Supplementary Information (SI) for RSC Advances.

Supplementary material

Structural and FTIR spectroscopic studies of matrix-isolated 3-thio-1,2,4-triazole complexes with carbon dioxide. The UV-induced formation of thiol···CO_2 complexes

K. Mucha*, M. Pagacz-Kostrzewa, M. Wierzejewska

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

* Corresponding author e-mail address: karolina.mucha@uwr.edu.pl

Table S1. Interatomic distances (Å), angle values (degrees) and electron density parameters (a.u.) determined for bond critical points (BCP) and ring critical points (RCP) in the complexes of the thione tautomer (STn) with CO_2 of the 1:1 stoichiometry calculated at the B3LYP-D3/6-311++G(3df,3pd) level.

Complex STn···CO_2	Intermolecular parameters[a]			AIM parameters			
	Interatomic distance		Angle value	BCP	ρ(r)	∇^2 ρ(r)	Ellipticity
	H ··· Y	X ··· Y	X-H ··· Y				
STn-C1	2.149	3.055	148.6	H9 ··· O11	0.014	0.053	0.025
		3.364		C10 ··· S6	0.007	0.025	1.965
			RCP (H9-O11-C10-S6-C5-N1)	6 at.	0.005	0.019	
STn-C2	2.093	3.024	152.4	H7 ··· O11	0.015	0.060	0.024
		3.352		C10 ··· S6	0.008	0.025	1.786
			RCP (H7-O11-C10-S6-C5-N4)	6 at.	0.005	0.020	
STn-C3	2.676	3.184	108.4	H8 ··· O11	0.006	0.025	1.003
		3.026		O11 ··· N1	0.009	0.036	1.419
			RCP (H8-O11-N2-C3)	4 at.	0.006	0.027	
STn-C4	2.401	3.032	120.0	H9 ··· O11	0.009	0.037	0.239
		3.023		N2 ··· O11	0.010	0.036	1.278
			RCP (H9-O11-N2-N1)	4 at.	0.008	0.035	

[a] X = N, C or S atom, Y = N, C or O atom.

Table S2. Interatomic distances (Å), angle values (degrees) and electron density parameters (a.u.) determined for bond critical points (BCP) and ring critical points (RCP) in the complexes of the thiol tautomer (STl) with CO_2 of the 1:1 stoichiometry, calculated at the B3LYP-D3/6-311++G(3df,3pd) level.

Complex STl···CO_2	Intermolecular parameters[a]			AIM parameters			
	Interatomic distance		Angle value	BCP	ρ(r)	∇^2 ρ(r)	Ellipticity
	H ··· Y	X ··· Y	X-H ··· Y				
STl-C1	2.298	3.128	139.0	H9 ··· O11	0.010	0.039	0.050
		3.434		O11 ··· S6	0.006	0.020	0.470
			RCP (H9-O11-S6-C5-N1)	5 at.	0.005	0.021	
STl-C2	2.374	3.644	156.3	H7 ··· O11	0.009	0.032	0.003
		2.851		C10 ··· N4	0.011	0.042	1.408
			RCP (H7-O11-C10-N4-C5-S6)	6 at.	0.005	0.020	
STl-C4	2.363	3.007	120.9	H9 ··· O11	0.010	0.039	0.172
		3.013		O11 ··· N2	0.010	0.037	1.391
			RCP (H9-O11-N2-N1)	4 at.	0.008	0.037	

[a] X = N, C or S atom, Y = N, C or O atom.

Table S3. Interatomic distances (Å), angle values (degrees) and electron density parameters (a.u.) determined for bond critical points (BCP) and ring critical points (RCP) in the complexes of the thione tautomer (STn) with CO_2 of the 1:2 stoichiometry, calculated at the B3LYP-D3/6-311++G(3df,3pd) level.

Complex STn···$(CO_2)_2$	Intermolecular parameters[a]			AIM parameters			
	Interatomic distance		Angle value	BCP	ρ(r)	∇^2 ρ(r)	Elipticity
	H ··· Y	X ··· Y	X-H ··· Y				
STn-2C1	2.095	3.026	152.7	H7 ··· O14	0.015	0.060	0.024
	2.152	3.058	148.7	H9 ··· O11	0.013	0.052	0.024
		3.364		S6 ··· C13	0.008	0.025	1.841
		3.354		S6 ··· C10	0.007	0.025	1.992
			RCP1 (H9-O11-C10-S6-C3-N2)	6 at.	0.005	0.019	
			RCP2 (H7-O14-C13-S6-C3-N4)	6 at.	0.005	0.020	
STn-2C2	2.170	3.069	147.6	H9 ··· O11	0.013	0.048	0.042
		2.991		C10 ··· O14	0.006	0.028	3.467
		3.449		S6 ··· C10	0.006	0.021	2.507
		3.532		S6 ··· O14	0.007	0.023	1.510
		3.362		N2 ··· O14	0.005	0.017	0.620
			RCP1 (H9-O11-C10-S6-C3-N2)	6 at.	0.004	0.018	
			RCP2 (N2-O14-S6-C3)	4 at.	0.004	0.016	
			RCP3 (O14-N2-H9-O11-C10)	5 at.	0.003	0.014	
			RCP4 (O14-S6-C10)	3 at.	0.003	0.013	
STn-2C3	2.477	3.071	117.2	H9 ··· O11	0.008	0.032	0.366
	2.180	3.070	146.2	H9 ··· O14	0.013	0.049	0.019
		3.354		S6 ··· C13	0.008	0.025	1.939
		3.010		N1 ··· O11	0.010	0.037	1.265
			RCP1 (H9-O14-C13-S6-C3-N2)	6 at.	0.005	0.019	
			RCP2 (H9-O11-N2-N1)	4 at.	0.007	0.033	

