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SUPPORTING INFORMATION

Title: 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

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Ref. No.: O040674

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1 General Remarks

(i) The numbering of compounds and the orbital notation is consistent with the information provided in the associated publication.

(ii) RI-BLYP/SVP//RI-BLYP/SVP-calculated energies *E* are provided in a.u. The electronic spectra were computed on a (TD)RI-BLYP/TZVPP//RI-BLYP/SVP (Section 3 and 5), or on a (TD)RI-B3LYP/TZVP//RI-BLYP/SVP level of theory (Section 4). The characters of the electronic excitations are indicated by their contributing configurations. The reported configurations have been restricted to those with a weight < 10 %.

2 X-Ray Crystallographic Data for *N*-(Hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (5a)[1,2]

The data for *N*-(hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) were collected on an Oxford Diffraction Xcalibur CCD with Sapphir CCD Detector [1] using Mo-K_α radiation (λ = 0.71073 Å) and have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-250006 (excluding structure factors). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

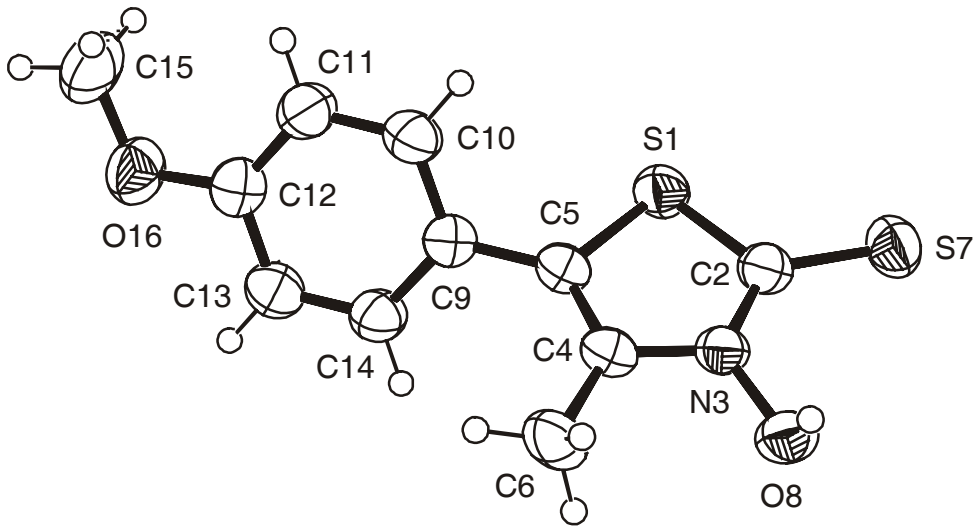


Figure 2.1. View of *N*-(hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) in the solid state. Thermal ellipsoids are drawn at the 50 % level. Hydrogen atoms are depicted as small circles of an arbitrary radius.[3]

Table 2.1. Crystallographic data and data collection parameters for thiazolethione **5a**

Empirical formula	$C_{11}H_{11}NO_2S_2$
Formula weight [g/mol]	253.33
Temperature [K]	299(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	*P*2/c
a [Å]	7.654 (1)
b [Å]	10.975(2)
c [Å]	14.201(2)
α [°]	90
β [°]	96.12 (1)
γ [°]	90
V [Å^3]	1186.1(3)
Z	4
$\rho_{calcd.}$ [mg/m^3]	1.419
μ(Mo-K_a) [mm^{-1}]	0.432
F(000)	528
Crystal size [mm]	0.80×0.64×0.60
Θ range [°]	4.61 to 26.36
Index ranges	$-9 \le h \le 9$
	$-13 \le k \le 13$
	$-14 \le l \le 17$
Reflections collected	3416
Independent reflections	2208
R (int.)	0.0233
Data/restraints/parameters	2208 / 0 / 148
Goodness-of-fit on F^2	1.080
Final *R* indices [$I > 4\sigma(I)$][a]	$R1 = 0.0529$, $wR2 = 0.1543$
R indices (all data)[a]	R1 = 0.0662, *wR*2 = 0.1696
Largest diff. peak and hole [eÅ^{-3}]	0.571 and –0.258

[a] *R* values defined as $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2)+(g_1P)^2+g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0)+2F_c^2]$.

The structure was solved with SHELXS-97[2] and refined by full-matrix least squares methods against F^2 (SHELXL-97).[2] All hydrogen atoms were positioned geometrically idealized and refined using a riding model.

