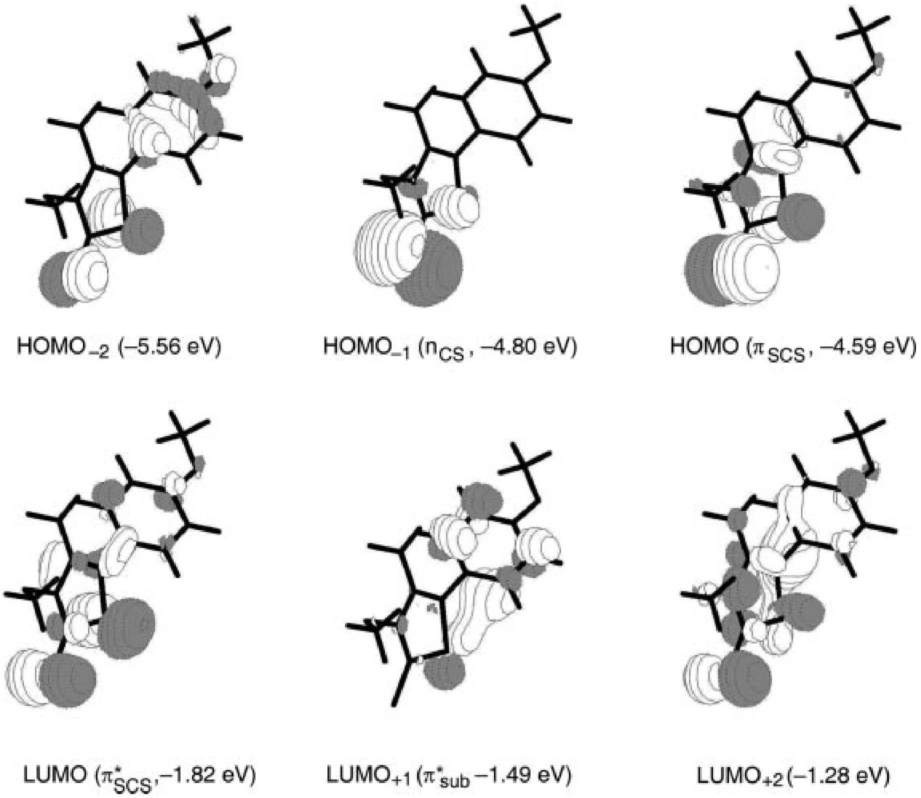
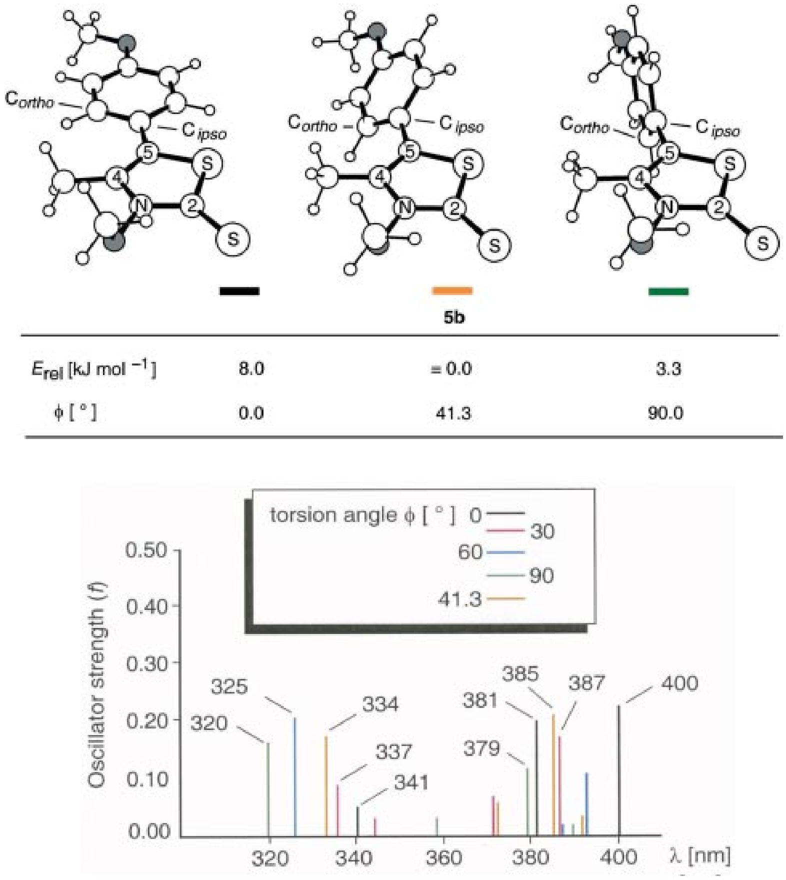


Figure 7. Visualization of the most important orbitals for an assignment of electronic transitions at the low energy end in the BLYP-calculated UV/Vis spectrum of *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (equilibrium geometry)[1]



		5b	
E_{rel} [kJ mol^{-1}]	8.0	≡ 0.0	3.3
φ [°]	0.0	41.3	90.0

Figure 8. Rotation of the *p*-methoxyphenyl group about the C5–C_{ipso} bond in *N*-methoxy-4-methyl-5-(*p*-methoxyphenyl)thiazolethione **5b**: RI-BLYP/SVP-calculated geometries and relative energies (top, ball and stick presentation with the oxygen atoms depicted in gray) and (TD)RI-BLYP-computed UV/Vis bands (bottom). φ = C4–C5–C_{ipso}–C_{ortho}

(TD)RI-B3LYP/TZVP calculations provide for symmetry-allowed energetically lowest excitations in 4-methylthiazolethiones **3a**–**b** bands that were blue-shifted by 21–23 nm in comparison with the experiment (Supporting Information). An even more critical dependence of the applied theory on the location of the symmetry-allowed bands was noted for the pyridine-2(1*H*)-thiones **1**. (Table 3 and Supporting Information). In view of the fact that thiazole-2(3*H*)-thiones constitute the majority of compounds that were analyzed in the present study, we restricted ourselves to a discussion of BLYP-computed spectroscopic data.[40] The B3LYP-values have been disclosed in the Supporting Information.

