

SUPPORTING INFORMATION

Photophysical investigation into room-temperature emission from xanthene derivatives

Kristen Harrington[a] David T. Hogan,[b] Todd C. Sutherland[b]* and Kevin Stamplecoskie[a]*

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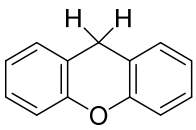
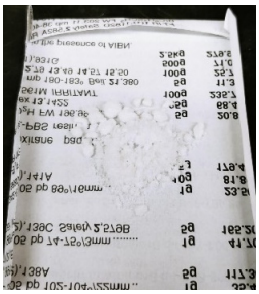
Xanthene (1) synthesis





This experimental was adapted from a literature procedure.[1] An oven-dried 100 mL RBF with an oven-dried magnetic stirbar was cooled to room temperature under a stream of N_2. Xanthone (2.0300 g, 1.0355×10^{-2} mol, 1.0 eq) and THF (60 mL) were added to the flask, it was stoppered with a rubber septum and the headspace was flushed with N_2. $BH_3{\cdot}SMe_2$ (2 M in THF, 7.8 mL, 1.56×10^{-2} mol, 1.5 eq) was added in one portion by syringe and the flask neck was equipped with a pre N_2-flushed water condenser. The flask was put into a 75-80 °C oil bath, stirred and refluxed for 1 hour under N_2, acquiring fluffy white precipitate as time passed. The mixture was allowed to cool to room temperature, then further to 0 °C in an ice-water bath. Slowly with manual swirling excess borane was quenched with brine (9 mL, added 1 mL at a time) and 1 M HCl (12 mL, added 1 mL at a time). Swirling was continued until the solution was no longer effervescent, then it was diluted with EtOAc (12 mL) and water (12 mL) and the layers were shaken then separated in a separatory funnel. The aqueous layer was extracted with EtOAc (3×12 mL), all combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressures into a white solid. This was dissolved in CH_2Cl_2 and adsorbed to silica, loaded onto a 3 cm wide × 5 cm tall silica column packed in hexanes. This solvent (~350 mL) was used to first elute remaining SMe_2, then all following eluate that contained shortwave UV-active fractions (visualized on TLC plates) was collected and concentrated under reduced pressures to yield xanthene (1.6630 g, 88%) as white hairy microcrystals: spectroscopic characterization was in accord with existing literature data;[2] m.p. (methanol) 102-103 °C (lit.[3] 100.5 °C from ethanol; *Anal. Calcd*. for $C_{13}H_{10}O$: C 85.69, H 5.53, Found C 85.38, H 5.61. For analysis, the solid was recrystallized from minimal boiling methanol. Colourless square plates were collected after allowing the supernatant solution to come to room temperature and sit un-agitated for 2-3 hours, then by chilling in an ice-water bath for 4-6 hours.

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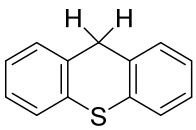
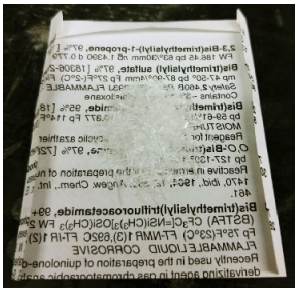
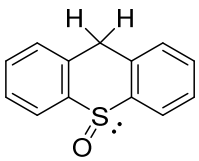
Thioxanthene (2) synthesis

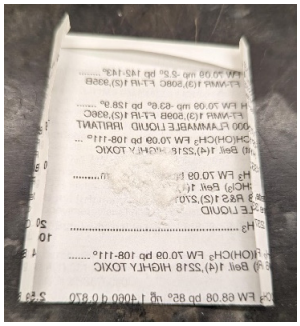




This experimental was adapted from a literature procedure.[1] An oven-dried 100 mL RBF with an oven-dried magnetic stirbar was cooled to room temperature under a stream of N_2. Thioxanthone (2.0412 g, 9.6269×10^{-3} mol, 1.0 eq) and THF (60 mL) were added to the flask, it was stoppered with a rubber septum and the headspace was flushed with N_2. $BH_3{\cdot}SMe_2$ (2 M in THF, 7.0 mL, 1.4×10^{-2} mol, 1.5 eq) was added in one portion by syringe and the flask neck was equipped with a pre N_2-flushed water condenser. The flask was put into a 75-80 °C oil bath, stirred and refluxed for 1 hour under N_2, acquiring fluffy brown precipitate as time passed. The mixture was allowed to cool to room temperature, then further to 0 °C in an ice-water bath. Slowly with manual swirling excess borane was quenched with brine (9 mL, added 1 mL at a time) and 1 M HCl (12 mL, added 1 mL at a time). Swirling was continued until the solution was no longer effervescent, then it was diluted with EtOAc (12 mL) and water (12 mL) and the layers were shaken then separated in a separatory funnel. The aqueous layer was extracted with EtOAc (3×12 mL), all combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressures into a beige solid. This was dissolved in CH_2Cl_2 and adsorbed to silica, loaded onto a 3 cm wide × 5 cm tall silica column packed in hexanes. This solvent (~500 mL) was used to first elute remaining SMe_2, then all following eluate that contained shortwave UV-active fractions (visualized on TLC plates) was collected and concentrated under reduced pressures to yield thioxanthene (1.6651 g, 87%) as fine white microneedles: spectroscopic characterization was in accord with existing literature data;[4] m.p. (methanol) 130-132 °C (lit.[5] 130-131 °C from methanol); *Anal. Calcd*. for $C_{13}H_{10}S$: C 78.75, H 5.08, S 16.17, Found C 78.84, H 5.13, S 16.17. For analysis, the solid was recrystallized from minimal boiling methanol. Colourless long needles were collected after allowing the supernatant solution to come to room temperature and sit un-agitated for 2-3 hours, then by chilling in an ice-water bath for 4-6 hours.

Thioxanthene Sulfoxide (3) synthesis

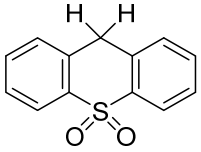


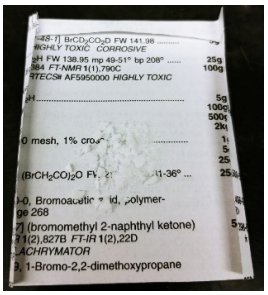


Into a 250 mL Schlenk flask were added a magnetic stirbar and thioxanthene (1.0019 g, 5.053×10^{-3} mol, 1 eq) which was dissolved in CH_2Cl_2 (80 mL) with stirring. The sidearm was opened and the solution was chilled in an ice-water bath. Separately, a solution of *m*-CPBA (0.4366 g, 2.530×10^{-3} mol, 0.5 eq) in CH_2Cl_2 (40 mL) was prepared with sonication, which was transferred with washing (2 mL CH_2Cl_2) into an addition funnel equipped to the flask neck. This solution was added over 20 mins to the

chilled and stirring thioxanthene solution, using CH_2Cl_2 (5 mL) to wash the addition funnel of any remaining *m*-CPBA. The reaction solution was stirred for a further 3 hours at 0 °C. After this time, the mixture was allowed to warm to room temperature and it was vigorously shaken with 1M NaOH (40 mL) in a separatory funnel. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organics were brine washed, dried over anhydrous Na_2SO_4 and concentrated under reduced pressures into a white solid. This was dissolved in CH_2Cl_2, adsorbed to silica and loaded onto a 5 cm tall × 4 cm wide silica column packed in hexanes. This solvent (~300 mL) eluted unreacted thioxanthene, which can be recovered and reused in subsequent sulfoxidations. The solvent was switched to 20% EtOAc/hexanes (~600 mL), the last ~300 mL of which contained a shortwave UV-active component on TLC plates, which was collected and concentrated to yield thioxanthene sulfoxide (0.4449 g, 38% yield, 82% brsm) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.37 (m, 6H), 4.20 (d, *J* = 16.7 Hz, 1H), 3.83 (d, *J* = 16.7 Hz, 1H); DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 133.0, 130.3, 128.3, 127.6, 124.7, 35.9; HRMS (EI, positive) calculated for $[M]^+$ $[C_{13}H_{10}SO]^+$ *m/z* = 214.0452, found *m/z* = 214.0447, -2.3 ppm difference; m.p. (methanol/ether) 118-120.5 °C (lit.[6] 116-118 °C from hexanes/CH_2Cl_2); *Anal. Calcd*. for $C_{13}H_{10}SO$: C 72.87, H 4.70, S 14.96, Found C 73.15, H 4.74, S 15.05. For analysis, the solid was recrystallized from minimal boiling 50/50 methanol/diethyl ether. Colourless microcrystalline lumps were collected after allowing the supernatant solution to come to room temperature and sit un-agitated for 2-3 hours, then by chilling in an ice-water bath for 4-6 hours.