3 UV/Vis Spectra, Relevant Orbitals, and Assignment of Bands of *N*-(Hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (5a) (BLYP, B3LYP)

Table 3.1. (TD)RI-BLYP/TZVPP//RI-BLYP/SVP-computed UV/VIS spectrum and assignment of the bands *N*-(hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a)** (equilibrium geometry, $\phi = 41.8\ °$)[a]

transition	ΔE [nm]	f	character	weight
1	389	3×10^{-3}	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.968
2	385	0.302	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.834
			$\pi_{SCS} \rightarrow$ LUMO$_{+2}$	0.106
3	357	0.017	$n_{CS} \rightarrow \pi^*_{SCS}$	0.969
4	333	0.083	$\pi_{SCS} \rightarrow$ LUMO$_{+2}$	0.501
			HOMO$_{-2} \rightarrow \pi^*_{SCS}$	0.354
5	323	0.012	$n_{CS} \rightarrow \pi^*_{sub}$	0.958
6	311	1×10^{-3}	$\pi_{SCS} \rightarrow$ LUMO$_{+3}$	0.897
7	295	0.0267	$n_{CS} \rightarrow$ LUMO$_{+2}$	0.915
8	285	4×10^{-3}	HOMO$_{-2} \rightarrow \pi^*_{SCS}$	0.406
			$\pi_{SCS} \rightarrow$ LUMO$_{+2}$	0.281
9	282	7×10^{-3}	HOMO$_{-2} \rightarrow \pi^*_{sub}$	0.708
			HOMO$_{-4} \rightarrow \pi^*_{SCS}$	0.226
10	275	0.015	$\pi_{SCS} \rightarrow$ LUMO$_{+4}$	0.446
			HOMO$_{-3} \rightarrow \pi^*_{SCS}$	0.351
			HOMO$_{-2} \rightarrow$ LUMO$_{+2}$	0.170
11	265	0.007	$\pi_{SCS} \rightarrow$ LUMO$_{+5}$	0.915
12	263	0.020	$n_{CS} \rightarrow$ LUMO$_{+3}$	0.513
			HOMO$_{-2} \rightarrow$ LUMO$_{+2}$	0.143
			HOMO$_{-4} \rightarrow \pi^*_{SCS}$	0.109
13	261	0.076	$\pi_{SCS} \rightarrow$ LUMO$_{+4}$	0.242
			$n_{CS} \rightarrow$ LUMO$_{+3}$	0.230
			HOMO$_{-3} \rightarrow \pi^*_{SCS}$	0.134
14	259	0.050	HOMO$_{-4} \rightarrow \pi^*_{SCS}$	0.377
			HOMO$_{-3} \rightarrow \pi^*_{sub}$	0.145
15	257	0.094	HOMO$_{-3} \rightarrow \pi^*_{SCS}$	0.344
			HOMO$_{-2} \rightarrow$ LUMO$_{+2}$	0.311
			$n_{CS} \rightarrow$ LUMO$_{+3}$	0.121
16	256	0.010	HOMO$_{-3} \rightarrow \pi^*_{sub}$	0.797
17	250	6×10^{-3}	$\pi_{SCS} \rightarrow$ LUMO$_{+6}$	0.961

[a] Definition of torsion angle ϕ = C4–C5–C$_{ipso}$–C$_{ortho}$ (for definition of atoms refer to Figure 8 in the associated publication).

Table 3.1. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-computed UV/VIS spectrum and assignment of the bands *N*-(hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**) (equilibrium geometry)

transition	ΔE [nm]	f	character	weight
1	336	0.474	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.953
2	314	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.756
3	314	0.012	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.875
4	287	0.038	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.744
			$HOMO_{-2}$ π^*_{SCS}	0.119
5	269	9×10^{-3}	$\pi_{SCS} \rightarrow LUMO_{+3}$	0.759
6	261	0.050	$HOMO_{-2} \rightarrow \pi^*_{SCS}$	0.569
			$\pi_{SCS} \rightarrow LUMO_{+2}$	0.127
			$n_{CS} \rightarrow \pi^*_{SCS}$	0.120
7	254	4×10^{-3}	$n_{CS} \rightarrow \pi^*_{sub}$	0.498
			$HOMO_{-2} \rightarrow \pi^*_{sub}$	0.246
			$HOMO_{-3} \rightarrow \pi^*_{sub}$	0.142

4 UV/Vis Spectra, Relevant Orbitals, and Assignment of Bands of Rotamers of *N*-(Methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (5b) (BLYP)

Table 4.1. (TD)RI-BLYP/TZVPP//RI-BLYP/SVP-computed UV/VIS spectrum and assignment of the bands *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione **5b** (ϕ = 0 °,[a] E_{rel} = + 8.0 kJ mol^{-1} [b])

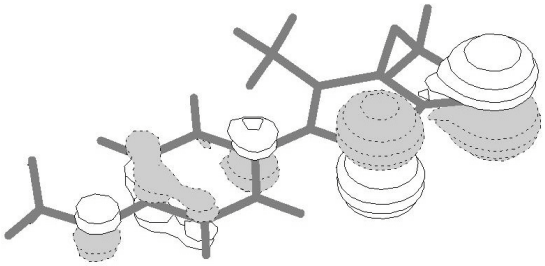
transition	ΔE [nm]	f	character	weight
1	433	< 10–3	$n_{CS} \rightarrow \pi^*_{SCS}$	0.995
2	397	0.344	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.854
3	382	0.034	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.820
4	368	< 10–3	$n_{CS} \rightarrow \pi^*_{sub}$	0.993
5	341	0.057	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.478
			$HOMO_{-2} \rightarrow \pi^*_{SCS}$	0.446
6	331	< 10–3	$n_{CS} \rightarrow LUMO_{+2}$	0.989

[a] Definition of torsion angle ϕ = C4–C5–C_{ipso}–C_{ortho} (for definition of atoms refer to Figure 8 in the associated publication). – [b] Referenced versus the equilibrium geometry (ϕ = 41.3 °).