2. Assignment of UV/Vis Spectra of *N*-hydroxypyridine-2(1*H*)-thione (1a) and *N*-(Methoxy)pyridine-2(1*H*)-thione (1b) – the Effect of Intramolecular Hydrogen Bonding

(i) Experimental Background. The UV/Vis spectrum of *N*-hydroxypyridine-2(1*H*)-thione (**1a**) shows three broad and featureless bands at λ_{exp} = 350 (halfwidth λ = 54 nm), 283, and 218 nm in 1:3:2.6 intensity ratio (in EtOH). The two bands at the low energy end of the spectrum are red-shifted by 5–9 nm in the experimental absorption spectrum of *N*-methoxypyridine-2(1*H*)-thione (**1b**) without showing major changes in relative intensities (Table 1).

(ii) FMOs in Pyridinethiones 1.[1] Two occupied and two virtual orbitals are required for an assignment of the most important UV/Vis bands of *N*-methoxypyridine-2(1*H*)-thione **1b** in the spectral region of $\lambda > 280$ nm (Figure 4). The HOMO_{-1} (π_{CS}), is dominated by contributions from the C=S π-orbital and exhibits further density at C3, C4, and C6. The HOMO (n_{CS}) of compound **1b** is largely governed by one of the lone pairs at sulfur (n-orbital). The LUMO (π^*_{ring}) shows π*-type interactions for the thiohydroxamate functionality and contributions at C3, C5, and C6. The LUMO_{+1} (π^*_{CS}) arises from a combination of the π* thiocarbonyl orbital and π-type orbitals at C3–C6. The illustration of FMOs in *N*-methoxypyridine-2(1*H*)-thione (**1b**) points to a more pronounced delocalization of electrons across the thiohydroxamate functionality and the bridging 1,3-butadiene-1,4-diyl entity in the virtual orbitals than in the occupied MOs. The latter orbitals are preferentially located at the C=S-group (Figure 4).

(iii) Calculated UV/Vis Bands. Transitions between one of the two highest occupied (n_{CS}, π_{CS}) into one of the two lowest unoccupied orbitals (π^*_{ring}, π^*_{CS}) give rise to two intense and two weak bands (Figure 4, Table 3). The excitation at λ_{calc} = 553 nm (2.24 eV) in *N*-methoxypyridine-

2(1*H*)-thione (**1b**) originates from the $n_{CS}\rightarrow\pi^*_{ring}$ transition. The next higher band at λ_{calc} = 422 nm (2.94 eV) arises from the $\pi_{CS}\rightarrow\pi^*_{ring}$ excitation. The third transition at λ_{calc} = 409 nm (3.03 eV) is predominantly due to the $n_{CS}\rightarrow\pi^*_{CS}$ transition. The strongest of the calculated bands is located at λ_{calc} = 297 nm (4.17 eV) and is due to a symmetry-allowed $\pi_{CS}\rightarrow\pi^*_{CS}$ transition. It is worth mentioning that all calculated UV/Vis excitations in thione **1b** ($\lambda > 280$ nm) are characterized by one dominant transition as shown by the statistical weight of its character.

In *N*-hydroxypyridine-2(1*H*)-thione (**1a**), the n_{CS}-orbital (ε = –5.44 eV) is significantly more stabilized than π_{CS} (ε = –5.11 eV) due to the presence of an intramolecular hydrogen bond (Figure 4). This effect causes the $n_{CS}\rightarrow\pi^*_{ring}$ transition in **1a** to be blue-shifted by 142 nm (0.78 eV) to 411 nm (3.02 eV). The $n_{CS}\rightarrow\pi^*_{CS}$ excitation exhibits a hypsochromic shift of 74 nm to 335 nm, for the same reason. These changes are not observed in the experimental spectrum, probably because excitations out of n_{CS} are associated with very weak oscillator strengths. The $\pi\rightarrow\pi^*$-type transitions in *N*-hydroxypyridinethione **1a** are not significantly affected by the stabilization of n_{CS} thus leading only to minor blue shifts in comparison to the corresponding excitation in *N*-methoxypyridinethione **1b** ($\Delta\lambda$ = 16 nm for $\pi_{CS}\rightarrow\pi^*_{ring}$ and 2 nm for $\pi_{CS}\rightarrow\pi^*_{CS}$).

(iv)Assignment of Spectral Transitions. The experimentally observed UV/Vis bands at λ_{exp} = 350 and 283 nm in *N*-hydroxypyridinethione **1a**, and at λ_{exp} = 359 and 288 nm in *N*-methoxypyridinethione **1b** are assigned on the basis of their intensity and spectral location to $\pi_{CS}\rightarrow\pi^*_{ring}$ and $\pi_{CS}\rightarrow\pi^*_{CS}$ transitions.

3. Electronic Spectra of Thiazole-2(3*H*)-thiones 2 and 3 – Similarities and Differences in Comparison to the Pyridine-2(1*H*)-thiones 1a–b

(i) Experimental Background. The UV/Vis spectroscopic fundamentals of *N*-oxy-substituted thiazole-2(3*H*)-thiones in the spectral region of $\lambda > 250$ nm have been explored for the least substituted derivatives, i.e. heterocycles **2a** and **2b**, for reasons of simplicity. Since the latter compounds have so far not been synthesized, the correlation between theory and experiment has been achieved by comparing computed UV/Vis spectral characteristics to experimental data of 4-methylthiazole-2(3*H*)-thiones **3a** and **3b**.[19,24,41] The experimental spectrum of *N*-hydroxy-4-methylthiazolethione **3a** in EtOH (Table 1) displays one featureless band with a halfwidth of $\Delta\lambda$ = 38 nm (λ_{exp} = 315 nm) and a shoulder at λ_{exp} = 233 nm (halfwidth: $\Delta\lambda$ = 44 nm) in a ratio of peak heights of ca. 1.5:1. For *N*-methoxy-4-methylthiazolethione **3b** one broad absorption band is observed experimentally with a maximum at λ_{exp} = 320 nm (halfwidth: λ = 43 nm).

(ii) FMOs in Thiazole-2(3*H*)-thiones 2. Two occupied and three unoccupied orbitals are necessary in order to assign electronic transitions in *N*-methoxythiazolethione **2b** in the spectral region of $\lambda > 250$ nm (Figure 5). The $HOMO_{-1}$ (n_{CS}) is dominated by a lone pair from the thiocarbonyl sulfur atom. The HOMO (π_{SCS}) shows large contributions with opposite orbital phases at the two sulfur atoms. The LUMO (π^*_{SCS}) is similarly dominated by contributions from the S–C=S fragment, this time with identical orbital phases at the two sulfur atoms. The $LUMO_{+1}$ and the $LUMO_{+2}$ are strongly delocalized and exhibit complex shapes.