Thioxanthene Sulfone (4) synthesis

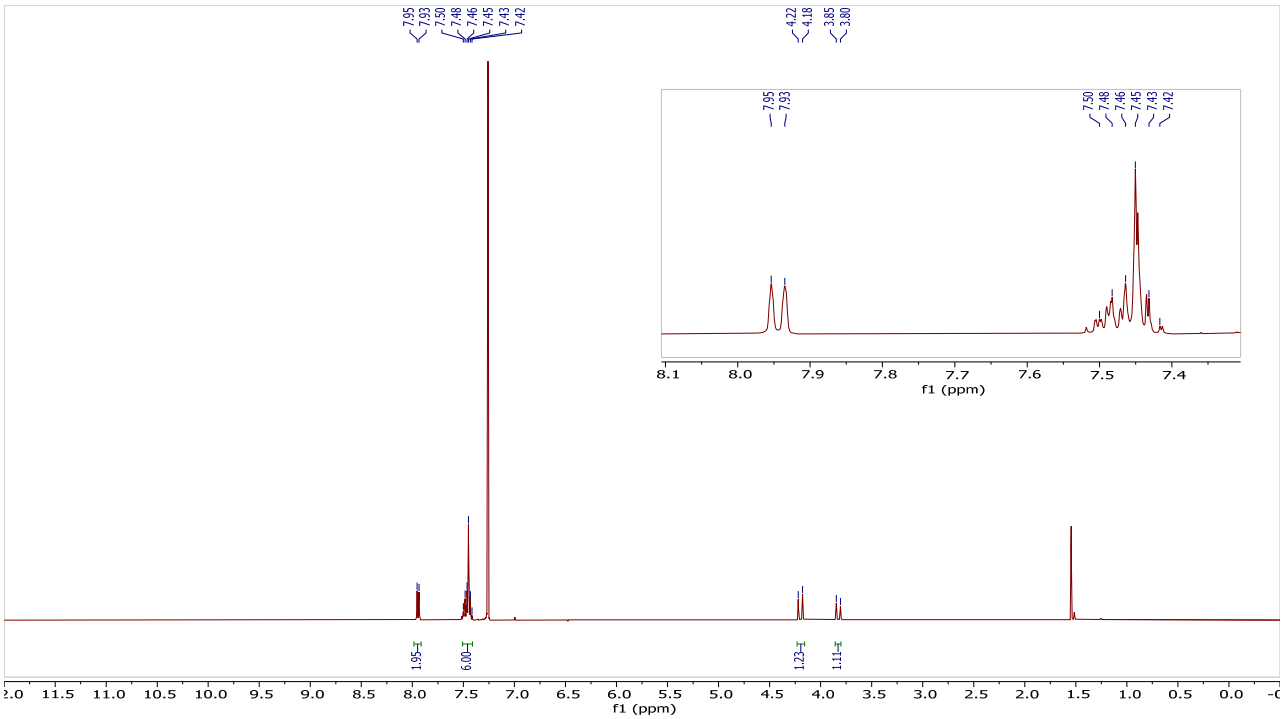




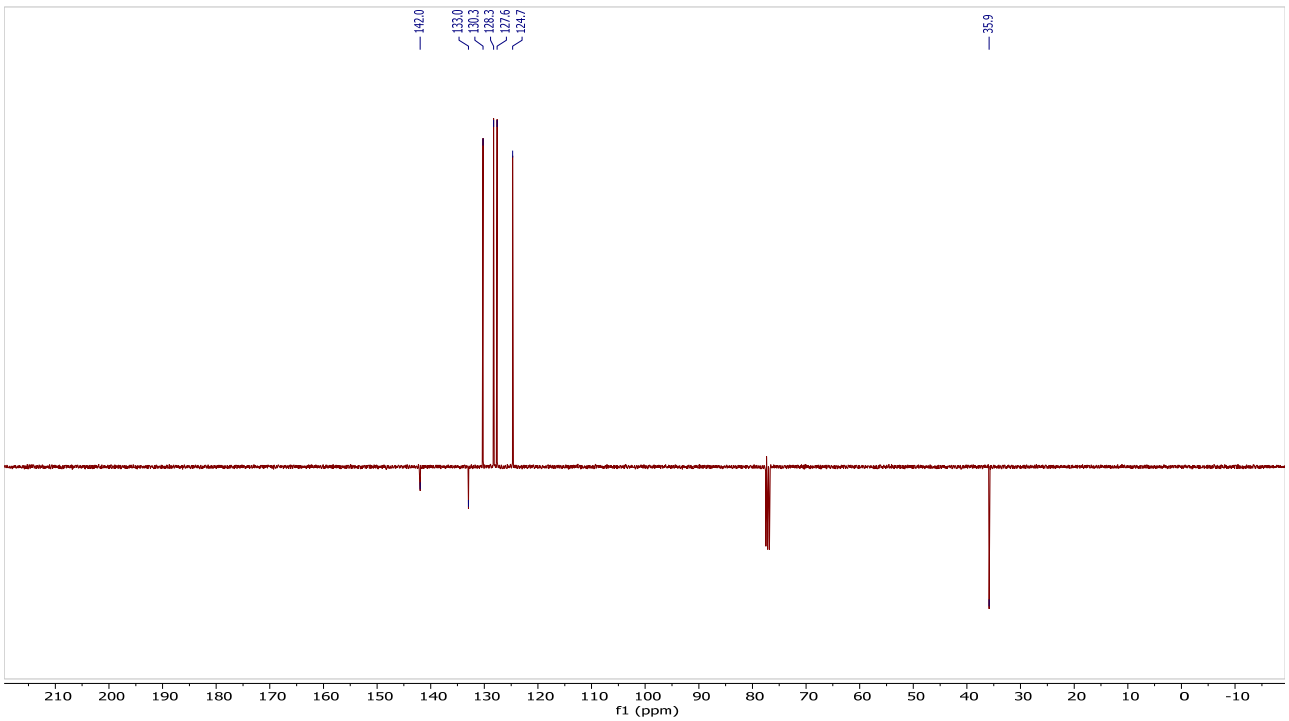
Into a 250 mL RBF were added a magnetic stirbar and thioxanthene (1.0093 g, 5.0903×10^{-3} mol, 1.0 eq), which was dissolved in CH_2Cl_2 (15 mL), with stirring. Separately, a solution of *m*-CPBA (2.6349 g, 1.5269×10^{-2} mol, 3.0 eq) in CH_2Cl_2 was prepared with sonication, and this was added in one portion to the stirring thioxanthene solution. After 1 hour stirring at room temperature the clear and colourless solution had become turbid with white precipitates. The mixture as diluted with CH_2Cl_2 (~120 mL) to dissolve all solids, and the solution was vigorously shaken with 1 M NaOH (3×15 mL) to quench remaining acids. The aqueous layer was extracted with CH_2Cl_2 (3×10 mL), all combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressures to yield thioxanthene-10,10-dioxide (1.1199 g, 95%) as a white amorphous solid: spectroscopic characterization was in accord with existing literature data;[7] m.p. (methanol) 174-176.5 °C (lit.[8] 174-177.5 °C from methanol); *Anal. Calcd*. for $C_{13}H_{10}SO_2$: C 67.81, H 4.38, S 13.92, Found C 67.29, H 4.48, S 14.04.

SUPPORTING INFORMATION

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for thioxanthene sulfoxide



DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) for thioxanthene sulfoxide



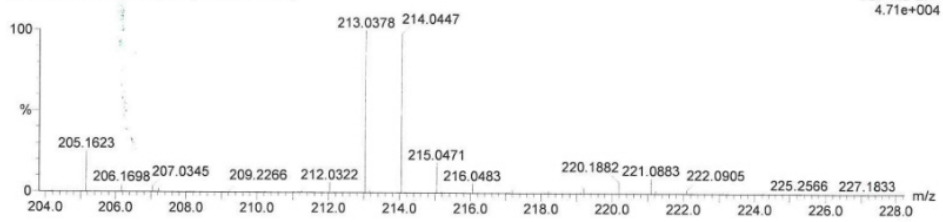
High-resolution mass spectrum (EI+) for thioxanthene sulfoxide

Elemental Composition Report Page 1

Multiple Mass Analysis: 4 mass(es) processed
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
10 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-13 H: 0-10 O: 0-1 32S: 0-1

Dave Hogan DTH-7-56ADave Hogan DTH-7-56A CAB072 24-Jul-2020 09:26:37
200724DTH1 324 (5.941) Cm (297:324-71:106) TOF MS EI+
4.71e+004



Minimum:	10.00				-1.5		
Maximum:	100.00		5.0	20.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
205.1623	24.83	---					
213.0378	100.00	213.0374	0.4	1.9	9.5	17821.6	C13 H9 O 32S
214.0447	97.62	214.0452	-0.5	-2.3	9.0	132.1	C13 H10 O 32S
215.0471	18.35	---					

Elemental analysis for recrystallized xanthene

University of Calgary
Department of Chemistry EA Date: 2-1-2023

Name:	DAVID	Group:	TCS
Sample:	XO-2	Weight (mg):	1.347
%C (Actual):	85.38	%C (Theorectical):	85.69%
%H (Actual):	5.61	%H (Theoretical):	5.53%
%N (Actual):	0.00	%N (Theoretical):	
%S (Actual):	0.00	%S (Theoretical):	

Elemental analysis for recrystallized thioxanthene

University of Calgary
Department of Chemistry EA Date: 2-1-2023

Name:	DAVID	Group:	TCS
Sample:	XS-1	Weight (mg):	1.566
%C (Actual):	78.84	%C (Theorectical):	78.75%
%H (Actual):	5.13	%H (Theoretical):	5.08%
%N (Actual):	0.00	%N (Theoretical):	
%S (Actual):	16.17	%S (Theoretical):	16.17%

Elemental analysis for recrystallized thioxanthene sulfoxide

University of Calgary
Department of Chemistry EA Date: 2-1-2023

Name:	DAVID	Group:	TCS
Sample:	XSO-2	Weight (mg):	1.911
%C (Actual):	73.15	%C (Theorectical):	72.87%
%H (Actual):	4.74	%H (Theoretical):	4.70%
%N (Actual):	0.00	%N (Theoretical):	
%S (Actual):	15.05	%S (Theoretical):	14.96%

Elemental analysis for recrystallized thioxanthene sulfone

University of Calgary
Department of Chemistry EA Date: 2-1-2023

Name:	DAVID	Group:	TCS
Sample:	XSO2-2	Weight (mg):	2.708
%C (Actual):	67.29	%C (Theorectical):	67.81%
%H (Actual):	4.48	%H (Theoretical):	4.38%
%N (Actual):	0.00	%N (Theoretical):	
%S (Actual):	14.04	%S (Theoretical):	13.92%

Gas Chromatograms of 1 -4.

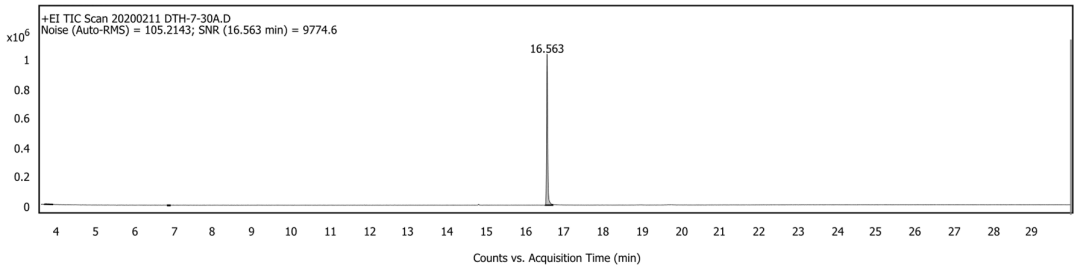


Figure 1. GC trace of **1** (X = O).

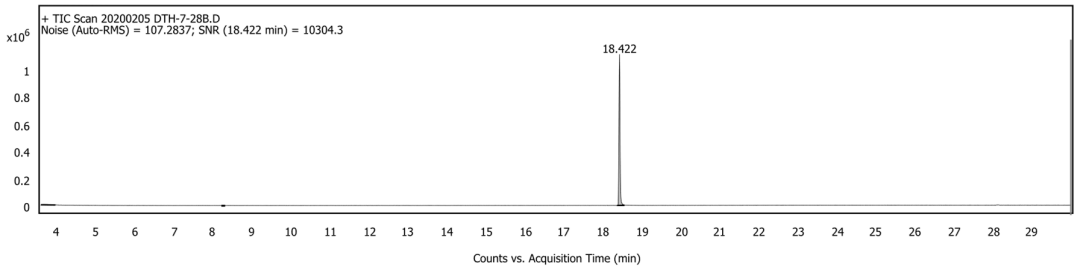


Figure 2. GC trace of **2** (X = S).

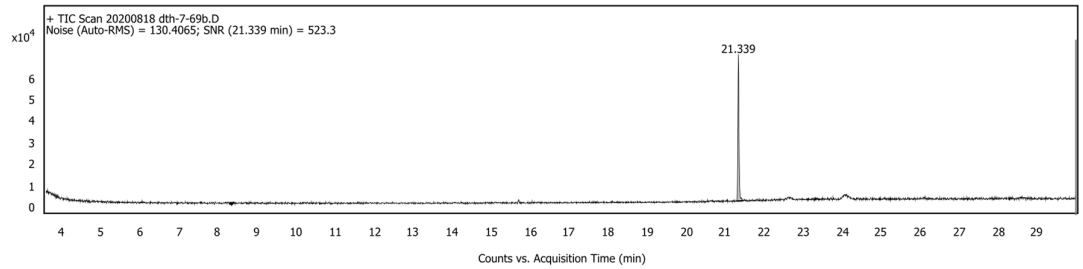


Figure 3. GC trace of **3** (X = SO).

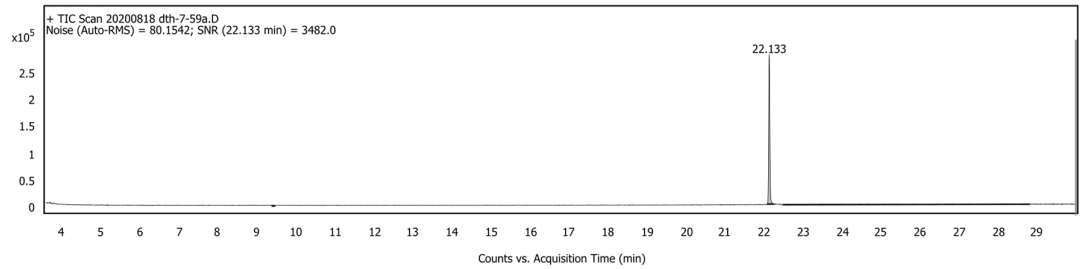


Figure 4. GC trace of **4** (X = SO_2).

Crystallographic Packing diagrams of 1 - 4.

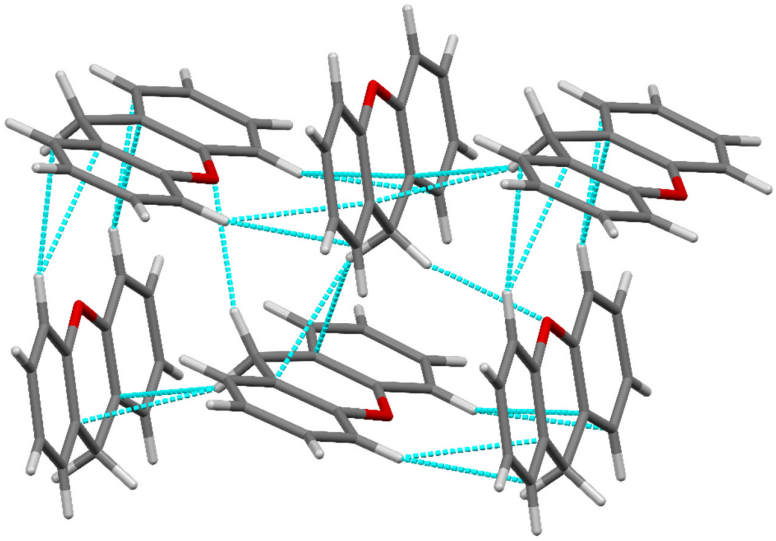


Figure 5. Solid-state packing arrangement of **1**.