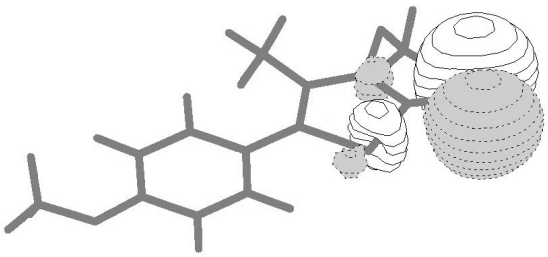
Table 4.2. (TD)RI-BLYP/TZVPP//RI-BLYP/SVP-computed UV/VIS spectrum and assignment of the bands *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazolethione **5b** (ϕ = 90 °,[a] E_{rel} = + 3.3 kJ mol^{-1} [b])

transition	ΔE [nm]	f	character	weight
1	388	7×10–3	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.781
			$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.194
2	386	< 10–3	$n_{CS} \rightarrow \pi^*_{SCS}$	0.956
3	372	< 10–3	$n_{CS} \rightarrow \pi^*_{sub}$	0.733
			$\pi_{SCS} \rightarrow LUMO_{+2}$	0.199
4	368	6×10–3	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.708
			$n_{CS} \rightarrow \pi^*_{sub}$	0.223
5	355	6×10–3	$n_{CS} \rightarrow LUMO_{+2}$	0.917
6	320	0.147	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.466
			$n_{CS} \rightarrow LUMO_{+3}$	0.260

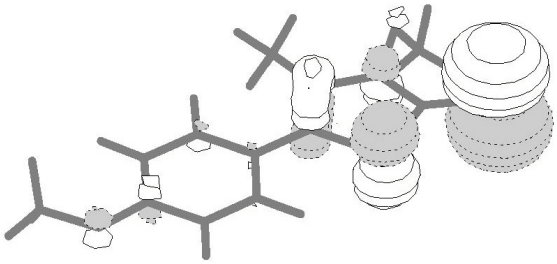
[a] Definition of torsion angle ϕ = C4–C5–C*ipso*–C*ortho* (for definition of atoms refer to Figure 8 in the associated publication). – [b] Referenced versus the equilibrium geometry (ϕ = 41.3 °).



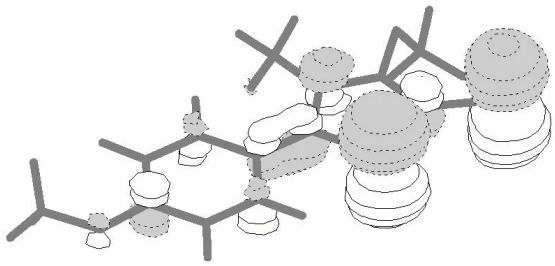
HOMO$_{-2}$ (–5.56 eV)



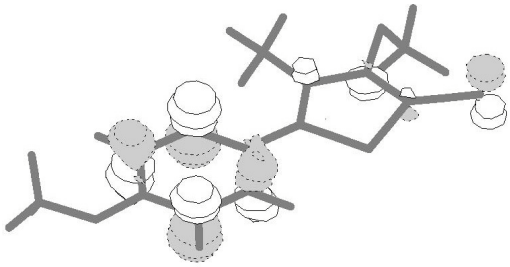
HOMO$_{-1}$ (n_{CS}, –4.82 eV)



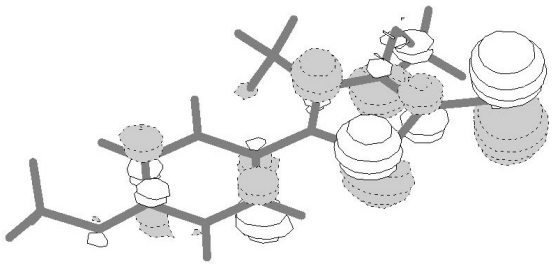
HOMO (π_{SCS}, –4.55 eV)



LUMO (π^*_{SCS}, –2.20 eV)

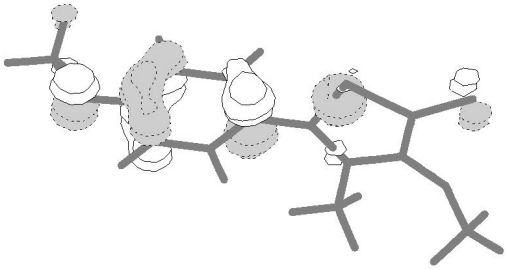


LUMO$_{+1}$ (π^*_{sub}, –1.46 eV)

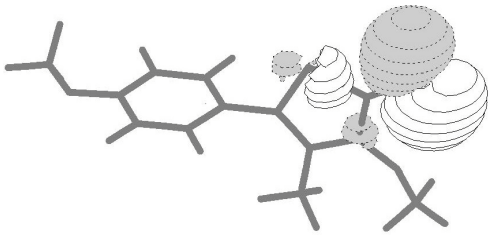


LUMO$_{+2}$ (–1.12 eV)

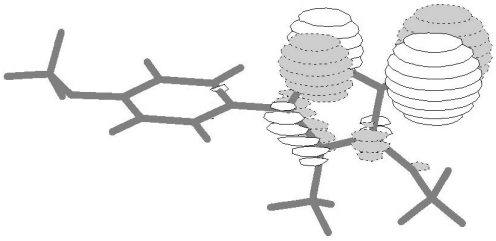
Figure 4.1. Visualization of the most important orbitals for an assignment of electronic transitions at the low energy end in the BLYP-calculated UV/Vis spectrum of *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (ϕ = 0 °; Table 3.1).