In *N*-hydroxythiazole-2(3*H*)-thione (**2a**), intramolecular hydrogen bonding causes a marked stabilization of n_{CS} and a change in its orbital shape, in comparison to n_{CS} in *N*-methoxythiazolethione **2b**. The remaining four photochemically relevant FMOs, i.e. π_{SCS}, π^*_{SCS}, $LUMO_{+1}$, $LUMO_{+2}$, exhibit similar shapes and energies in thiones **2a** and **2b**.

(iii) Electronic Transitions in Thiazole-2(3*H*)-thiones 2a–b. The UV/Vis spectrum of *N*-methoxythiazole-2(3*H*)-thione (**2b**) shows strong bands at λ_{calc} = 325 nm (3.82 eV) and λ_{calc} = 277 nm (4.48 eV). The former originates from an $\pi_{SCS}\rightarrow\pi^*_{SCS}$ excitation with minor contributions from a $n_{CS}\rightarrow LUMO_{+1}$ transition, while the band at λ_{calc} = 277 nm is due to a $\pi_{SCS}\rightarrow LUMO_{+2}$ and a $\pi_{SCS}\rightarrow\pi^*_{SCS}$ excitation. In addition, four less intense bands are present in the computed UV/Vis spectrum of thione **2b**, which originate from a symmetry-forbidden and therefore weak $n_{CS}\rightarrow\pi^*_{SCS}$ excitation (λ = 383 nm, 3.2 eV), $\pi_{SCS}\rightarrow LUMO_{+1}/LUMO_{+2}$ transitions (λ = 314 nm, 3.95 eV), $n_{CS}\rightarrow LUMO_{+1}/LUMO_{+2}$ excitations (λ = 306 nm, 4.05 eV), and a multicharacter band (298 nm 4.29 eV).

A stabilization by 0.51 eV causes excitations out of n_{CS} in *N*-hydroxythiazolethione **2a** to be blue-shifted versus the corresponding bands in *N*-methoxythiazolethione **2b**. π_{SCS} Orbitals in thiones **2a** and **2b**, on the other hand, exhibit similar orbital energies thus leading to approximately the same transition energies (Tables 5 and 6).

(iv) Assignment of the UV/Vis Band in 4-Methylthiazolethiones 3 and Structurally Related Derivatives. On the basis of their spectral location and associated intensity, the UV/Vis absorption bands at λ_{exp} = 315 nm for *N*-hydroxythiazolethione **3a** and λ_{exp} = 320 nm for *N*-methoxy-4-methylthiazolethione **3b** are correlated with excitations that predominantly originate from $\pi_{SCS}\rightarrow\pi^*_{SCS}$ transitions. In view of the predicted small effect of a methyl substituent onto the spectral characteristics of thiazole-2(3*H*)-thiones, the UV/Vis absorption at λ_{exp} = 317 nm for *N*-hydroxy-4,5-dimethylthiazolethione **4a** and λ_{exp} = 323 nm for *N*-methoxy-4,5-dimethylthiazolethione **4b** are also considered to originate from $\pi_{SCS}\rightarrow\pi^*_{SCS}$ excitations as dominating character. It is tempting to draw the same conclusion for the origin of the experimentally observed UV/Vis bands of 4-(*p*-chlorophenyl)-substituted thiazolethiones **7a**–**7b**. It should, however, be noted that an aryl substituent affects orbital energies and shapes considerably stronger than a CH_3 group (see below).

(v) Comparison between UV/Vis Spectra of the Pyridine-2(1*H*)-thiones 1a–b and Thiazolethiones 2a–b (and 3a–b). The n_{CS} orbitals in pyridine-2(1*H*)-thiones **1a**–**b** and thiazole-2(3*H*)-thiones **2a**–**b** (and also **3a**–**b**) are similar in terms of shape and energy. These similarities are not visible from the experimental spectra probably due to the fact that $n_{CS}\rightarrow\pi^*_{CS}$ (for **1**) and $n_{CS}\rightarrow\pi^*_{SCS}$ excitations (for

2 and **3**) are associated with very small intensities. The major differences in electronic excitations between the two groups of heterocyclic thiones relate to the $\pi\rightarrow\pi^*$-type transitions. Most of the excited states in thiazole-2(3*H*)-thiones are determined by more than one significant configuration, whereas for pyridinethiones **1** one configuration suffices in order to adequately describe the nature of an excited state in the spectral region of $\lambda > 280$ nm. This aspect originates from a very small energy gap between π_{SCS} and n_{CS} ($\Delta\varepsilon <$ 0.1 eV for **2b**) on one side and the $LUMO_{+1}$ and $LUMO_{+2}$ on the other side. In pyridinethione **1b**, the two occupied orbitals as well as the two virtual orbitals, are separated by larger energy differences.

4. UV/Vis Spectra of *N*-(Methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (5b)

(i) Experimental Background. The absorption band at the low energy end in the experimental UV/Vis spectra of *N*-hydroxy- and *N*-methoxythiazole-2(3*H*)-thiones shows a progressive red shift along the series of 4-/5-substituents 4-(p-ClC_6H_4)/5-H < 4-(CH_3)/5-H < 4-(CH_3)/5-(CH_3) < 4-(CH_3)/5-(p-$H_3COC_6H_4$) ≈ 4-(CH_3)/5-[3,4-$(H_3CO)_2C_6H_3$] (Table 1).

The experimental electronic spectrum of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5a** shows three broad and featureless bands at λ_{exp} = 334, 255, and 203 nm in a 2.3:1:4.5 intensity ratio (in EtOH). The UV/Vis absorptions for *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5b** are located at λ_{exp} = 335, 258, and 228 nm (4.6:1:2.5 intensity ratio, in EtOH). The bathochromic shift exerted by the *p*-methoxyphenyl group at position 5 onto the energetically lowest band is noteworthy since it is the basis for an application of thiazolethiones **5** in visible light-induced photoreactions.