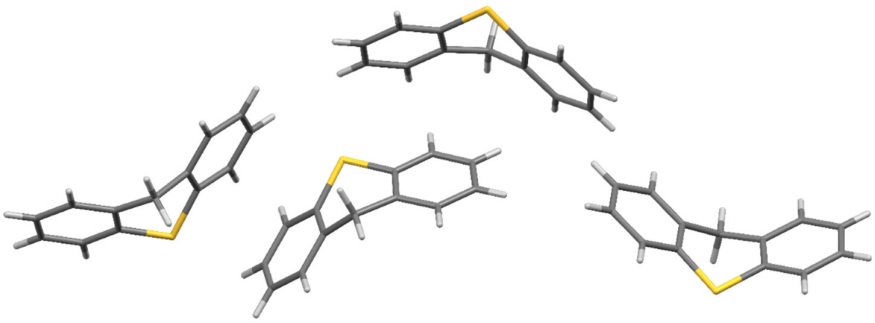


Figure 6. Solid-state packing arrangement of **2**.

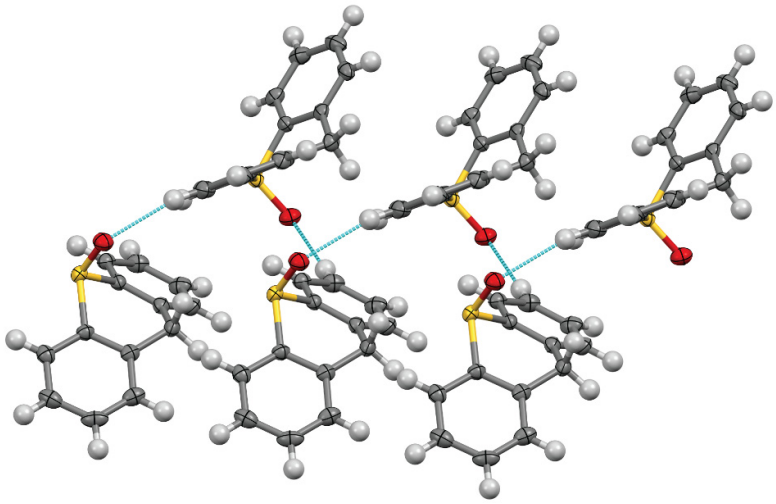


Figure 7. Solid-state packing arrangement of **3**, highlighting the intermolecular H-bonding chains

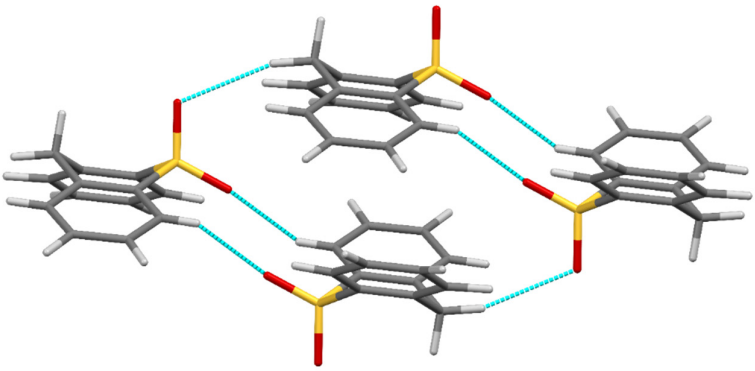


Figure 8. Solid-state packing arrangement of **4**.

Solution (10^{-5} M, ACN) absorbance, emission, and excitation spectra.

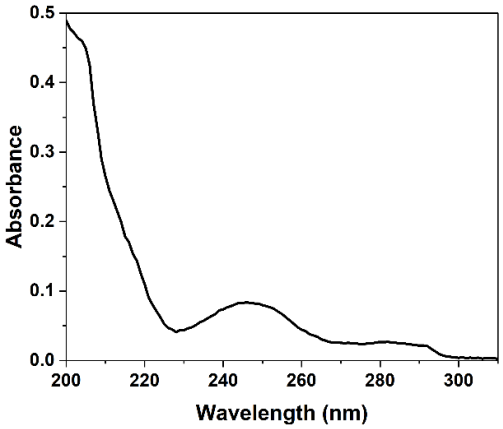


Figure 9.a Absorption spectrum of **1** (X = O) in acetonitrile (10^{-5} M).

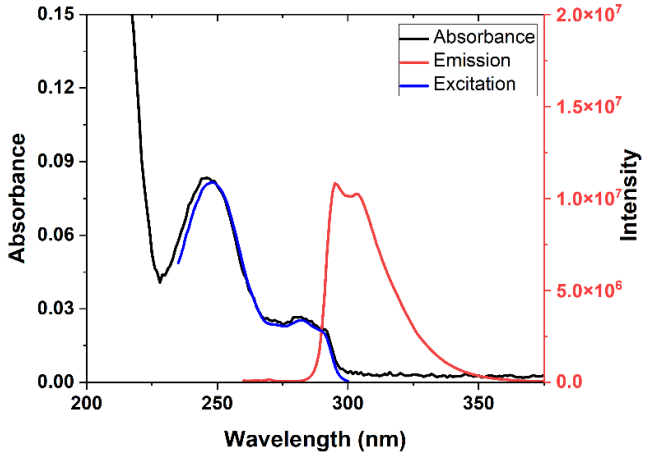


Figure 9.b Absorption, Emission (λ_{ex} =250 nm) and excitation (λ_{em} =310 nm) spectra of **1** (X = O) in acetonitrile (10^{-5} M).

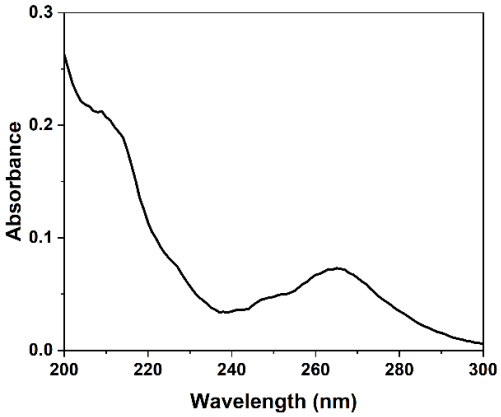


Figure 10.a Absorption spectrum of **2** (X = S) in acetonitrile (10^{-5} M).

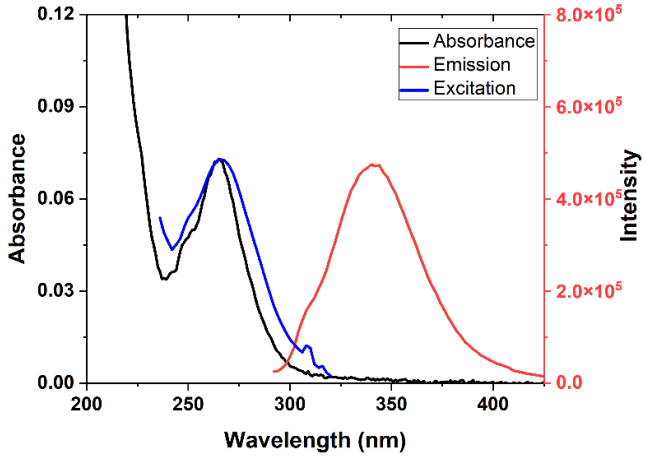


Figure 10.b Absorption, Emission (λ_{ex} =265 nm) and excitation (λ_{em} =340 nm) spectra of **1** (X = S) in acetonitrile (10^{-5} M).

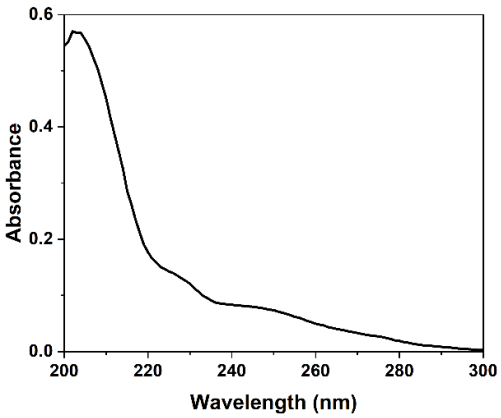


Figure 11.a Absorption spectrum of **3** (X = SO) in acetonitrile (10^{-5} M).

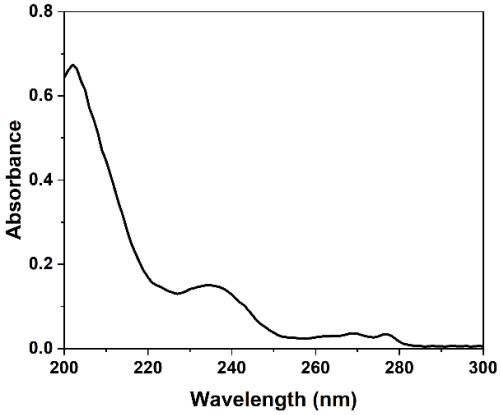


Figure 12.a Absorption spectrum of **4** (X = SO_2) in acetonitrile (10^{-5} M).

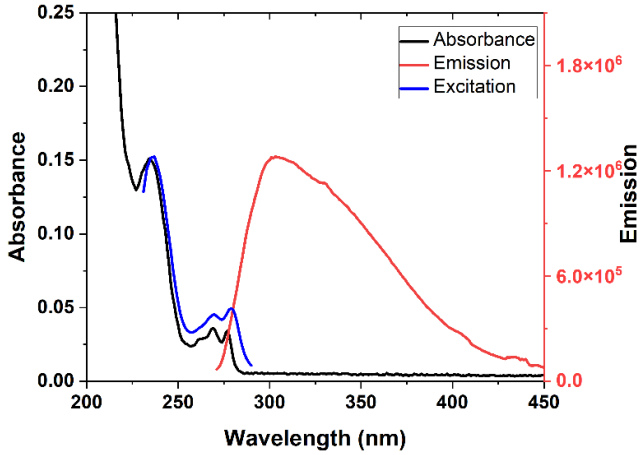


Figure 12.b Absorption, Emission (λ_{ex} =240 nm) and excitation (λ_{em} =306 nm) spectra of **4** (X = SO_2) in acetonitrile (10^{-5} M).

Solution (5-50 mM, ACN) absorbance spectra.

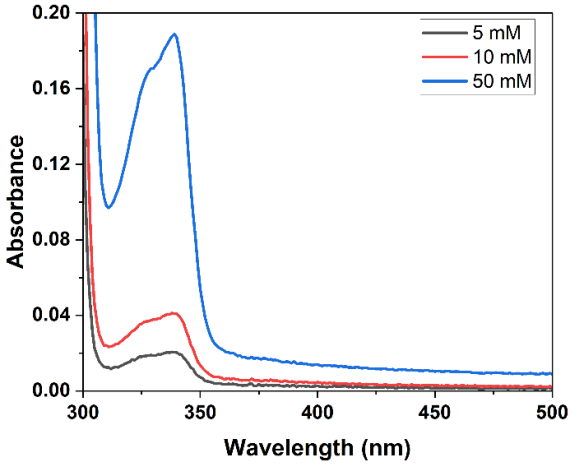


Figure 13.a Absorption spectra of **1** (X = O) at different concentrations in acetonitrile.

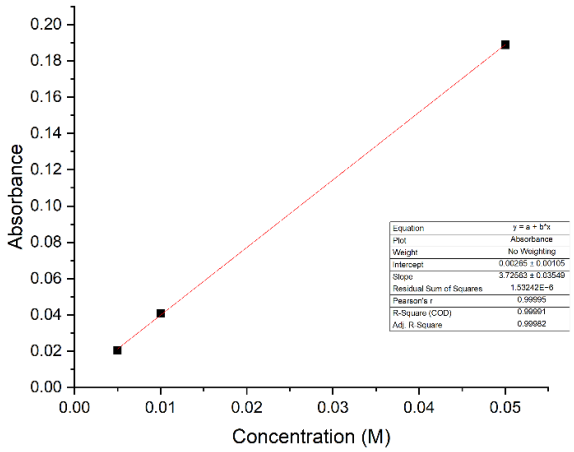


Figure 13.b Beer-Lambert plot of variable concentrations of **1**.