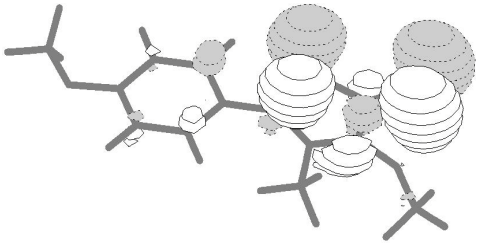
HOMO$_{-2}$ (–5.59 eV)



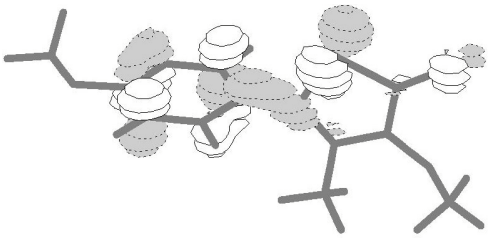
HOMO$_{-1}$ (n_{CS} , –4.76 eV)



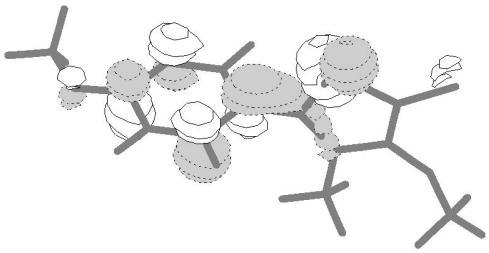
HOMO (π_{SCS}, –4.65 eV)



LUMO (π^*_{SCS}, –1.62 eV)



LUMO (π^*_{sub}, –1.44 eV)



LUMO$_{+2}$ (–1.29 eV)

Figure 4.2. 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**) (ϕ = 90 °; Table 3.2).

5 UV/Vis Spectra and Assignment of Bands for Pyridine-2(1*H*)-thiones 1 and Thiazole-2(3*H*)-thiones 2, 3, and 5 (B3LYP)

Table 5.1. Assignment of (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated electronic transitions in the spectruml range of λ > 280 nm in *N*-(hydroxy)pyridine-2(1*H*)-thione (**1a**) and *N*-(methoxy)pyridine-2(1*H*)-thione **1b** [a]

character	**1a**			**1b**		
	Δ*E* [nm]	*f*	weight	Δ*E* [nm]	*f*	weight
$n_{CS} \rightarrow \pi^*_{ring}$	349	$< 10^{-3}$	0.962	448	$< 10^{-3}$	0.921
$\pi_{CS} \rightarrow \pi^*_{ring}$	361	0.040	0.921	372	0.051	0.852
$nCS \rightarrow \pi^*_{CS}$	293	$< 10^{-3}$	0.958	347	$< 10^{-3}$	0.884
$\pi_{CS} \rightarrow \pi^*_{CS}$	278	0.238	0.866	81	0.272	0.811

[a] All computations are performed for the equilibrium geometry of thiones **1a** and **1b**; configurations with weights below 0.11 have, for the sake of clarity, not been considered.

Table 5.2. Correlation of (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies Δ*E* and the assignment of the UV/Vis spectrum (λ > 250 nm) of *N*-(hydroxy)thiazole-2(3*H*)-thione (**2a**)

transition	Δ*E* [nm]	*f*	character	weight
1	311	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.974
2	296	0.177	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.927
3	277	$< 10^{-3}$	$\pi_{SCS} \rightarrow LUMO_{+1}$	0.992

Table 5.3. Correlation of (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies Δ*E* and the assignment of the UV/Vis spectrum (λ > 250 nm) of *N*-(methoxy)thiazole-2(3*H*)-thione (**2b**)

transition	Δ*E* [nm]	*f*	character	weight
1	356	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.978
2	298	0.133	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.867
3	282	$< 10^{-3}$	$\pi_{SCS} \rightarrow LUMO_{+1}$	0.780
			$\pi_{SCS} \rightarrow LUMO_{+2}$	0.210

Table 5.4. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies ΔE and assignment of the UV/Vis transitions ($\lambda > 250$ nm) in *N*-(hydroxy)-4-methylthiazole-2(3*H*)-thione (**3a**)

transition	ΔE [nm]	f	character	weight
1	307	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.981
2	294	0.191	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.936
3	276	$< 10^{-3}$	$\pi_{SCS} \rightarrow LUMO_{+1}$	0.991

Table 5.5. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies ΔE and assignment of the UV/Vis transitions ($\lambda > 250$ nm) in *N*-(methoxy)-4-methylthiazole-2(3*H*)-thione (**3b**)

transition	ΔE [nm]	f	character	weight
1	351	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.985
2	292	0.159	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.902
3	313	$< 10^{-3}$	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.550
			$\pi_{SCS} \rightarrow LUMO_{+1}$	0.441