(ii) FMOs in *N*-Methoxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione 5b. Three filled and three unoccupied levels are relevant in order to assign the calculated electronic spectrum of thione **5b** in the range of $\lambda \geq 334$ nm. The $HOMO_{-2}$ is delocalized over the whole molecule and may be classified as a combination of a thiazolethione π_{SCS}-orbital and a π-type orbital of the *p*-methoxyphenyl substituent. The $HOMO_{-1}$ is destabilized by 0.2 eV but otherwise similar in shape as the n_{CS} in thiazolethione **2b**. The HOMO corresponds to the π_{SCS} orbital in **2b**, but it is destabilized by 0.4 eV and exhibits additional density predominantly located at the *ortho*- and *para*-position of the *p*-methoxyphenyl entity in **5b**. The LUMO in **5b** is a combination of the π_{SCS} in **2b**,with additional contributions from the *para*- and *ortho*-position of the *p*-methoxyphenyl substituent, and a π-type interaction between C5 and C_{ipso}. The $LUMO_{+1}$ exhibits significant density at the *ortho*- and *meta*-position of the *p*-methoxyphenyl entity and a lone pair from the endocyclic sulfur atom. Such linear combinations are possible for the equilibrium structure on the basis of a tilt angle of φ = 41.3° between the aryl and the thiazolethione ring. The $LUMO_{+2}$ in **5b** resembles the π^*_{SCS} orbital of the parent thione **2b** with additional contributions from orbitals of the *ortho*- and *para*-carbon atoms of the *p*-methoxyphenyl group. It should be kept in mind that additional occupied and virtual orbitals besides those outlined above contribute to the calculated UV/Vis spectrum **5b** in the region of $250 < \lambda < 334$ nm. Their orbital shapes shall, however, not be addressed in a similar explicit way due to their complexity.

(iii) UV/Vis Excitations in *N*-Methoxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione 5b. The UV/Vis spectrum of thiazolethione **5b** (equilibrium geometry, φ = 41.3°) displays four stronger bands at λ_{calc} = 385, 334, 266, and 265 nm. The excitation at λ_{calc} = 385 nm is attributed to a $\pi_{SCS}\rightarrow\pi^*_{SCS}$ transition, which is located at 325 nm for *N*-methoxythiazole-2(3*H*)-thione (**2b**). The calculated red shift of 60 nm originates predominantly from a destabilization of π_{SCS} of 0.4 eV in **5b**. An observed increase in oscillator strength of this excitation from 0.052 in **2b** to 0.176 in **5b** may be caused by the presence of additional configurations (for **2b**: $n_{CS}\rightarrow LUMO_{+1}$ with a weight of 0.280; for **5b**: $\pi_{SCS}\rightarrow LUMO_{+2}$, with a weight of 0.115). The transition at λ_{calc} = 334 nm originates from a multicharacter excitation ($\pi_{SCS}\rightarrow LUMO_{+2}$, $HOMO_{-2}\rightarrow\pi^*_{SCS}$, and $n_{CS}\rightarrow LUMO_{+2}$). In a similar way, the two intense bands at λ_{calc} = 266 and 265 nm, are due to three major characters each. In addition, the calculated spectrum of **5b** further displays fourteen weak bands. The energetically lowest transition at λ_{calc} = 409 nm is attributed to a $n_{CS}\rightarrow\pi^*_{SCS}$ transition. This excitation is red-shifted by 26 nm, if compared to the equivalent band in the unsubstituted *N*-methoxythiazolethione **2b**, or 32 nm versus the corresponding excitation in 4-methyl derivative **3b** (Tables 5 and 6). The observed bathochromic shift may be explained by a destabilization of the n_{CS} orbital in going from **2b** to **5b**. The weak $\pi_{SCS}\rightarrow\pi^*_{sub}$ excitation at λ_{calc} = 392 nm has been assigned to a charge transfer from the endocyclic sulfur atom to the aromatic substituent.[42] The band at λ_{calc} = 372 nm is dominated by a $n_{CS}\rightarrow\pi^*_{sub}$ transition. The character and weight of all succeeding higher energy transitions are given in Table 7. A similar explicit assignment of transitions were in the latter two instances difficult to attain, since the bands generally exhibit contributions from three configurations and are associated with transitions between orbitals of complex shape.

(iv) Assignment of the UV/Vis Band in 5-Aryl-4-methylthiazolethiones. On the basis of spectral intensities and the above mentioned orbital analysis, the band located at λ_{exp} = 335 nm for thione **5b** is correlated with the multicharacter transition at λ_{calc} = 334 nm ($\pi\rightarrow LUMO_{+2}$, $HOMO_{-2}\rightarrow\pi^*_{SCS}$, $n_{CS}\rightarrow LUMO_{+2}$). The band located at λ_{exp} = 258 nm has been assigned to the two excitations located at λ_{calc} = 266 and 265 nm. Due to the complexity of transitions occurring at the high energy end of the spectrum it was refrained from searching for equivalent excitations that would characterize the third band located at λ_{exp} = 228 nm in the experimental spectrum of thione **5b**. Based on the close structural analogy, a similar assignment of experimentally observed bands to electronic transitions should be valid for the *N*-oxy-substituted 5-(dimethoxyphenyl)-4-methylthiazolethiones **6a**–**b**.

(v) Spectral Changes upon Rotation of the *p*-Methoxyphenyl Substituent in Thiazolethione (5b). A calculated barrier of 8.0 kJ·mol^{-1} points to an almost unhindered rotation of the *p*-methoxyphenyl group about the C5,C$_{ipso}$ bond at room temperature. This torsional movement alters energies of n_{CS}, π_{SCS}, π^*_{SCS}, π^*_{sub}, LUMO$_{+2}$, characters, and intensities of electronic excitations in thione **5b**. For example, a 90° variation of φ changes the position, intensity, and $\pi_{SCS}\rightarrow\pi^*_{SCS}$ character of an intense band that theory predicts to be located at λ_{calc} = 385 nm (f = 0.176, φ = 41.3°) [for φ = 0°: λ_{calc} = 397 nm (f = 0.344), for φ = 90°: 388 nm ($f = 7\cdot10^{-3}$) (see also Figure 8 and the Supporting Information)]. Since a planar arrangement (φ = 0°) is 4.7 kJ·mol^{-1} higher in energy than the orthogonal configured structure of thione **5b** (φ = 90°), the energy profile for the variation of dihedral angle φ is asymmetric thus leading to a more significant population of conformers with torsion angles $41° < \varphi < 90°$ than in between $0° < \varphi < 41°$. The spectral changes that are associated with a variation of the dihedral angle φ therefore should lead to a decrease in the intensity of this band thus offering an explanation for the fact that this absorption has so far not been detected in the experimental UV/Vis spectrum of *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5b**.