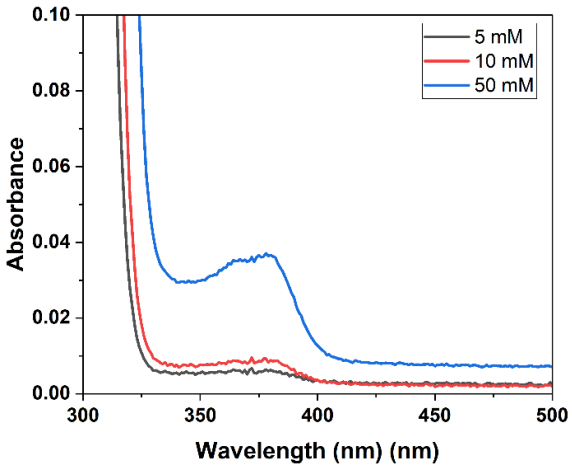


Figure 14.a Absorption spectra of **2** (X = S) at different concentrations in acetonitrile.

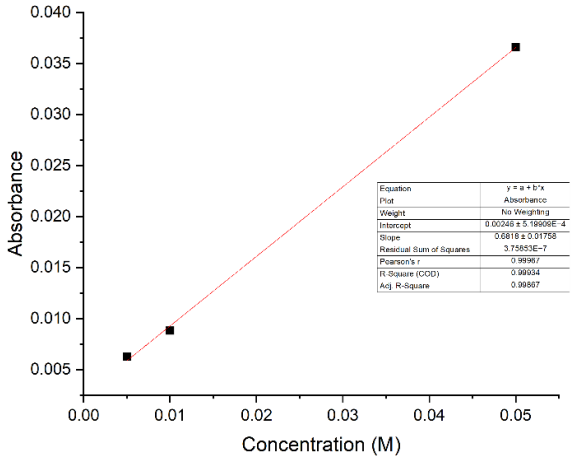


Figure 14.b Beer-Lambert plot of variable concentrations of **2**.

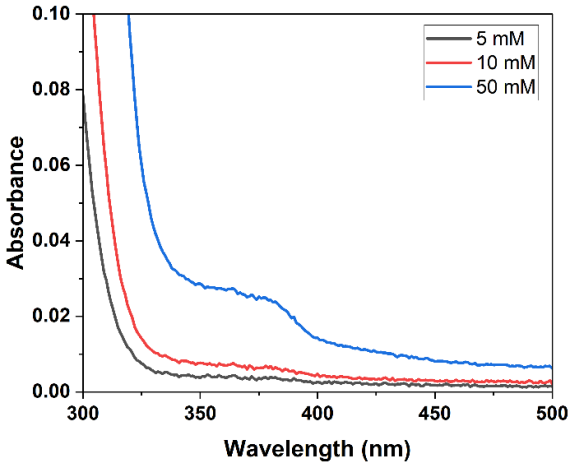


Figure 15.a Absorption spectra of **3** (X = SO) at different concentrations in acetonitrile.

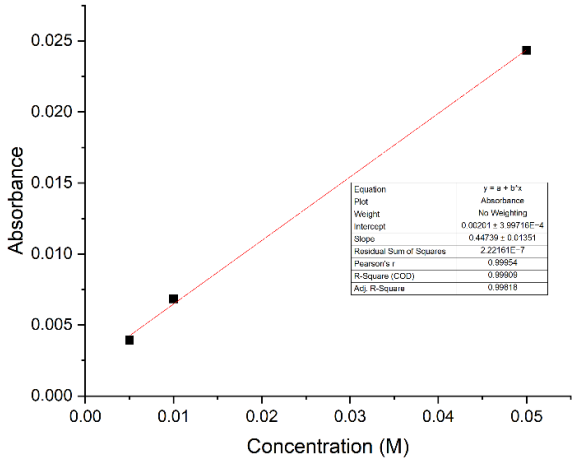


Figure 15.b Beer-Lambert plot of variable concentrations of **3**.

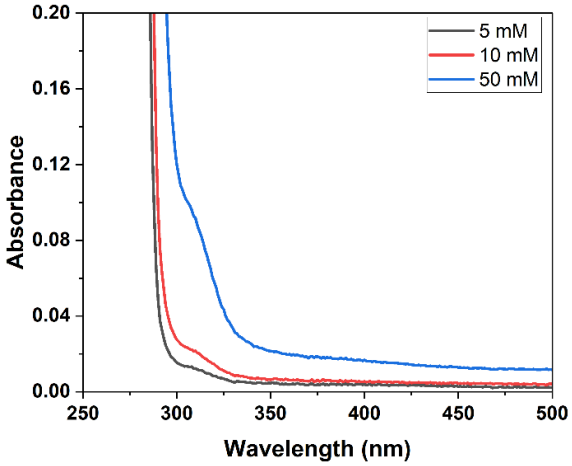


Figure 16.a Absorption spectra of **4** (X = SO_2) at different concentrations in acetonitrile.

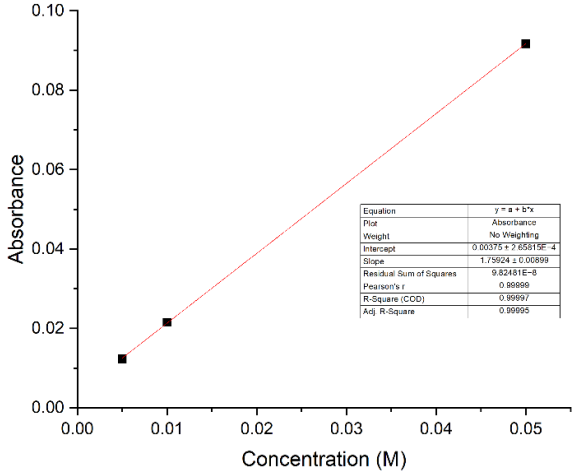


Figure 16.b Beer-Lambert plot of variable concentrations of **4**.

Emission and Excitation spectra of 1 – 4 (50 mM, ACN)

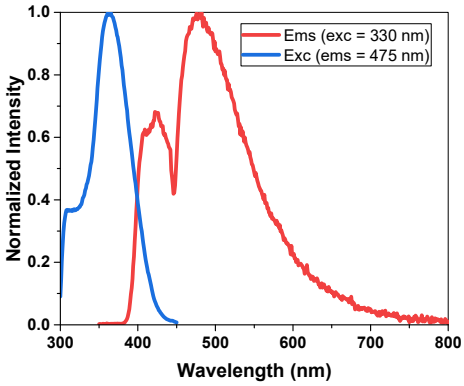


Figure 17.a Emission and excitation spectra of 50 mM **1** (X = O) in ACN.

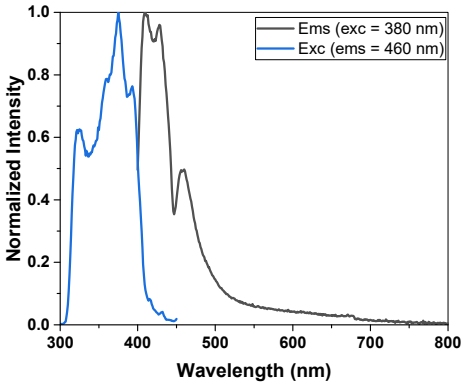


Figure 17.b Emission (λ_{ex} =380 nm) and excitation(λ_{em} =460 nm) spectra of 50 mM **2** (X = S) in ACN.

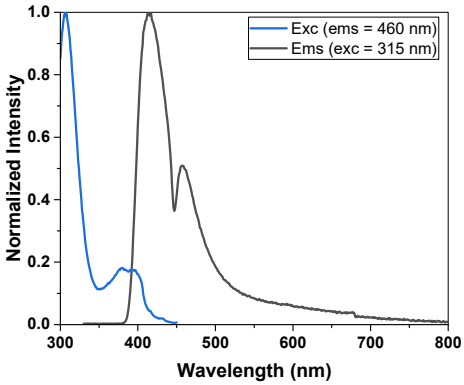


Figure 18.a Emission (λ_{ex} =315 nm) and excitation (λ_{em} =460 nm) spectra of 50 mM **3** (X = SO) in ACN.

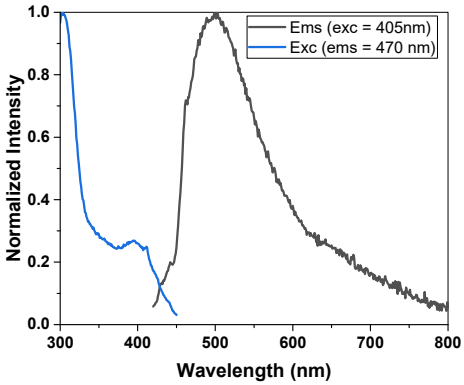


Figure 18.b Emission (λ_{ex} =405 nm) and excitation (λ_{em} =470 nm) spectra of 50 mM **4** (X = SO_2) in ACN.

Solution (50 mM, ACN) variable temperature absorbance spectra of 1 - 4.

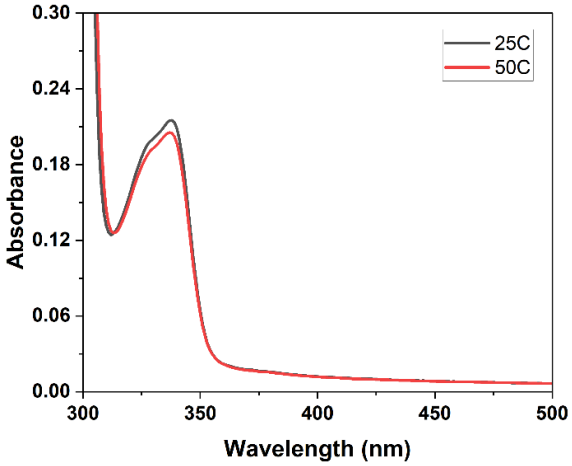


Figure 19.a Absorption spectra of **1** (X = O) at different temperatures in acetonitrile (50 mM).

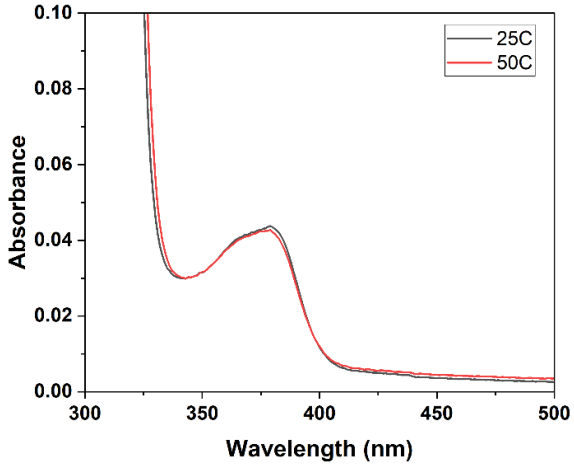


Figure 19.b Absorption spectra of **2** (X = S) at different temperatures in acetonitrile (50 mM).

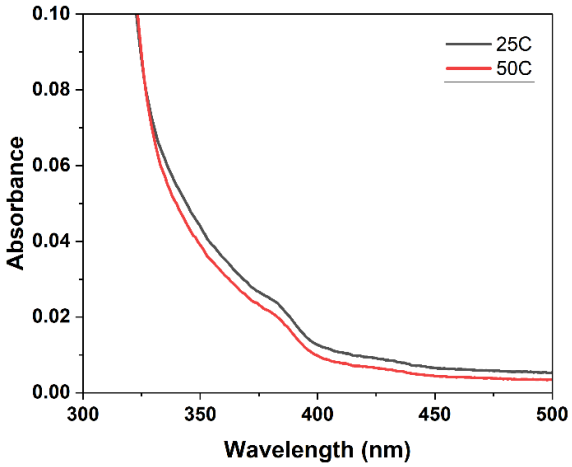


Figure 20.a Absorption spectra of **3** (X = SO) at different temperatures in acetonitrile (50 mM).