Table 5.6. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies and assignment of calculated electronic transitions ($\lambda > 250$ nm) for *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (equilibrium geometry, $\phi = 44.5\,^\circ$ [a])

transition	ΔE [nm]	f	character	weight
1	361	5×10^{-3}	$n_{CS} \rightarrow \pi^*_{SCS}$	0.801
			$n_{CS} \rightarrow \pi^*_{sub}$	0.156
2	332	0.381	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.912
3	316	6×10^{-3}	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.932
4	293	0.032	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.817
5	282	0.039	$n_{CS} \rightarrow LUMO_{+2}$	0.706
			$n_{CS} \rightarrow \pi^*_{SCS}$	0.149
6	277	0.030	$n_{CS} \rightarrow \pi^*_{sub}$	0.831
7	273	0.015	$\pi_{SCS} \rightarrow LUMO_{+3}$	0.863
8	261	0.040	$HOMO_{-2} \rightarrow \pi^*_{SCS}$	0.768
9	254	5×10^{-3}	$HOMO_{-2} \rightarrow \pi^*_{sub}$	0.719
			$HOMO_{-3} \rightarrow \pi^*_{SCS}$	0.150

[a] Definition of torsion angle ϕ = C4–C5–C_{ipso}–C_{ortho} (for definition of atoms refer to Figure 8 in the associated publication).

Table 5.7. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies and assignment of calculated electronic transitions (λ > 250 nm) for *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (equilibrium geometry, ϕ = 0 °,[a] E_{rel} = 10.7 kJ mol^{-1} [b])

transition	Δ*E* [nm]	*f*	character	weight
1	377	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.872
2	351	0.517	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.971
3	313	0.013	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.922
4	288	0.036	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.544
			$HOMO_{-2} \rightarrow \pi^*_{SCS}$	0.207
5	286	7×10^{-3}	$n_{CS} \rightarrow \pi^*_{sub}$	0.486
			$n_{CS} \rightarrow LUMO_{+2}$	0.264
6	331	6×10^{-3}	$\pi_{SCS} \rightarrow LUMO_{+4}$	0.851

[a] Definition of torsion angle ϕ = C4–C5–C*ipso*–C*ortho* (for definition of atoms refer to Figure 8 in the associated publication). – [b] Referenced versus the equilibrium geometry (ϕ = 44.5 °).

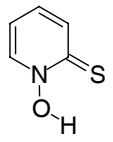
Table 5.8. (TD)RI-B3LYP/TZVP//RI-BLYP/SVP-calculated excitation energies and assignment of calculated electronic transitions (λ > 250 nm) for *N*-(methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**) (equilibrium geometry, ϕ = 90 °,[a] E_{rel} = 10.7 kJ mol^{-1} [b])

transition	Δ*E* [nm]	*f*	character	weight
1	356	$< 10^{-3}$	$n_{CS} \rightarrow \pi^*_{SCS}$	0.939
2	307	0.048	$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.622
			$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.294
3	304	0.122	$\pi_{SCS} \rightarrow \pi^*_{SCS}$	0.490
			$\pi_{SCS} \rightarrow LUMO_{+2}$	0.306
			$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.126
4	294	0.040	$\pi_{SCS} \rightarrow LUMO_{+2}$	0.607
			$\pi_{SCS} \rightarrow \pi^*_{sub}$	0.233
5	277	$< 10^{-3}$	$\pi_{SCS} \rightarrow LUMO_{+3}$	0.854
6	275	0.033	$n_{CS} \rightarrow \pi^*_{sub}$	0.906

[a] Definition of torsion angle ϕ = C4–C5–C*ipso*–C*ortho* (for definition of atoms refer to Figure 8 in the associated publication). – [b] Referenced versus the equilibrium geometry (ϕ = 44.5 °).

6 Energies and Atomic Coordinates of Pyridine–2(1*H*)–thiones 1 and Thiazole–2(3*H*)–thiones 2–11 (RI-BLYP/SVP//RI-BLYP/SVP)

6.1 *N*–(Hydroxy)pyridine-2(1*H*)-thione (**1a**): E = –721.69842205401



1a

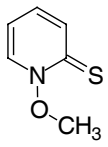
Coordinates:

Atom	x [Å]	y [Å]	z [Å]
C	–3.60798905	0.00064979	–2.37763661
C	–4.53410100	0.00048092	0.14545077
C	–2.80290007	0.00048169	2.11795976
N	–0.27858847	–0.00082779	1.60690682
C	0.80060315	–0.00066271	–0.83895402
C	–1.01994973	–0.00164485	–2.84386985
O	1.34777383	–0.00037078	3.62401521
H	3.05576220	0.00009576	2.66362322
S	4.00897090	0.00068122	–1.04450653
H	–0.27128642	–0.00106257	–4.77784522
H	–4.94304780	0.00149790	3.97008009
H	–6.56293524	0.00231051	0.57104269
H	–3.29133811	0.00116052	4.13272553

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 33^2$

ΔE [nm]	Oscillator strength f	Transition	Contributing configurations
411	< 0.0001	32 → 34	99.7 %
406	0.0177	33 → 34	89.4 %
336	< 0.0001	32 → 35	99.7 %
295	0.1936	33 → 35	81.2 %