Conclusions

The experimental UV/Vis spectra of pyridine-2(1*H*)-thiones **1a**–**b** and the thiazole-2(3*H*)-thiones **2**–**7** have been assigned on the basis of time-dependent density functional theory. The information from the present study is essential in order to guide a future rational design of new derivatives of *N*-alkoxythiazole-2(3*H*)-thiones, to serve as oxygen radical precursors for specific purposes in photochemistry and photobiology. In detail, three major results were obtained:

(i) The UV/Vis bands in the experimental spectra of the pyridine-2(1*H*)-thiones **1**, 4-methylthiazolethiones **3**, and 5-(*p*-methoxyphenyl)-4-methylthiazolethiones **5** have been assigned to $\pi\rightarrow\pi^*$-type transitions.

(ii) (TD)RI-BLYP/TZVPP//RI-BLYP/SVP-calculated energetically lowest transitions agree within ±5 nm to the experimental data for thiazole-2(3*H*)-thiones (spectra in EtOH). The correlation is less satisfactory for the pyridinethiones **1a**–**b**, where the computed transitions are comparatively strongly dependent on the selected computational method (BLYP/TZVPP versus B3LYP/TZVP).

(iii) The orbital shapes, number of relevant orbitals required for an assignment of computed spectra, and characters of the calculated bands increase in complexity in going from pyridine-2(1*H*)-thiones **1a**–**b** via thiazole-2(3*H*)-thiones **2a**–**b**, 4-methylthiazole-2(3*H*)-thiones **3a**–**b** to 4-methyl-5-(*p*-methoxyphenyl)thiazolethiones **5a**–**b**. According to theory, these differences originate in particular from contributions of the endocyclic sulfur atom and effects of substituents such as a *p*-methoxyphenyl group located in position 5 of thiazole-2(3*H*)-thiones.

Computational Details

All calculations were performed using the TURBOMOLE program package.[43] Structures were optimized using the BLYP density functional[27] in combination with the Resolution of Identity approximation (RI-BLYP) and the SVP basis,[28] which is implemented in TURBOMOLE. The electronic excitations were computed using the time dependent (TD)RI-BLYP density functional in association with the TZVPP (triple-zeta-valence basis set with double polarization functions) and the (TD)RI-B3LYP/TZVP method (TZVP = triple-zeta-valence basis set including polarization functions).[31,32] (TD)RI-BLYP/TZVPP-calculated UV/Vis spectra of the φ = 0 and 90° rotamers of *N*-methoxy-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5b** and (TD)RI-B3LYP/TZVP-computed UV/Vis spectra of pyridinethiones **1a**–**b** and thiazolethiones **2**, **3**, and **5** have been enclosed in the Supporting Information.

Experimental Section

General Remarks

For spectroscopic equipment and general laboratory practice see ref.[22,44] UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer at 20 °C using analytical grade EtOH or *n*-hexane as solvents in 1-cm quartz cuvettes. *N*-hydroxypyridine-2(1*H*)-thione (**1a**),[45]*N*-methoxypyridine-2(1*H*)-thione (**1b**),[16]*N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**),[20]*N*-hydroxy-4,5-dimethylthiazole-2(3*H*)-thione (**4a**), *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**), *N*-hydroxy-5-(3,4-dimethoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**6a**), *N*-hydroxy-4-(*p*-chlorophenyl) thiazole-2(3*H*)-thione (**7a**)[22] were prepared according to, or in extension of, published procedures.[21,22,46]*N*-hydroxythiazole-2(3*H*)-thione tetraalkylammonium salts were prepared from the parent thiohydroxamic acids according to ref.[23]

Synthesis of *N*-Methoxythiazole-2(3*H*)-thiones. General Procedure: A solution of a *N*-hydroxythiazole-2(3*H*)-thione tetraalkylammonium salt (2.2 mmol) in anhydrous DMF (5 mL) was treated at 20 °C under argon atmosphere with a solution of methyl *p*-toluenesulfonate (2.2 mmol) in anhydrous DMF (2 mL). The mixture was stirred for 4–6 d at 20 °C in the dark. Afterwards, it was poured into a mixture of H_2O/*tert*-butyl methyl ether (MTB) [30 mL, 1:1 (v/v)]. The phases were separated and the aqueous layer was extracted with MTB (3 × 20 mL). The combined organic phases were washed successively with a satd. aq. $NaHCO_3$ solution (10 mL) and brine (10 mL). The solution was dried ($MgSO_4$) and the solvent removed under reduced pressure to furnish an oil that was purified either by column chromatography [SiO_2, petroleum ether/Et_2O], or by recrystallization from petroleum ether/Et_2O to afford analytically pure thiones **3b**–**7b**.

***N*-(Methoxy)-4-methylthiazole-2(3*H*)-thione (3b):** 102 mg (63%) from *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**) [147 mg (1.0 mmol)], NEt_4OH [1.50 mL of a solution in MeOH, (25% w/w, equivalent to 1.0 mmol of base)], and methyl *p*-toluenesulfonate [187 mg (1.0 mmol)]; yellow oil, R_f = 0.35 [SiO_2, petroleum ether/Et_2O = 2:1 (v/v)]. UV/Vis (EtOH): λ_{max} (lg ε) = 320 nm (4.09). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.29 (d, J = 1.2 Hz, 3 H, CH_3), 4.16 (s, 3 H, OCH_3), 6.16 (q, J = 1.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.2 (CH_3), 53.5 ($NOCH_3$), 102.1 (5-C), 137.0 (4-C), 180.5 (C=S). MS (70 eV, EI): m/z (%) = 161 [M^+] (100), 131

[$C_4H_5NS_2^+$] (32), 86 [$C_3H_4NS^+$] (50). $C_5H_7NOS_2$ (161.2): calcd. C 37.25, H 4.38, N 8.69, S 39.72; found: C 37.58, H 4.48, N 8.56, S 39.05.