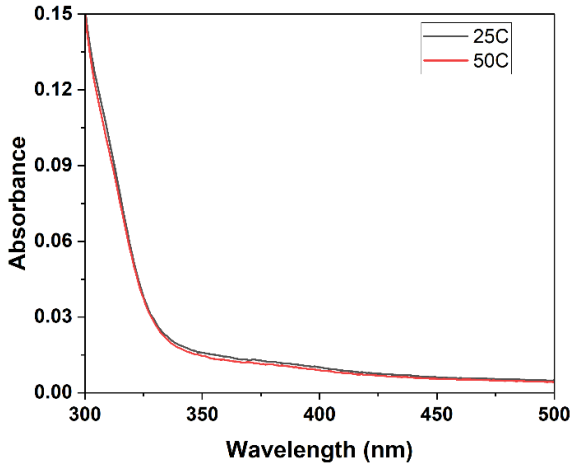


Figure 20.b Absorption spectra of **4** (X = SO_2) at different temperatures in acetonitrile (50 mM).

Emission lifetimes of solutions (50 mM, ACN) of 1 – 4.

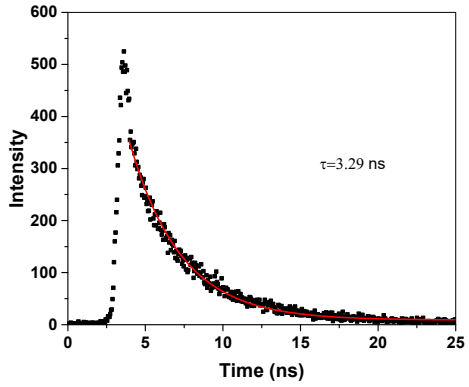


Figure 21.a Emission lifetime of 50 mM **1** (X = O) in ACN with excitation at 405 nm.

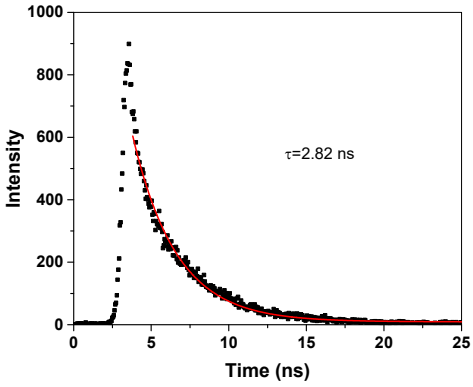


Figure 21.b Emission lifetime of 50 mM **2** (X = S) in ACN with excitation at 405 nm.

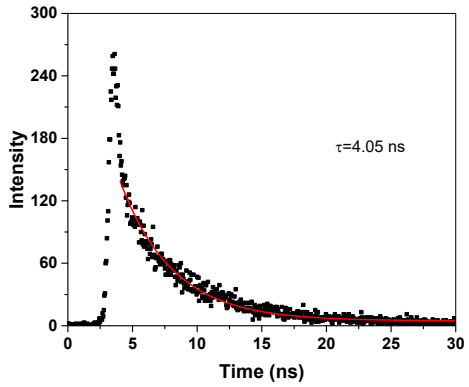


Figure 22.a Emission lifetime of 50 mM **3** (X = SO) in ACN with excitation at 405 nm.

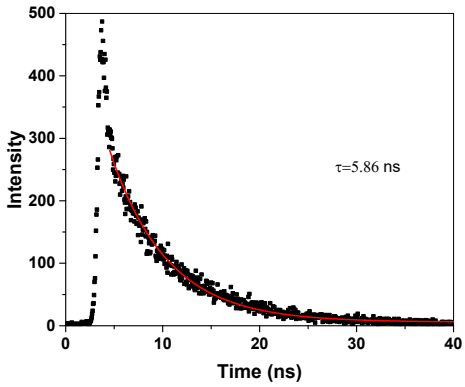
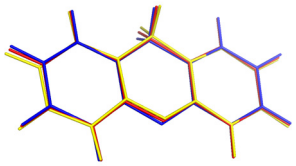


Figure 22.b Emission lifetime of 50 mM **4** (X = SO_2) in ACN with excitation at 405 nm.

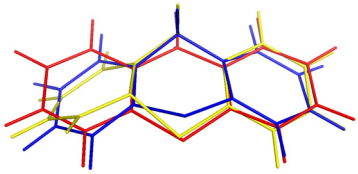
DFT calculated excited-state structure changes for 1 – 4.

X = O



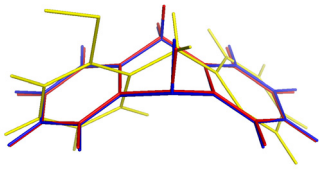
RMSD S_0 and S_1 = 0.118 Å
RMSD S_0 and T_1 = 0.180 Å
RMSD S_1 and T_1 = 0.199 Å

X=S



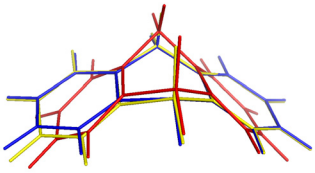
RMSD S_0 and S_1 = 0.696 Å
RMSD S_0 and T_1 = 0.489 Å
RMSD S_1 and T_1 = 0.590 Å

X = SO



RMSD S_0 and S_1 = 0.116 Å
RMSD S_0 and T_1 = N/A
RMSD S_1 and T_1 = N/A

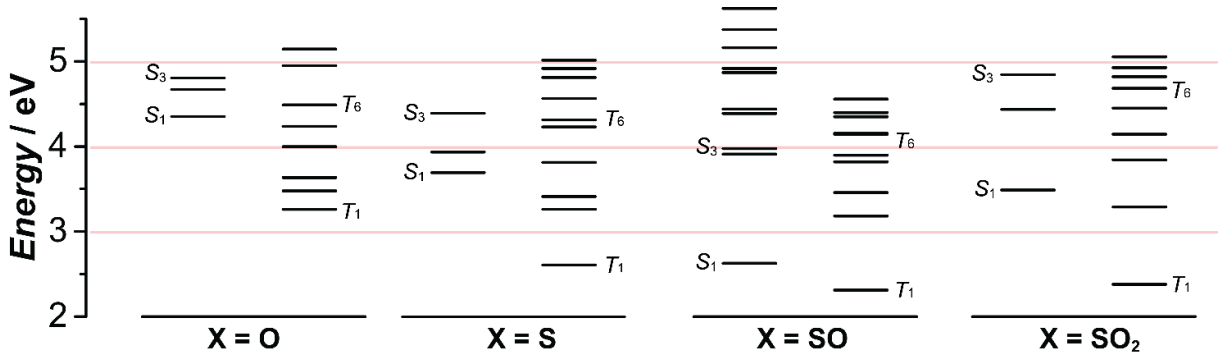
X = SO_2



RMSD S_0 and S_1 = 0.602 Å
RMSD S_0 and T_1 = 0.217 Å
RMSD S_1 and T_1 = 0.407 Å

Figure 23. Calculated RMSD in structures **1** – **4** between their ground state (S_0), singlet excited state (S_1) and excited state triplet (T_1) using PyMol2.5 pair fit function. For all structures shown, the following colours are used for each state: blue = S_0; red = S_1; yellow = T_1.

Computationally determined relevant S_n and T_n energies, and selected SOC constants for 1 – 4 in optimised S_1 geometries.



State	ΔE / eV	ξ / cm^{-1}	State	ΔE / eV	ξ / cm^{-1}	State	ΔE / eV	ξ / cm^{-1}	State	ΔE / eV	ξ / cm^{-1}
S_1, T_6	-0.13	0.00	S_1, T_6	-0.62	0.11	S_1, T_6	-1.51	0.66	S_1, T_6	-0.96	1.07
S_1, T_5	0.12	0.05	S_1, T_5	-0.54	0.02	S_1, T_5	-1.27	0.46	S_1, T_5	-0.66	2.37
S_1, T_4	0.36	0.00	S_1, T_4	-0.12	0.03	S_1, T_4	-1.19	11.44	S_1, T_4	-0.36	0.41
S_1, T_3	0.72	0.00	S_1, T_3	0.28	0.03	S_1, T_3	-0.83	7.40	S_1, T_3	-0.35	0.01
S_1, T_2	0.88	0.01	S_1, T_2	043	0.16	S_1, T_2	-0.55	7.42	S_1, T_2	0.20	0.72
S_1, T_1	1.10	0.01	S_1, T_1	1.09	0.04	S_1, T_1	0.32	0.78	S_1, T_1	1.11	0.51
S_0, T_1	3.26	0.02	S_0, T_1	2.61	1.87	S_0, T_1	2.31	11.41	S_0, T_1	2.38	3.37

Figure 24. Using the S_1-optimised geometry, the relevant singlet and triplet energies (eV) of **1** – **4**. In addition, below each energy diagram contains the magnitude of SOC constants (ξ) in units of cm^{-1}.

Computationally determined S_n and T_n energies (eV) at optimised S_1 geometries for 1 - 4.

1 (X = O) S_n and T_n energies / eV			2 (X = S) S_n and T_n energies / eV			3 (X = SO) S_n and T_n energies / eV			4 (X = SO_2) S_n and T_n energies / eV		
State	S_n	T_n	State	S_n	T_n	State	S_n	T_n	State	S_n	T_n
1	4.355	3.260	1	3.703	2.613	1	2.629	2.313	1	3.487	2.380
2	4.670	3.479	2	3.945	3.270	2	3.911	3.183	2	4.435	3.288
3	4.803	3.632	3	4.402	3.419	3	3.972	3.459	3	4.846	3.840
4	5.506	3.999	4	5.078	3.823	4	4.389	3.816	4	5.044	3.844
5	5.544	4.237	5	5.277	4.243	5	4.440	3.898	5	5.073	4.142
6	5.913	4.488	6	5.299	4.324	6	4.869	4.142	6	5.215	4.448
7	5.973	4.951	7	5.643	4.575	7	4.918	4.153	7	5.417	4.681
8	5.974	5.146	8	5.760	4.826	8	5.159	4.347	8	5.850	4.819
9	6.220	5.423	9	5.884	4.933	9	5.373	4.395	9	5.934	4.926
10	6.268	5.744	10	6.079	5.028	10	5.621	4.556	10	5.968	5.052

Computationally determined SOC constants (cm^{-1}) for singlet and triplet states in optimised S_1 geometries for 1 – 4.

1 (X = O) SOC constants / cm^{-1}			2 (X = S) SOC constants / cm^{-1}			3 (X = SO) SOC constants / cm^{-1}			4 (X = SO_2) SOC constants / cm^{-1}		
T_n	S_n	ξ	T_n	S_n	ξ	T_n	S_n	ξ	T_n	S_n	ξ
1	0	0.022	1	0	1.864	1	0	11.413	1	0	3.368
1	1	0.010	1	1	0.042	1	1	0.778	1	1	0.508
1	2	0.010	1	2	0.010	1	2	2.360	1	2	0.400
1	3	0.000	1	3	0.010	1	3	2.094	1	3	3.179
2	0	0.000	2	0	0.086	2	0	5.375	2	0	0.968
2	1	0.000	2	1	0.156	2	1	7.418	2	1	0.725
2	2	0.010	2	2	0.010	2	2	2.531	2	2	1.094
2	3	0.000	2	3	0.079	2	3	1.005	2	3	1.200
3	0	0.000	3	0	0.047	3	0	1.091	3	0	0.750
3	1	0.000	3	1	0.033	3	1	7.396	3	1	0.014
3	2	0.036	3	2	0.010	3	2	3.245	3	2	0.072
3	3	0.028	3	3	0.032	3	3	0.825	3	3	2.145
4	0	0.120	4	0	0.624	4	0	15.492	4	0	1.223
4	1	0.000	4	1	0.032	4	1	11.436	4	1	0.411
4	2	0.010	4	2	0.017	4	2	1.980	4	2	0.024
4	3	0.000	4	3	0.022	4	3	1.612	4	3	1.113
5	0	0.045	5	0	1.001	5	0	4.220	5	0	2.226
5	1	0.050	5	1	0.022	5	1	0.457	5	1	2.369
5	2	0.010	5	2	0.032	5	2	1.239	5	2	1.337
5	3	0.010	5	3	0.010	5	3	0.367	5	3	0.261
6	0	0.000	6	0	0.112	6	0	1.480	6	0	0.073
6	1	0.000	6	1	0.114	6	1	0.658	6	1	1.071
6	2	0.014	6	2	0.024	6	2	1.610	6	2	0.311
6	3	0.036	6	3	0.073	6	3	1.104	6	3	0.042
7	0	0.022	7	0	0.579	7	0	0.997	7	0	1.851
7	1	0.000	7	1	0.041	7	1	2.942	7	1	0.500
7	2	0.000	7	2	0.010	7	2	0.553	7	2	0.408
7	3	0.010	7	3	0.010	7	3	1.737	7	3	3.309
8	0	0.000	8	0	0.372	8	0	9.113	8	0	0.726
8	1	0.010	8	1	0.041	8	1	6.555	8	1	2.044
8	2	0.036	8	2	0.022	8	2	0.272	8	2	0.686
8	3	0.010	8	3	0.024	8	3	1.126	8	3	11.640
9	0	0.010	9	0	108.55	9	0	13.883	9	0	3.343
9	1	0.010	9	1	8.407	9	1	27.915	9	1	4.398
9	2	0.000	9	2	4.999	9	2	2.243	9	2	3.465
9	3	0.000	9	3	1.233	9	3	2.486	9	3	0.422
10	0	0.000	10	0	0.578	10	0	2.982	10	0	0.175
10	1	0.000	10	1	0.193	10	1	7.023	10	1	1.291
10	2	0.010	10	2	0.024	10	2	2.587	10	2	1.655
10	3	0.036	10	3	0.064	10	3	0.134	10	3	0.993

Computationally determined S_n and T_n energies (eV) at optimised S_0 geometries for 1 - 4.