6.2 *N*–(Methoxy)pyridine-2(1*H*)-thione (**1b**): $E = -760.97237099843$



1b

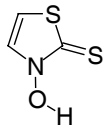
Coordinates:

Atom	x [Å]	y [Å]	z [Å]
C	–1.21146536	0.01275905	–4.63597205
C	–2.50688463	–0.35273884	–2.40205373
N	–1.25388744	–0.33943379	–0.12625979
C	1.39750370	–0.04302909	0.19094824
C	2.68855531	0.35550336	–2.19393331
C	1.46366839	0.38329293	–4.50311263
O	–2.75600823	–0.95323870	1.96360587
C	3.39699648	1.25325513	3.46042688
S	2.83157048	–0.16317279	3.02300162
H	4.74162161	0.61539110	–2.05631381
H	2.55337761	0.67904874	–6.24847119
H	–2.23621431	0.00234081	–6.43795790
H	–4.54812217	–0.68907308	–2.26023158
H	–4.57202293	0.49174118	5.01069472
H	–1.67198652	2.13938796	4.24574088
H	–4.51426672	2.62553989	2.32895295

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 37^2$

ΔE [nm]	f	Transition	Contributing configurations
553	< 0.0001	37 → 38	99.6 %
422	0.0236	36 → 38	85.9 %
		36 → 39	10.4 %
409	0.0005	37 → 39	98.4 %
297	0.2294	36 → 39	79.6 %
		36 → 38	10.1 %
276	0.0013	37 → 40	99.4 %
265	0.0248	35 → 38	88.4 %
258	0.0003	36 → 40	99.7 %

6.3 *N*–(Hydroxy)thiazole-2(3*H*)-thione (**2a**): $E = -1042.48285263138$



2a

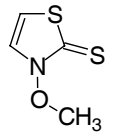
Coordinates:

Atom	x [Å]	y [Å]	z [Å]
N	0.09834533	–0.00022516	–1.93633165
C	–0.70215281	–0.00145845	0.54654440
S	2.09053510	–0.00012549	2.44845100
C	4.06506939	0.00086349	–0.24293409
C	2.67223160	0.00079441	–2.42087432
S	–3.76758415	0.00042751	1.35447492
O	–1.64486294	–0.00048050	–3.87555169
H	–3.26991838	0.00241947	–2.86558298
H	3.31900970	0.00061639	–4.38633290
H	6.12485981	–0.00426404	–0.06786826

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 34^2$

ΔE [nm]	f	Transition	Contributing configurations
337	0.0001	33 → 35	99.7 %
323	0.1074	34 → 35	82.1 %
313	0.0001	34 → 36	99.7 %
277	0.0055	33 → 36	49.0 %
		34 → 37	40.4 %
267	< 0.0001	33 → 37	99.8 %
266	0.0957	33 → 36	45.7 %
		34 → 37	35.8 %
		34 → 35	10.9 %

6.4 *N*–(Methoxy)thiazole-2(3*H*)-thione (**2b**): $E = -1081.76504353469$



2b

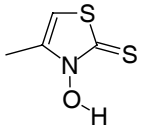
Coordinates:

Atom	x [Å]	y [Å]	z [Å]
C	0.19593094517303	1.08117478865918	0.10291896955559
S	3.58429126323979	0.86309371797398	–0.32607628747839
C	3.56730932506690	–2.46644512865728	–0.04650444736104
C	1.17152403518060	–3.34066027026218	0.30618340160093
N	–0.62581910649430	–1.40861147392700	0.35042832647511
O	–3.11624670372238	–1.99135782248748	0.96679909249826
C	–4.75491093253559	–1.94024080599108	–1.23348274281529
H	0.51974617797553	–5.28696443486310	0.57323740370721
H	5.30780786314655	–3.58004008761875	–0.14890025238966
S	–1.51609620237925	3.70508290515416	0.16710091738980
H	–4.15046219860205	–3.36048406524757	–2.65656743384281
H	–4.81406358351260	–0.02216727163034	–2.06726873245543
H	–6.63624996271853	–2.44830316790636	–0.48123392396115

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 38^2$

ΔE [nm]	Oscillator strength f	Transition	Contributing configurations
383	0.0001	37 → 39	99.7 %
325	0.0523	38 → 39	61.1 %
		37 → 40	28.0 %
314	0.0005	38 → 40	88.6 %
		38 → 41	11.0 %
306	0.0171	37 → 40	51.8 %
		37 → 41	36.0 %
298	0.0252	37 → 41	56.5 %
		37 → 40	16.5 %
		38 → 41	13.8 %
277	0.0863	38 → 41	61.2 %
		38 → 39	14.0 %

6.5 *N*-(Hydroxy)-4-methylthiazole-2(3*H*)-thione (**3a**): *E* —1081.79341944725



3a

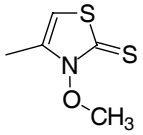
Coordinates:

Atom	x [Å]	y [Å]	z [Å]
C	–3.03743957736828	0.00144322877665	–0.16802256718127
C	–2.82648430640527	0.00426784223971	2.41674940563412
S	0.36112803807790	–0.00094319728892	3.41304788432250
C	1.46975485728616	–0.00180125472346	0.23284116195885
S	4.41621771130739	0.00044028778602	–0.94729625846030
N	–0.64750045321566	–0.00173618124454	–1.28564884068672
O	–0.38462368856743	0.00115498886208	–3.88433389227744
H	1.52727969525580	0.00472953766002	–4.02415100607058
H	–4.37589993432561	0.00026154126693	3.78494472184058
C	–5.35397578763369	–0.00172986496323	–1.80570864589373
H	–7.07545681037425	0.05129823023361	–0.62447942961572
H	–5.36483066561105	1.65334466385316	–3.09176567663649
H	–5.41735505391431	–1.71382000144172	–3.01400099868998

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 38^2$

ΔE [nm]	f	Transition	Contributing configurations
330	0.0002	37 → 39	99.7 %
316	0.1229	38 → 39	85.2 %
310	0.0001	38 → 40	99.7 %
275	0.0151	38 → 41	59.6 %
		37 → 40	22.1 %
		36 → 39	12.0 %
265	0.0606	37 → 40	72.4 %
		38 → 41	15.6 %
260	< 0.0001	37 → 41	99.8 %

6.6 *N*-(Methoxy)-4-methylthiazole-2(3*H*)-thione (**3b**): E = –1121.07437928088



3b

Coordinates:

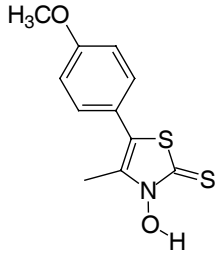
Atom	x [Å]	y [Å]	z [Å]
O	–0.62127038779085	0.00516462355696	–3.36588513862092
N	–0.57504199917986	–0.11264095000350	–0.76049412578400
C	1.66731358316783	–0.10451323470219	0.55129947068750
S	0.85678704856787	–0.64242399046066	3.75621578413272
C	–2.36379132124034	–0.96507217811810	3.03764524913214
C	–2.81513746818172	–0.64417009809572	0.54443787239430
S	4.56179879322042	0.32711928145025	–0.57356423276144
C	–5.26144938272072	–0.82091436324708	–0.85617855651323
C	–0.41850836298630	2.57932412028490	–4.26545560370160
H	1.38469547996228	3.39777050022960	–3.68755444775567
H	–0.49784287676902	2.40239088244576	–6.31773489777523
H	–2.00906124037893	3.71304119415621	–3.58157478499632
H	–5.17457107924192	–2.28240456406836	–2.31683916723516
H	–5.73839376994843	0.96394590089894	–1.78883813922374
H	–6.77649066380436	–1.28837421127524	0.46463281661901
H	–3.74078805390257	–1.38224639392869	4.48552941643344

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 42^2$

ΔE [nm]	f	Transition	Contributing configurations
377	0.0001	41 → 43	99.7 %
315	0.0750	42 → 43	68.8 %
		41 → 44	17.4 %
303	0.0007	42 → 44	73.7 %
		42 → 45	26.0 %
300	0.0104	41 → 44	68.6 %
		41 → 45	23.8 %
291	0.0271	41 → 45	67.2 %
		41 → 44	11.6 %
280	0.0567	42 → 45	55.8 %
		42 → 44	18.3 %
261	0.0022	42 → 46	90.0 %
256	0.0297	41 → 46	87.2 %

6.7 *N*-(Hydroxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5a**):

E –1427.37276282508



5a

Coordinates:

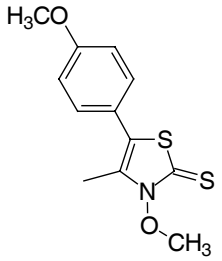
Atom	x [Å]	y [Å]	z [Å]
C	3.48498912	–1.69128340	1.11866636
C	1.91869690	0.10366622	–0.10777420
C	3.13274395	2.16086174	–1.34844649
C	5.76282076	2.39135186	–1.37967266
C	7.30088801	0.56092023	–0.17141760
C	6.13605847	–1.49115980	1.08392748
C	–0.86095913	–0.10822596	–0.06683745
C	–2.38704314	–2.21523284	–0.34355294
N	–4.93953934	–1.57342512	–0.14991786
C	–5.62099378	0.91054843	0.21440961
S	–2.76444060	2.65764866	0.40748196
O	–6.79335853	–3.39862446	–0.38874737
H	–8.35757843	–2.30152011	–0.21922776
C	–1.70586565	–4.91625216	–0.90291761
S	–8.65443072	1.83968773	0.40623857
O	9.85282542	0.95135652	–0.31525856
C	11.51973964	–0.80750498	0.86843468
H	11.31726598	–2.74017855	0.06570922
H	11.21248275	–0.90001622	2.94590589
H	13.45571107	–0.11722380	0.49729196
H	1.97960426	3.58631504	–2.32700230
H	6.69137258	3.97668353	–2.34726860
H	7.26572934	–2.92236984	2.06996502
H	2.61925925	–3.25699758	2.17249556
H	–2.91599965	–5.66344851	–2.43971507
H	–2.01478612	–6.15063190	0.76542868
H	0.29480764	–5.06349882	–1.47515473