***N*-(Methoxy)-4,5-dimethylthiazole-2(3*H*)-thione (4b):** 106 mg (68%) from *N*-hydroxy-4,5-dimethylthiazole-2(3*H*)-thione (**4a**) [144 mg (0.89 mmol)], NBu_4OH [0.71 mL of a solution in MeOH, (25% w/w, equivalent to 0.89 mmol of base)], and methyl *p*-toluenesulfonate [167 mg (0.89 mmol)]; yellow solid, m.p. 53–55 °C, $R_f = 0.45$ [SiO_2, petroleum ether/Et_2O = 2:1 (v/v)]. UV/Vis (EtOH): λ_{max} (lg ε) = 323 nm (4.12), 244 (3.38). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.12 (q, 3 H, J^5 = 0.9 Hz, CH_3), 2.19 (q, 3 H, J^5 = 0.9 Hz, CH_3), 4.13 (s, 3 H, $NOCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 11.3 (CH_3), 12.4 (CH_3), 63.9 ($NOCH_3$), 115.0 (5-C), 132.6 (4-C), 178.6 (C=S). MS (70 eV, EI): *m*/*z* (%) = 175 [M^+] (100), 144 [$M^+ - OCH_3$] (12), 85 [$C_4H_6S^+$] (44). $C_6H_9NOS_2$ (175.3): calcd. C 41.12, H 5.18, N 7.99, S 36.59; found C 41.24, H 5.24, N 8.06, S 36.91.

***N*-(Methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (5b):** 137 mg (64%) from *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) [202 mg (0.80 mmol)], NBu_4OH [0.64 mL of a solution in MeOH, (equivalent to 0.80 mmol of base)], methyl *p*-toluenesulfonate[150 mg (0.80 mmol)]; colorless powder, m.p. 102–104 °C, $R_f = 0.40$ [SiO_2, petroleum ether/Et_2O = 2:1(v/v)]. UV/Vis (EtOH) λ_{max} (lg ε) = 335 nm (4.31), 258 (3.78), 228 (4.18). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.35 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.20 (s, 3 H, $NOCH_3$), 6.95 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.24 (d, *J* = 8.8 Hz, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.0 (CH_3), 56.5 (OCH_3), 64.1 ($NOCH_3$), 114.6, 119.4, 122.5, 129.9, 131.8, 160.0 (Ar-C), 178.6 (C=S). MS (70 eV, EI): *m*/*z* (%) = 267 [M^+] (100), 236 [$M^+ - OCH_3$] (36), 178 [$C_{10}H_{10}SO^+$] (41), 163 [$C_9H_7SO^+$] (19). $C_{12}H_{13}NO_2S_2$ (267.4): calcd. C 53.91, H 4.90, N 5.24, S 23.99; found: C 53.82, H 4.75, N 4.93, S 24.21.

***N*-(Methoxy)-5-(3,4-dimethoxyphenyl)-4-methylthiazole-2(3*H*)-thione (6b):** 112 mg (78%) from *N*-hydroxy-5-(3,4-dimethoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**6a**) [135 mg (0.48 mmol)], NBu_4OH [0.38 mL of a solution in MeOH (equivalent to 0.48 mmol of base)], methyl *p*-toluenesulfonate [90 mg (0.48 mmol)]; yellow solid, m.p. 105–107 °C, $R_f = 0.35$ [SiO_2, petroleum ether/Et_2O = 2:1(v/v)]. UV/Vis (EtOH) λ_{max} (lg ε) = 335 nm (4.45), 232 (4.23), 208 (4.69). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.36 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.22 (s, 3 H, $NOCH_3$), 6.78 (d, *J* = 1.9 Hz, 1 H, Ar-H), 6.89 (d, *J* = 1.9 Hz, 1 H, Ar-H), 6.90 (s, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.4 (CH_3), 56.4 (OCH_3), 56.5 (OCH_3), 64.1 ($NOCH_3$), 111.7, 112.8, 119.9, 121.8, 123.1, 132.4, 149.7, 150.1 (Ar-C), 179.0 (C=S). MS (70 eV, EI): *m*/*z* (%) = 297 [M^+] (100), 266 [$M^+ - OCH_3$] (51), 235 [$C_{10}H_7NS_2^+$] (59), 176 [$C_{10}H_{10}SO^+$] (18). $C_{13}H_{15}NO_3S_2$ (297.4): calcd. C 52.50, H 5.08, N 4.71, S 21.56; found: C 52.64, H 4.97, N 4.81, S 21.68.

***N*-(Methoxy)-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione (7b):** 160 mg (62%) from *N*-hydroxy-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione (**7a**) [243 mg (1.0 mmol)], NBu_4OH [0.80 mL of a solution in MeOH (25% w/w, equivalent to 1.0 mmol of base)], and methyl *p*-toluenesulfonate [187.0 mg (1.0 mmol)]; colorless powder, m.p. 115–117 °C, $R_f = 0.35$ [SiO_2, petroleum ether/Et_2O = 3:2 (v/v)]. UV/Vis (EtOH) λ_{max} (lg ε) = 317 nm (4.40), 232 (4.46). ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.85 (s, 3 H, $NOCH_3$), 6.53 (s, 1 H, CH), 7.46 (s, *J* = 6.7 Hz, 2 H, Ar-H), 7.55 (s, *J* = 6.7 Hz, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 63.9 ($NOCH_3$), 105.9 (5-C), 126.8, 129.3, 129.5, 136.8, 139.9 (Ar-C), 181.0 (C=S). MS (70 eV, EI): *m*/*z* (%) = 257 [M^+] (10), 226 [$M^+ - OCH_3$] (64), 191 [$M^+ - Cl - OCH_3$] (30), 168 [$C_8H_5ClS^+$] (100), 133 [$C_8H_5S^+$] (20).– $C_{10}H_8NOS_2Cl$ (257.8): calcd. C 46.60, H 3.13, N 5.43, S 24.88; found: C 46.68, H 3.21, N 5.59, S 24.52.

X-ray Crystallographic Studies: Suitable crystals were grown by slowly concentrating a solution of *N*-hydroxy-4-methyl-5-(*p*-methoxyphenyl)thiazole-2(3*H*)-thione (**5a**)in petroleum ether/CH_2Cl_2 [2:1 (v/v)] at 20 °C. CCDC-250006 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. For details on the crystallographic investigation see the Supporting Information.

Acknowledgments

This work was funded by the Deutsche Forschungsgemeinschaft (grants Ha 1705/5-2 and Graduiertenkolleg 690, Elektronendichte – Theorie und Experiment). Further, we express our gratitude to all our colleagues from the former Graduiertenkolleg 690 for helpful discussions and to Prof. U. Holzgrabe for providing access to the UV/Vis spectrophotometer.