1 (X = O) S_n and T_n energies / eV			2 (X = S) S_n and T_n energies / eV			3 (X = SO) S_n and T_n energies / eV			4 (X = SO_2) S_n and T_n energies / eV		
State	S_n	T_n	State	S_n	T_n	State	S_n	T_n	State	S_n	T_n
1	4.599	3.415	1	4.589	3.424	1	3.988	3.438	1	5.064	3.488
2	4.847	3.615	2	4.640	3.434	2	4.779	3.523	2	5.135	3.580
3	5.021	3.890	3	4.933	4.089	3	4.934	3.739	3	5.271	4.359
4	5.672	4.220	4	5.004	4.353	4	5.082	4.344	4	5.567	4.398
5	5.728	4.393	5	5.546	4.381	5	5.084	4.384	5	5.601	4.532
6	6.019	4.592	6	5.625	4.395	6	5.156	4.457	6	5.830	4.598
7	6.066	5.029	7	5.783	4.828	7	5.294	4.606	7	5.937	5.006
8	6.139	5.187	8	5.954	4.848	8	5.341	4.757	8	6.027	5.089
9	6.348	5.628	9	5.990	5.031	9	5.702	4.843	9	6.126	5.291
10	6.423	5.854	10	6.054	5.221	10	5.717	4.898	10	6.170	5.596

Computationally determined SOC constants (cm^{-1}) for singlet and triplet states in optimised S_0 geometries for 1 – 4.

1 (X = O) SOC constants / cm^{-1}			2 (X = S) SOC constants / cm^{-1}			3 (X = SO) SOC constants / cm^{-1}			4 (X = SO_2) SOC constants / cm^{-1}		
T_n	S_n	ξ	T_n	S_n	ξ	T_n	S_n	ξ	T_n	S_n	ξ
1	0	0.180	1	0	13.353	1	0	3.787	1	0	2.560
1	1	0.148	1	1	1.051	1	1	6.862	1	1	0.154
1	2	0.050	1	2	3.602	1	2	0.345	1	2	0.811
1	3	0.120	1	3	1.474	1	3	0.440	1	3	0.037
2	0	0.130	2	0	1.185	2	0	6.799	2	0	1.238
2	1	0.130	2	1	0.187	2	1	4.496	2	1	1.788
2	2	0.014	2	2	7.175	2	2	20.273	2	2	0.024
2	3	0.022	2	3	1.429	2	3	2.590	2	3	2.359
3	0	0.130	3	0	9.392	3	0	12.709	3	0	0.269
3	1	0.060	3	1	1.916	3	1	2.854	3	1	0.717
3	2	0.190	3	2	2.446	3	2	31.249	3	2	0.072
3	3	0.032	3	3	0.485	3	3	2.268	3	3	0.313
4	0	0.316	4	0	3.511	4	0	0.335	4	0	0.975
4	1	0.362	4	1	2.458	4	1	1.168	4	1	0.078
4	2	0.100	4	2	1.194	4	2	2.442	4	2	0.586
4	3	0.030	4	3	1.909	4	3	1.721	4	3	0.022
5	0	0.187	5	0	30.106	5	0	4.220	5	0	3.133
5	1	0.076	5	1	1.901	5	1	10.853	5	1	0.020
5	2	0.020	5	2	2.624	5	2	0.180	5	2	0.348
5	3	0.020	5	3	0.289	5	3	0.528	5	3	0.054
6	0	0.350	6	0	2.635	6	0	6.897	6	0	1.970
6	1	0.040	6	1	1.771	6	1	16.639	6	1	2.465
6	2	0.064	6	2	5.321	6	2	0.033	6	2	0.017
6	3	0.054	6	3	0.222	6	3	4.386	6	3	2.932
7	0	0.061	7	0	6.967	7	0	2.761	7	0	2.009
7	1	0.067	7	1	0.528	7	1	6.337	7	1	0.088
7	2	0.160	7	2	3.031	7	2	5.210	7	2	0.589
7	3	0.050	7	3	0.871	7	3	0.889	7	3	0.057
8	0	0.200	8	0	48.335	8	0	32.621	8	0	0.734
8	1	0.060	8	1	2.067	8	1	46.112	8	1	0.558
8	2	0.184	8	2	2.766	8	2	0.453	8	2	0.051
8	3	0.030	8	3	1.211	8	3	1.824	8	3	1.808
9	0	0.972	9	0	103.819	9	0	7.757	9	0	1.268
9	1	0.340	9	1	3.955	9	1	0.174	9	1	0.732
9	2	0.020	9	2	1.542	9	2	1.835	9	2	1.564
9	3	0.080	9	3	1.774	9	3	1.417	9	3	1.446
10	0	0.290	10	0	0.790	10	0	58.578	10	0	8.087
10	1	0.070	10	1	1.738	10	1	23.222	10	1	8.021
10	2	0.971	10	2	2.073	10	2	0.127	10	2	0.437
10	3	0.193	10	3	0.559	10	3	3.030	10	3	8.771

Excitation and emission spectra of crystalline samples of 1 – 4 (200 μs delay).

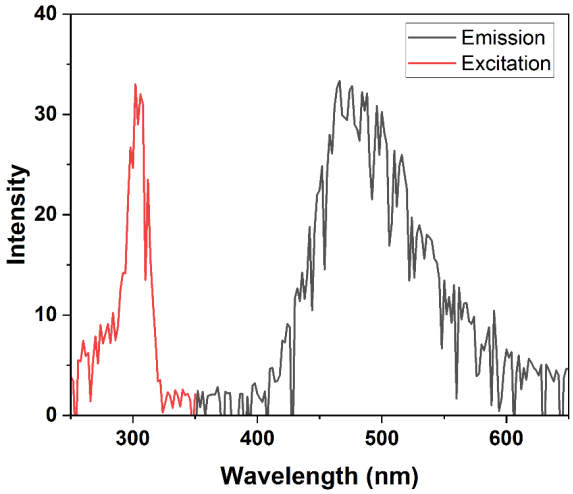


Figure 25.a Solid-state emission (λ_{ex} = 306 nm) and excitation (λ_{em} = 475 nm) spectra of **1** (X = O).

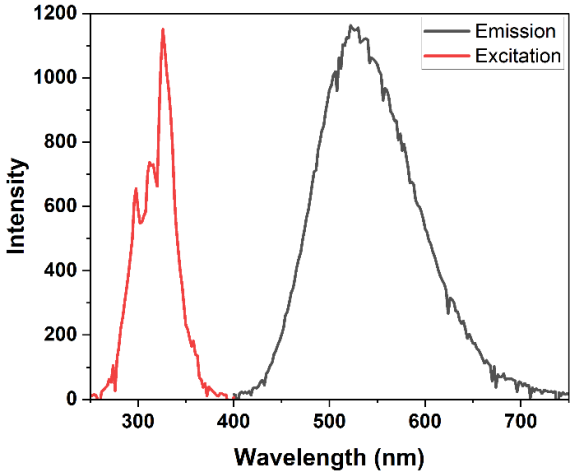


Figure 25.b Solid-state emission (λ_{ex} = 326 nm) and excitation (λ_{em} = 530 nm) spectra of **2** (X = S).

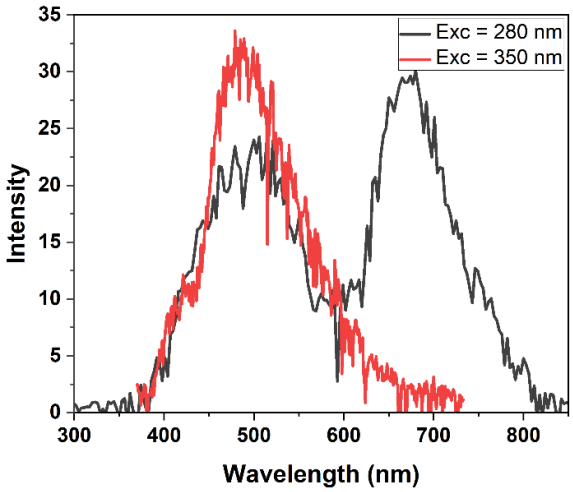


Figure 26.a Solid-state emission (λ_{ex} = 280 nm or 350 nm) spectra of **3** (X = SO).

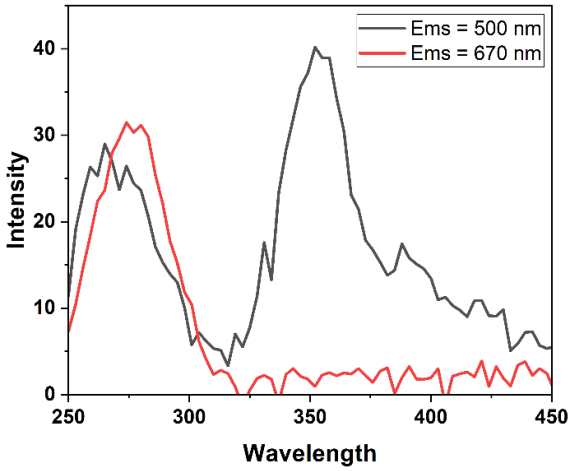


Figure 26.b Solid-state excitation (λ_{em} = 500 nm or 670 nm) spectra of **3** (X = SO).

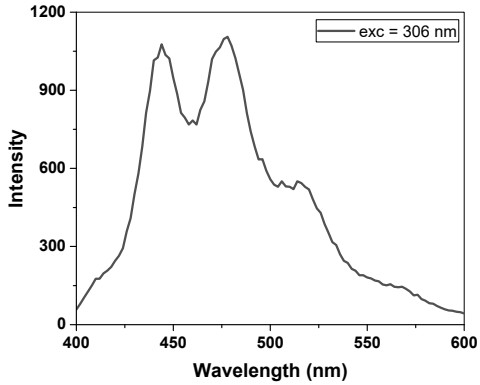


Figure 27.a Solid-state emission (λ_{ex} = 306 nm) spectrum of **4** (X = SO_2).

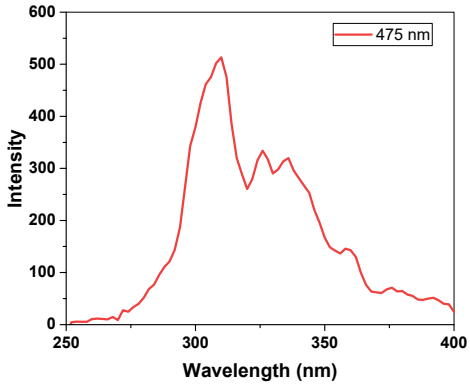


Figure 27.b Solid-state excitation (λ_{em} = 475 nm) spectrum of **4** (X = SO_2).

Variable Temperature Emission of Crystalline Samples of 1 – 4 (200 μs delay).