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 66^2$

ΔE [nm]	f	Transition	Contributing configurations
389	0.0039	66 → 68	96.8 %
385	0.3017	66 → 67	83.4 %
		66 → 69	10.6 %
357	0.0172	65 → 67	96.9 %
333	0.0833	66 → 69	50.1 %
		64 → 67	35.4 %
323	0.0115	65 → 68	95.8 %
311	0.0010	66 → 70	89.7 %
295	0.02667	65 → 69	91.5 %
285	0.0038	64 → 67	40.6 %
		66 → 69	28.1 %
282	0.0070	64 → 68	70.8 %
		62 → 67	22.6 %
275	0.0148	66 → 71	44.6 %
		63 → 67	35.1 %
		64 → 69	17.0 %
265	0.0066	66 → 72	91.5 %
263	0.0202	65 → 70	51.3 %
		64 → 69	14.3 %
		62 → 67	10.9 %
261	0.0761	66 → 71	24.2 %
		65 → 70	23.0 %
		63 → 67	13.4 %
259	0.0502	62 → 67	37.7 %
		63 → 68	14.5 %
257	0.0938	63 → 67	34.4 %
		64 → 69	31.1 %
		65 → 70	12.1 %
256	0.0095	63 → 68	79.7 %
250	0.0064	66 → 73	96.1 %

6.8 *N*-(Methoxy)-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (**5b**):

E = –1466.65294983657



5b

Coordinates:

Atom	x [Å]	y [Å]	z [Å]
N	–4.60692580699321	–1.20832167320535	0.12024766807035
C	–2.05510764825331	–1.96150695498194	–0.01466246030102
C	–0.43592069003149	0.07906919681186	0.02842574451458
S	–2.21248271062294	2.95649365322890	0.23722152161428
C	–5.19310711299697	1.34355954125182	0.33831417087360
O	–6.45689493566768	–3.06322309184757	0.41190133943988
C	–7.98477367751742	–3.37533431919841	–1.84683538830005
C	2.35282573142824	0.16509571901100	–0.07896321408819
C	11.93067927239541	–1.01296968880982	0.84212124307811
C	3.61848833141854	2.01553083681613	–1.56797078074614
C	6.25479264013302	2.13445434276180	–1.66841029153367
C	7.74654780656627	0.39772840836205	–0.27829854027789
C	6.53074853152813	–1.44407446179736	1.22895174071524
S	–8.02135800900907	2.67813340985327	0.64891360837708
C	3.87460341975044	–1.53130736854112	1.32887358217126
O	10.30934763500839	0.66532488607515	–0.50867917716223
C	–1.46286516633030	–4.73219369758328	–0.25983411935471
H	–6.80637933330502	–3.94526520075833	–3.48772239124144
H	–9.04677021499057	–1.62221806444287	–2.26536276839734
H	–9.30977797323537	–4.91448272443901	–1.35676069307373
H	11.63967664642404	–3.01464479022360	0.26759357434282
H	11.66044103456677	–0.85973093394079	2.92135200654095
H	13.88422878803865	–0.44615758299162	0.36761854080560
H	2.49936254263039	3.36535075465910	–2.68338725982163
H	7.22348350271992	3.55939028483312	–2.82721949683736
H	7.62467690824992	–2.79375748627235	2.35974967066366
H	2.97227653631617	–2.92304702266781	2.57817405740753
H	–2.59262402101783	–5.61416448929578	–1.78698149613642
H	–1.90845890761559	–5.77664144490891	1.50337099720379
H	0.55863131725431	–5.00306284136985	–0.69746097256406

Calculated Electronic Spectrum: $\Psi_0 = 1^2 - 70^2$

ΔE [nm]	f	Transition	Contributing configurations
409	0.0031	69 → 71	97.7 %
392	0.0147	70 → 72	91.0 %
385	0.1762	70 → 71	66.3 %
		70 → 73	11.5 %
372	0.0338	69 → 72	88.3 %
350	0.0024	69 → 73	70.3 %
		70 → 73	23.7 %
334	0.1133	70 → 73	30.3 %
		68 → 71	27.1 %
		69 → 73	24.3 %
312	0.0054	70 → 74	97.2 %
300	0.0055	69 → 74	69.3 %
		68 → 71	18.0 %
288	0.0155	70 → 75	28.2 %
		69 → 74	26.4 %
		70 → 73	13.8 %
284	0.0088	68 → 72	72.2 %
		67 → 71	15.7 %
275	0.0419	70 → 76	35.1 %
		70 → 75	29.1 %
		68 → 73	23.3 %
272	0.0328	70 → 76	54.6 %
		70 → 75	16.5 %
		68 → 73	10.9 %
266	0.1031	70 → 75	38.2 %
		68 → 73	23.1 %
		69 → 75	17.2 %
265	0.1793	69 → 75	62.6 %
		68 → 73	18.0 %
262	0.0201	69 → 76	89.7 %
		67 → 71	13.0 %
259	0.0101	67 → 71	64.4 %
		67 → 73	15.3 %
		68 → 74	10.3 %
255	0.0030	70 → 77	97.7 %
250	0.0029	68 → 74	84.3 %

7 References

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