[a] X = N or S atom, Y = N, C or O atom.

Table S4. Selected shifts of wavenumbers Δν (cm^{-1}) and band intensities (km mol^{-1}, in brackets) calculated at the B3LYP-D3/6-311++G(3df,3pd) level for 1:2 complexes of the thione tautomer (STl) with a CO_2 molecule, compared with the experimental shifts.

Theoretical shifts (Δν)			Mode [16][a]	Experimental shifts[b]	Assignment
STn-2C1	STn-2C2	STn-2C3			
-39 (202)	-11 (85)	-11 (89)	νN2H	-41.5	STn-2C1
-44 (276)	-30 (221)	-44 (235)	νN4H	-42.0	STn-2C1
+4 (89)	0 (85)	+3 (84)	υCN + δNH	+5.5	STn-2C1
+10 (390)	+6 (364)	+5 (484)	υCN + δNH + δ_{ring}	+10.5	STn-2C1
+9 (29)	+5 (25)	+7 (36)	δ_{ring}	+7.5	STn-2C1
+48 (0)	+12 (20)	+15 (43)	γNH + γ_{ring}	n.o.	STn-2C1

[a] Abbreviations: ν - bond stretching, δ - in-plane bending, γ - out-of-plane bending.
[b] Positions of the ST monomer bands: 3498.0, 3491.0, 1558.0, 1474.5, 932.5, 566.0 cm^{-1}.

Table S5. Experimental and theoretical (B3LYP-D3/6-311++G(3df,3pd)) values of the νN2H band intensities for both ST monomers and their respective N_2 and CO_2 complexes used to estimate the efficiency of photoinduced hydrogen atom transfer.

Species	I_{theo}	Integrated intensity		I_{exp}/I_{theo} x10^4	
		t = 0 min	t = 16 min	t = 0 min	t = 16 min
STn monomer	101	0.213	0.036	21.09	3.56
STl monomer	90	0.0015	0.076	0.17	8.44
N_2 complexes [16]					
STn2 complex	255	0.084	0.051	3.29	1.86
STl2 complex	167	0.001	0.011	0.00	0.65
CO_2 complexes					
STn-C2 complex	249	0.010	0.0035	0.402	0.14
STl-C2 complex	87	0.0005	0.0011	0.057	0.128

Intensity ratio for the monomer: STl (16 min)/STn (0 min) = 0.400
Intensity ratio for the N_2 complex: STl2 (16 min)/STn2 (0 min) = 0.197
Intensity ratio for the CO_2 complex: STl-C2 (16 min)/STn-C2 (0 min) = 0.318

Table S6. Experimental and theoretical (B3LYPD3/6-311++G(3df,3pd)) intensities of the most intense bands of STn and STl monomers (1474.5 cm^{-1} and 1437.0 cm^{-1}, respectively) before and after irradiation, in ST/Ar and ST/CO_2/Ar matrices.

Species	I_{theor}	Integrated intensity		I_{exp}/I_{theor} x10^4	
		t = 0 min	t = 16 min	t = 0 min	t = 16 min
ST/Ar matrix					
STn	420	0.64	0.063	15.24	1.50
STl	81	0.009	0.071	1.11	8.76
ST/N_2/Ar matrix [16]					
STn	420	0.65	0.09	15.48	2.14
STl	81	0.009	0.048	1.11	5.92
ST/CO_2/Ar matrix					
STn	420	0.64	0.10	15.25	2.36
STl	81	0.005	0.034	0.62	4.21

Intensity ratio for monomer in Ar matrix: STl (16 min)/STn (0 min) = 0.548
Intensity ratio for monomer in N_2/Ar matrix: STl (16 min)/STn (0 min) = 0.382
Intensity ratio for monomer in CO_2/Ar matrix: STl (16 min)/STn (0 min) = 0.452