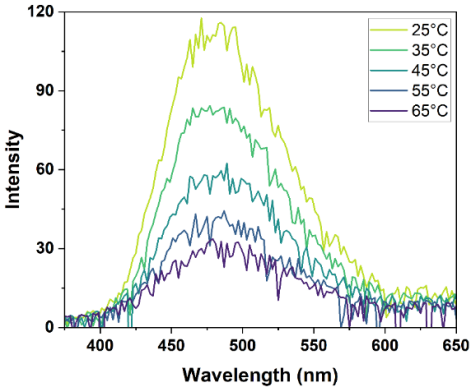


Figure 28.a Emission spectra of **1** (X = O, λ_{ex} = 310 nm) at various temperatures.

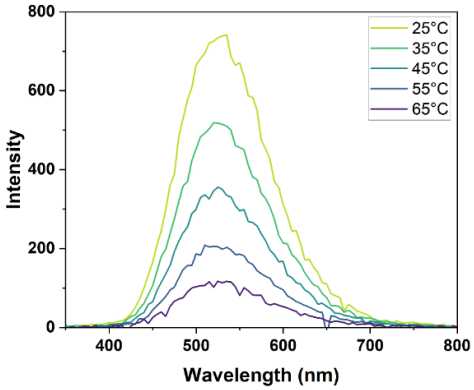


Figure 28.b Emission spectra of **2** (X = S, λ_{ex} = 326 nm) at various temperatures.

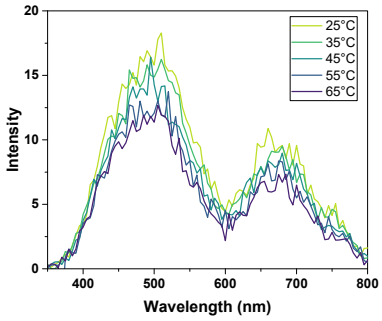


Figure 29.a Emission spectra of **3** (X = SO, λ_{ex} = 280 nm) at various temperatures..

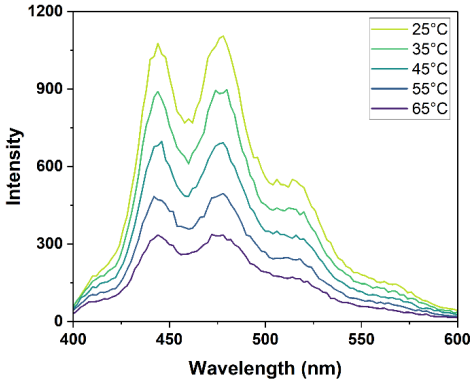


Figure 29.b Emission spectra of **4** (X = SO_2, λ_{ex} = 306 nm) at various temperatures.

Emission lifetimes of crystalline solids 1 – 4 (200 μs delay).

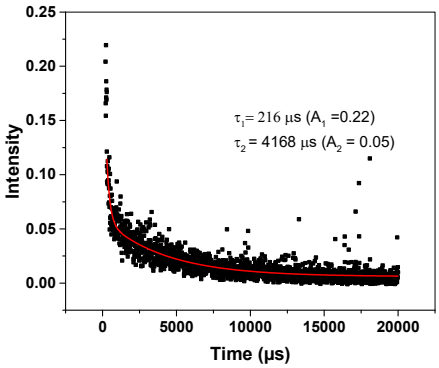


Figure 30.a Emission (475 nm) lifetime of solid **1** (X = O) with excitation at 310 nm.

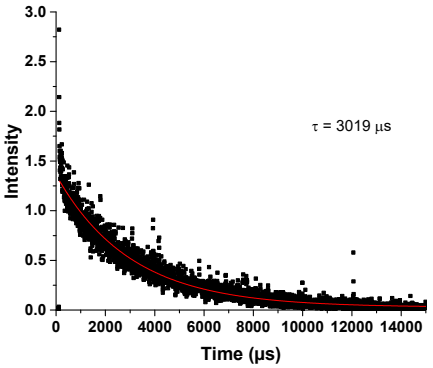


Figure 30.b Emission (530 nm) lifetime of solid **2** (X = S) with excitation at 326 nm.

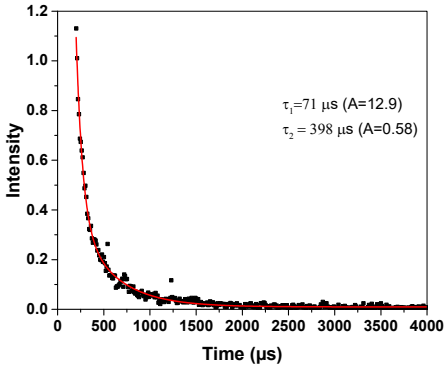


Figure 31.a Emission (500 nm) lifetime of solid **3** (X = SO) with excitation at 280 nm.

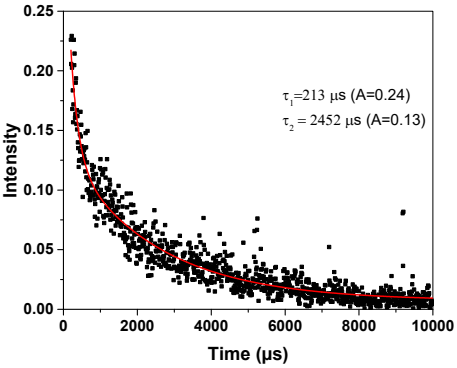


Figure 31.b Emission (670 nm) lifetime of solid **3** (X = SO) with excitation at 280 nm.

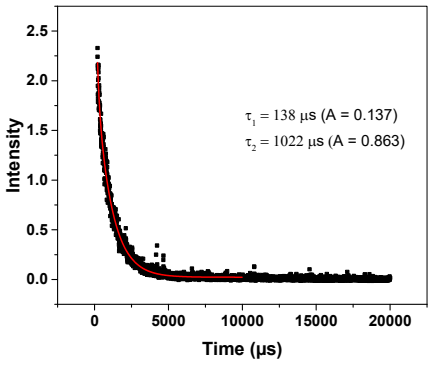


Figure 32.a Emission (475 nmm) lifetime of solid **4** (X = SO_2) with excitation at 306 nm.

Emission of Crystalline Samples under either air or N_2 atmosphere (200 μs delay).

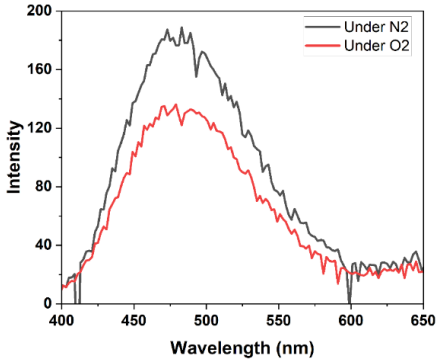


Figure 33.a X = O

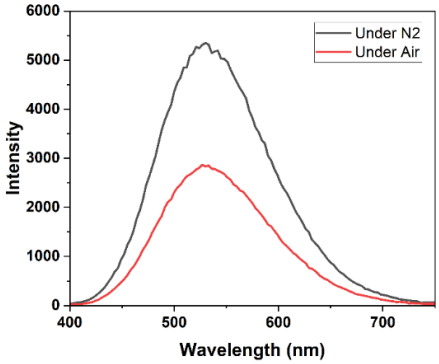


Figure 33.b X = S

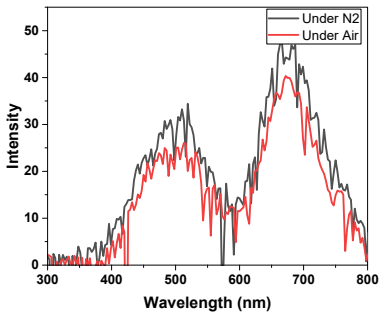


Figure 34.a X = SO.

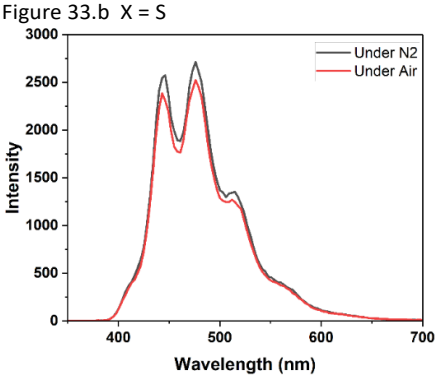


Figure 34.b X = SO_2

Steady-state fluorescence of crystalline samples of 1, 2, and 4.

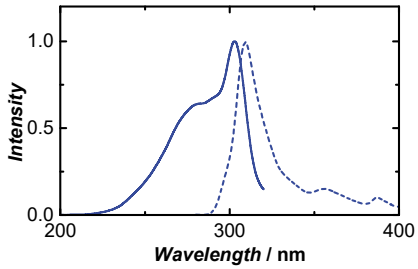


Figure 35.a Emission (dashed line, λ_{ex} = 260 nm) and excitation (solid line, λ_{em} = 340 nm) spectra of **1** (X = O).

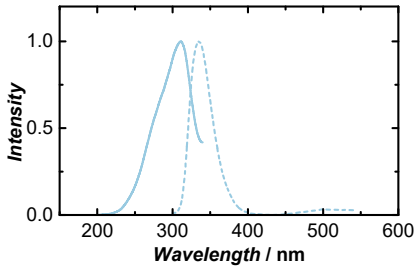


Figure 35.b Emission (dashed line, λ_{ex} = 285 nm) and excitation (solid line, λ_{em} = 360 nm) spectra of **2** (X = S).

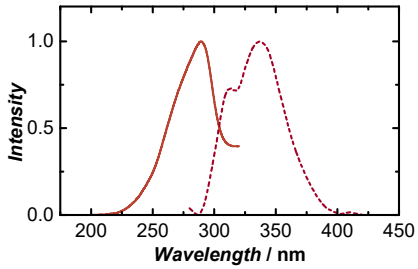


Figure 36.b Emission (dashed line, λ_{ex} = 260 nm) and excitation (solid line, λ_{em} = 340 nm) spectra of **4** (X = SO_2).

Emission lifetimes of crystalline solids 1 – 4 (prompt).

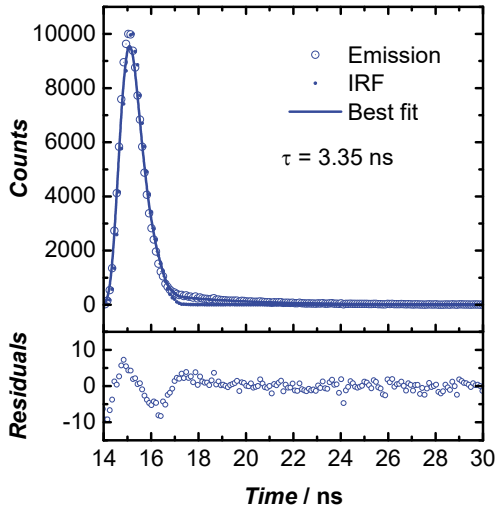


Figure 37.a Emission (320 nm) lifetime of solid **1** (X = O) with excitation at 290 nm. Raw data (open circles), Instrument response factor (IRF, solid points), best fit (line) and residuals plot of best-fit line.

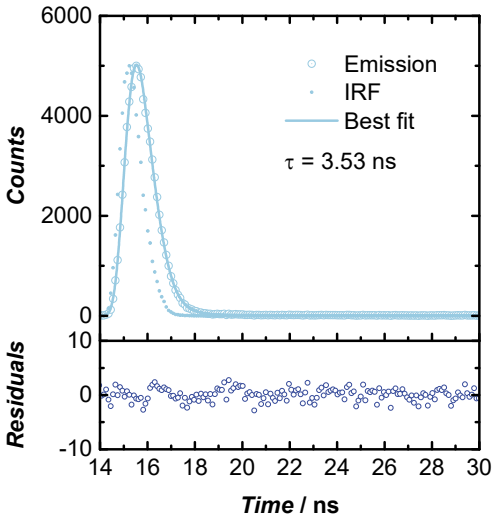


Figure 37.b Emission (385 nm) lifetime of solid **2** (X = S) with excitation at 310 nm. Raw data (open circles), Instrument response factor (IRF, solid points), best fit (line) and residuals plot of best-fit line.