---

[1] The following abbreviations have been used: ΔE = transition energies [nm]; FMO = frontier molecular orbital; *f* = oscillator strength; HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; MTB = methyl *tert*-butyl ether. The torsional angle φ = C4–C5—C_{ipso}–C_{ortho} (for atom notation refer to Figure 8) refers to the tilt between the heterocyclic and the aromatic entity in 5-aryl-substituted thiazole-2(3*H*)-thiones such as **5a** and **5b**. The term *character* in the Tables abbreviates *characterization of contributing configurations.* All configurations are characterized by the given excitations, which describe their differences in comparison to the corresponding electronic ground states. – *Orbital nomenclature: (i) bonding orbitals*: $HOMO_{-n}$ = orbital located *n* energetic levels (*n* = 1, 2, 3, ...) below the HOMO; π_{CS} = orbital with major contributions from the thiocarbonyl π-orbital; π_{SCS} = occupied orbital with major contributions from the S–C=S entity; *(ii) nonbonding orbitals*: n_{CS} = nonbonding occupied orbital located predominantly at a thiocarbonyl sulfur atom; *(iii) virtual orbitals*: $LUMO_{+n}$ = orbital located *n* energetic levels (*n* = 1, 2, 3, ...) above the LUMO; π^*_{ring} = orbital that extends over the heterocyclic ring and exhibits contributions from the thiocarbonyl sulfur atom; π^*_{CS} = combination of π* orbitals of a thiocarbonyl-group and a heterocyclic ring; π^*_{SCS} = unoccupied orbital with major contributions from the S–C–S entity; π^*_{sub} = orbital of low symmetry obtained from mixing of orbitals with π-symmetry from an aryl substituent and those of σ-symmetry from a thiazole-2(3*H*)-thione entity.

[2] J. Hartung, T. Gottwald, K. Špehar, *Synthesis* **2002**, 1469–1498.

[3] a) W. Adam, J. Hartung, H. Okamoto, C. R. Saha-Möller, K. Špehar, *Photochem. Photobiol.* **2000**, *72*, 619–624; b) W. Adam, J. Hartung, H. Okamoto, S. Marquardt, W. M. Nau, U. Pischel, C. R. Saha-Möller, K. Špehar, *J. Org. Chem.* **2002**, *67*, 6041–6049; c) W. Adam, G. N. Grimm, C. R. Saha-Möller, *Free Rad. Biol. Med.* **1998**, *24*, 234–238; d) B. M. Aveline, R. W. Redmond, *J. Am. Chem. Soc.* **1999**, *121*, 9907–9985; e) B. M. Aveline, R. W. Redmond, *Photochem. Photobiol.* **1998**, *68*, 266–275; f) W. Adam, G. N. Grimm, S. Marquardt, C. R. Saha-Möller, *J. Am. Chem. Soc.* **1999**, *121*, 1179–1185.

[4] For recent photobiological applications of thiocarbonyl compounds: a) M. Borges, A. Romao, O. Matos, C. Marzano, S. Caffieri, R. S. Becker, A. L. Macanita, *Photochem. Photobiol.***2002**, *75*, 97–106; b) C. Miolo, S. Caffieri, D. Vedaldi, F. Baccichetti, C. Marzano, V. Lucchini, P. Rodighiero, F. Dall'Acqua, *Farmaco* **1999**, *54*, 134–144.

[5] a) J. Hartung, F. Gallou, *J. Org. Chem.* **1995**, *60*, 6706–6716; b) J. Boivin, E. Crépon, S. Z. Zard, *Tetrahedron Lett.* **1990**, *31*, 6869–6872.

[6] a) J. Hartung, R. Kneuer, *Tetrahedron: Asymmetry* **2003**, *14*, 3019–3031; b) J. Hartung, R. Kneuer, S. Laug, P. Schmidt, K. Špehar, I. Svoboda, H. Fuess, *Eur. J. Org. Chem.* **2003**, 4033–4052; c) J. Hartung, T. M. Kopf, R. Kneuer, P. Schmidt, *C. R. Acad. Sci. Ser. II: Chim.* **2001**, 649–666.

[7] a) J. Hartung, *Eur. J. Org. Chem.* **2001**, 619–632; b) A. L. J. Beckwith, B. P. Hay, *J. Am. Chem. Soc.* **1988**, *110*, 4115–4416.

[8] J. Hartung, T. Gottwald, K. Špehar, *Synlett* **2003**, 227–229.

[9] A. Maciejewski, R. P. Steer, *Chem. Rev.* **1993**, *93*, 67–98.

[10] A. Albini, M. Alpegiani, *Chem. Rev.* **1984**, *84*, 43–71.

[11] a) J. Tatchen, M. Waletzke, M. C. Marian, S. Grimme, *Chem. Phys.* **2001**, *264*, 245–254; b) J. D. Coyle, *Tetrahedron* **1985**, *41*, 5393–5425.

[12] a) D. C. Moule, E. C. Lim, *J. Phys. Chem. A* **2002**, *106*, 3072–3076; b) R. P. Steer, V. Ramamurhty, *Acc. Chem. Res.* **1988**, *21*, 380–386; c) P. de Mayo, *Acc. Chem. Res.* **1976**, *9*, 52–59; d) N. J. Turro, V. Ramamurthy, W. Cherry, W. Farneth, *Chem. Rev.* **1978**, *78*, 125–145.

[13] a) O. Korver, J. U. Veenland, Th. J. De Boer, *Rec. Trav. Chim.* **1965**, *84*, 289–303; b) R. Mayer, J. Morgenstern, J. Fabian, *Angew. Chem.* **1964**, *76*, 157–196; c) G. Oster, L. Citarel, M. Goodman, *J. Am. Chem. Soc.* **1962**, *84*, 703–706.

[14] M. Petiau, J. Fabian, *J. Mol. Struct. (Theochem.)* **2001**, *538*, 253–260.

[15] For related work see: a) M. A. El-Kemary, M. E. El-Khouly, O. Ito, *J. Photochem. Photobiol. A* **2000**, *137*, 105–113; b) A. Puszko, *Chem. Pap.* **1998**, *52*, 29–33.

[16] J. Hartung, M. Hiller, M. Schwarz, I. Svoboda, H. Fuess, *Liebigs Ann.* **1996**, 2091–2097.

[17] E. K. U. Gross, W. Kohn, *Adv. Quantum Chem.* **1990**, *21*, 255–291.

[18] J. Hartung, T. Gottwald, R. Kneuer, *Synlett* **2001**, 749–751.

[19] a) D. H. R. Barton, S. I. Parekh, *Half a Century of Free Radical Chemistry*, Cambridge, University Press, Cambridge, **1993**; b) W. B. Motherwell, C. Imboden, in: *Radicals in Organic Synthesis* (Eds.: P. Renaud, M. P. Sibi), Vol. 1, 109–134, Wiley-VCH, Weinheim, **2000**; c) D. Crich, L. Quintero, *Chem. Rev.* **1989**, *89*, 1413–1432.

[20] D. H. R. Barton, D. Crich, G. Kretzschmar, *J. Chem. Soc., Perkin Trans. 1* **1986**, 39–53.

[21] T. Gottwald, J. Hartung, K. Špehar, I. Svoboda, H. Fuess, manuscript in preparation.

[22] J. Hartung, M. Schwarz, I. Svoboda, H. Fuess, M. T. Duarte, *Eur. J. Org. Chem.* **1999**, 1275–1290.

[23] J. Hartung, R. Kneuer, M. Schwarz, I. Svoboda, H. Fuess, *Eur. J. Org. Chem.* **1999**, 97–106.

[24] K. Špehar, Ph. D. Dissertation, University of Würzburg, **2004**.

[25] U. Wille, C. Jargstorff, *J. Chem. Soc., Perkin Trans. 1* **2002**, 1036–1041.

[26] a) E. Shaw, J. Bernstein, K. Losee, W. A. Lott, *J. Am. Chem. Soc.* **1950**, *72*, 4362–4364; b) E. Shaw, *J. Am. Chem. Soc.* **1949**, *71*, 67–73.

[27] a) A. D. Becke, *Phys. Rev. B* **1988**, *17*, 3098–3100; b) C. Lee, Y. Weitao, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[28] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.

[29] Selected geometrical parameter for *N*-hydroxypyridine-2(1*H*)-thione (**1a**) (X-ray diffraction N3–C2 = 1.367(3) Å, C2–C3 = 1.400(4) Å, C3–C4 = 1.349(4) Å, C4–C5 = 1.372(5) Å, C5–C6 = 1.344(4) Å, N1–O8 = 1.377(3) Å, C2–S7 = 1.684(2) Å, C2–N1–C6 = 125.5(2)°, C3–C2–N1 = 113.5(2)°, C2–C3–C4 = 122.1°, C3–C4–C5 = 120.8°.[23]

[30] Selected geometrical parameter for *N*-[*trans*-(*tert*-butylcyclohexyl)-4-oxy]pyridine-2(1*H*)-thione (X-ray diffraction): C2–C3 = 1.411(6) Å, C3–C4 = 1.338(6) Å, C4–C5 = 1.392(7) Å, C5–C6 = 1.344(6) Å, C3–C2–N1 = 112.4(4)°, C2–N1–C6 = 125.3(3)°, C2–N1–O8–C9 = 99.9(3)°.[16]

[31] R. Bauernschmitt, M. Häser, O. Treutler, R. Ahlrichs, *Chem. Phys. Lett.* **1997**, *264*, 573–578.

[32] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[33] Selected geometrical parameter for *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**3a**): S1–C2 = 1.715(10) Å, C2–N3 = 1.330(12) Å, N3–C4 = 1.392(12) Å, C4–C5 = 1.342(14) Å, C5–S1 = 1.712(10) Å, C2–S7 = 1.687(10) Å, N3–O8 = 1.380(10) Å, C2–N3–C4 = 118.1(8)°, S1–C2–N3 = 107.9(7)°, C5–S1–C2 = 92.2(5)°, N3–C4–C5 = 109.5(8)°.[34]

[34] A. D. Bond, N. Feeder, S. T. Teat, W. Jones, *Tetrahedron* **2000**, *56*, 6617–6624.

[35] J. Hartung, M. Schwarz, I. Svoboda, H. Fuess, *Acta Crystallogr., Sect. C* **2003**, *59*, 682–684.

[36] Selected geometrical parameter for 2-(4-methyl-2-thioxo-2,3-dihydrothiazol-3-yloxy)propanoate: S1–C2 = 1.724(2) Å, C2–N3 = 1.352(2) Å, N3–C4 = 1.399(2) Å, C4–C5 = 1.332(3) Å, C5–S1 = 1.724 (2) Å, C2–S7 = 1.658(2) Å, N3–O8 = 1.385(2) Å, C2–N3–C4 = 117.8(1)°, S1–C2–N3 = 107.0(1)°, C5–S1–C2 = 92.50(8)°, N3–C4–C5 = 110.2(2)°.[35]

[37] A. L. Speck, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[38] The uncertainty of relative energies in accurate quantum chemical calculations usually exceeds $1\ \mathrm{kJ{\cdot}mol^{-1}}$. The computed data are reported in the given accuracy in order to indicate that the relative energy of the two compounds is similar but not identical.

[39] Comparison BLYP data versus spectral location of experimentally determined absorption bands: for **3a**: $\lambda_{\mathrm{calc}} = 316$ nm, $\lambda_{\mathrm{exp}} = 315$ nm; for **3b**: $\lambda_{\mathrm{calc}} = 315$ nm, $\lambda_{\mathrm{exp}} = 320$ nm, for **5a**: $\lambda_{\mathrm{calc}} = 333$ nm (see Supporting Information), $\lambda_{\mathrm{exp}} = 334$ nm; for **5b**: $\lambda_{\mathrm{calc}} = 334$ nm, $\lambda_{\mathrm{exp}} = 335$ nm.

[40] D. Tozer, R. Amos, N. C. Handy, B. Roos, L. Serrano-Andrés, *Mol. Phys.* **1999**, *97*, 859–868.

[41] J. L. Esker, M. Newcomb, *Adv. Heterocycl. Chem.* **1993**, *58*, 1–45.

[42] The failure of TD-DFT for the description of CT is considered to originate from an inadequate asymptotic behavior of the XC-potential (A. Dreuw, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007–4016). The computed CT transitions in the present work, however, exhibit almost vanishing oscillator strenghths and therefore have little effect onto the interpretation of the calculated UV/Vis spectra of aryl-substituted thiazole-2(3*H*)-thiones.

[43] R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehring, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häsler, H. Horn, H. Huber, U. Huniar, M. Kattaneck, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneder, O. Treutler, M. v. Arnim, F. Weigend, P. Weis, *TURBOMOLE*, University of Karlsruhe, Germany, since 1988.

[44] W. L. F. Armarego, D. D. Perrin, in: *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, **1997**.

[45] M. Newcomb, T. M. Deeb, D. J. Marquardt, *Tetrahedron* **1990**, *46*, 2317–2328.

[46] J. Hartung, M. Schwarz, *Org. Synth.* **2003**, *79*, 228–234.

Received September 22, 2004