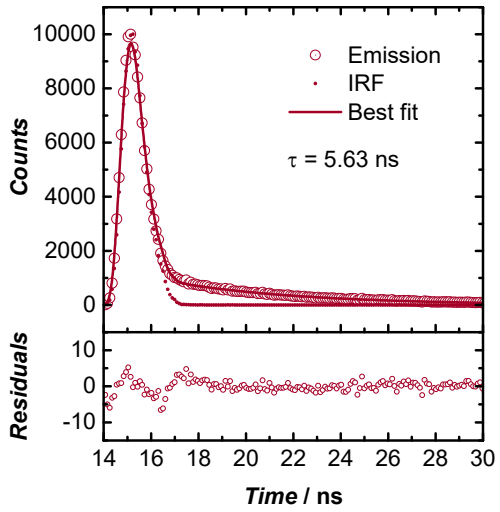


Figure 38.b Emission (340 nm) lifetime of solid **4** (X = SO_2) with excitation at 290 nm. Raw data (open circles), Instrument response factor (IRF, solid points), best fit (line) and residuals plot of best-fit line.

Irradiance power (transmittance) versus emission intensity of crystalline solids 1 – 4.

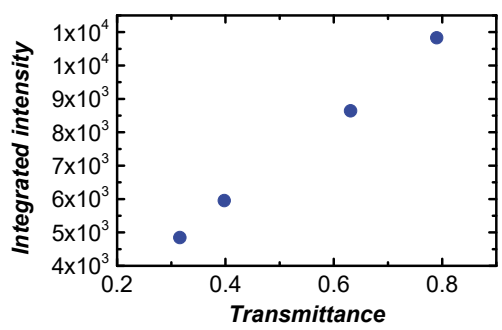


Figure 39.a X = O

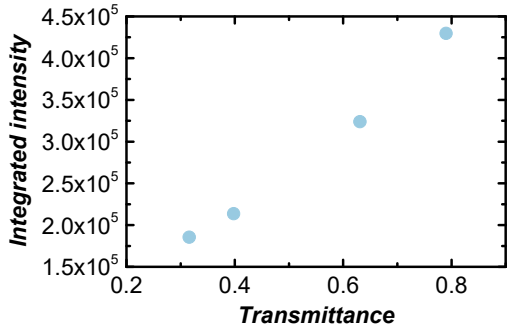


Figure 39.b X = S

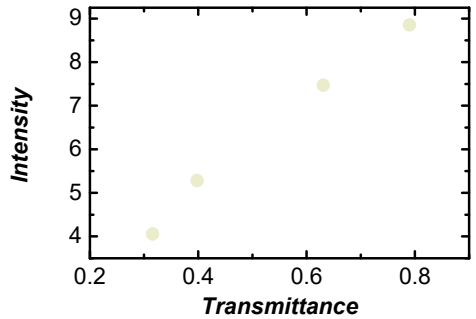


Figure 40.a X = SO.

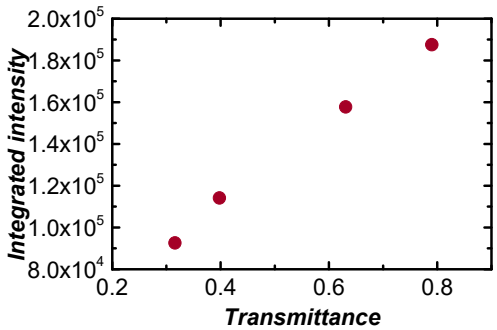


Figure 40.b X = SO_2

Natural Transition orbitals (NTOs) of 1 - 4.

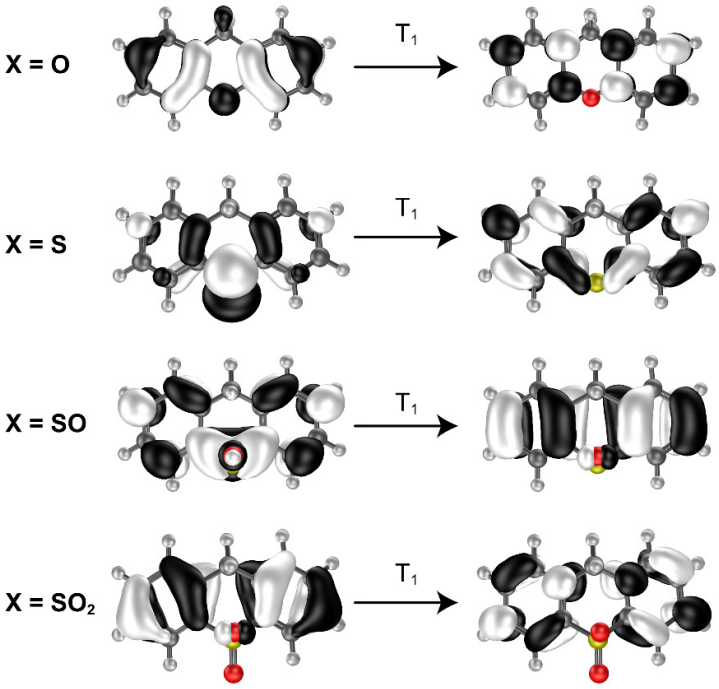


Figure 41. Natural transition orbitals (NTOs) of T_1 state for **1** - **4**.

DFT Computations Orca 5.0.3, PBE0 D4 def2-TZVP – Ground states (S_0) of 1 – 4.

X = O

Energy: -576.052695817400Eh Lowest IR freq: 119.48 cm^{-1}

Cartesian coordinates:

O	3.23983454815159	5.22175728558252	1.25235369268813
C	2.95508470565381	4.04505663058156	0.62540811840521
C	3.40783991635032	2.89644987166393	1.26142152707945
H	3.94883590411115	2.99915099782478	2.19437547447434
C	3.16477837408518	1.65864733584873	0.69810987099807
H	3.51843805268470	0.76373790103818	1.19650981479866
C	2.47437058999743	1.56623850735745	-0.50351555153170
H	2.28342723880574	0.59939463598296	-0.95323939358014
C	2.03085261185120	2.72061017642900	-1.12335924738511
H	1.48866461105057	2.65521667969880	-2.06181377698351
C	2.25571210184204	3.97762935274973	-0.57260457142553
C	1.74442909097180	5.22175956457739	-1.23305089152757
H	0.64699140887812	5.22176045231195	-1.21399419383046
H	2.02310343275352	5.22176036264947	-2.29252922167147
C	2.95508588705778	6.39845888248882	0.62540952832051
C	3.40784250952764	7.54706406485029	1.26142474059103
H	3.94883926592380	7.44436070479144	2.19437794924400
C	3.16478295937631	8.78486766311407	0.69811425948705
H	3.51844420791213	9.67977610862680	1.19651490613376
C	2.47437449735559	8.87727879839778	-0.50351051601065
H	2.28343310390368	9.84412348880488	-0.95323344618967
C	2.03085487122529	7.72290848896143	-1.12335577888865
H	1.48866705907779	7.78830372416279	-2.06181031661697
C	2.25571305145280	6.46588832150524	-0.57260297657877

X = S

Energy: -898.936764454031Eh Lowest IR freq: 56.24 cm^{-1}

Cartesian coordinates:

C	0.95167393509505	0.45435963483867	0.59502651019526
C	5.07958695528255	-2.56712200400958	0.18249101312026
C	5.28927959558528	-1.89985429219280	1.38017639764037
C	4.48484193560784	-0.82691502830488	1.72551645845916
C	3.48788495998840	-0.40294800218172	0.85516905065091
C	-0.23772620176672	0.77008900891377	1.24055973500243
C	-1.44615484838030	0.38267054293573	0.68619774693924
C	-1.46624388695895	-0.34110422255046	-0.49699570312058
C	-0.27537487961367	-0.65907168703725	-1.13134874842676
C	0.94344533619894	-0.24982160040173	-0.60875148399299
C	2.24499894867926	-0.51399202479884	-1.30173722470699
C	3.28694707832020	-1.04620433680577	-0.36561225295192
C	4.07900883953388	-2.14232068993634	-0.67777515541329
H	5.69619912437423	-3.41770146676271	-0.08257642078374
H	6.06811869390247	-2.22677185318637	2.05902596401995
H	4.61715400265511	-0.32261822363353	2.67570787689932
H	-0.21075928185721	1.30640856195226	2.18209483492994
H	-2.37248289610863	0.63208634373862	1.19001938969607
H	-2.40912177797461	-0.65927522419541	-0.92552070837899
H	-0.28823687057256	-1.22216691455895	-2.05883979215692
H	2.61152815025448	0.44064236222222	-1.70883365294196
H	2.10300200867235	-1.19075479803045	-2.14569475265459
H	3.91639580738460	-2.65919455128378	-1.61792702538807
S	2.47893527169799	0.96738046526930	1.30142794336389

X = SO

Energy: -974.098803947903 Eh Lowest IR freq: 55.34 cm^{-1}

Cartesian coordinates:

S	5.59317398115394	0.82678385017596	13.38862043355899
O	4.63244306501793	-0.23861544475183	13.00496755534847
C	5.06178777988837	1.45156471267884	14.97218634346463
C	5.84718016520031	1.20852591755411	16.08602657141257
H	6.80483237054276	0.71286454103941	15.96964571947892
C	5.39450492675197	1.59510131387897	17.33853324017266
H	6.00130507754494	1.41093535730088	18.21688263575961
C	4.15931490784075	2.21209476413914	17.45694320548213
H	3.79831604961765	2.51561545801456	18.43274424537232
C	3.38086017918804	2.45392684758564	16.33231885492220
H	2.42137212152406	2.94983067169898	16.43528830131152
C	3.82123289792701	2.07940532417784	15.07265500199709
C	3.02359046720496	2.34406005909480	13.83032972892309
H	2.58033492292410	1.39562931384908	13.50067413574008
H	2.20712613652967	3.03603256542441	14.04013238106344
C	3.88229738271209	2.86842710420871	12.71770864596401
C	3.49392965502536	3.93113925954382	11.91700876595198
H	2.53217860114273	4.40317006450863	12.08864855904235
C	4.32715297729031	4.40252633080951	10.91069648174634
H	4.00607500128822	5.23629715104806	10.29716439410340
C	5.56551779542255	3.82024965498959	10.69217769886528
H	6.21473645600459	4.19231892861238	9.90881312980056
C	5.96675619192191	2.75218212324388	11.48046242940798
H	6.92596551550633	2.27227978750198	11.31964537950926
C	5.12691537482939	2.28775434367262	12.47802616160096

X = SO2

Energy: -1049.312794972365 Eh Lowest IR freq: 56.35 cm^{-1}

Cartesian coordinates:

C	4.18616782941285	-2.28151204889230	2.20367642609250
C	3.71351079767973	-3.18233494959390	1.26142123239435
C	3.24013971487582	-4.41016852755999	1.72020406505592
C	1.81757763661600	-4.50544308645496	-0.56344877977066
C	2.38851509434498	-3.26909961487884	-0.85847228603835
C	4.18705368871365	-2.60497196871270	3.55347905278815
C	3.69975880214856	-3.82892368235576	3.98666781340433
C	3.21341802886866	-4.74062511382595	3.06318864940288
C	0.61107826574264	-4.91441416100636	-1.10290198265198
C	-0.043330747489 04	-4.07587445077535	-1.99095211683013
C	0.51041579260091	-2.84476363820273	-2.30894439862744
C	1.71186116504312	-2.44207962732521	-1.74226461371170
C	3.68169114336561	-2.86461859107913	-0.20755047390468
H	4.55098425446821	-1.31338101996595	1.87793513802151
H	4.56089906571405	-1.88715940958125	4.27434621993304
H	3.69189280943149	-4.07103755191549	5.04245009473341
H	2.81203219777663	-5.69951384879129	3.36784417193226
H	0.19991852776361	-5.87550940322005	-0.81904109341814
H	-0.98730567217887	-4.37947937214103	-2.42701089157280
H	-0.00380676961872	-2.18311676406103	-2.99625680943795
H	2.12554521853927	-1.46885496220092	-1.98338429175334
H	3.86360588490268	-1.80074109758770	-0.36381652249941
H	4.49913134644287	-3.41071760596088	-0.69591009505804
O	3.88298216127496	-6.02753944918450	-0.19525225287997
O	1.82127488106420	-6.53164025991587	1.09991422412977
S	2.71328888249613	-5.57317979481080	0.50987952026648

DFT Computations Orca 5.0.3, PBE0 D4 def2-TZVP – S_1 of 1 – 4.

X = O

Energy: -576.024706556601 Eh Lowest IR freq: 59.55 cm^{-1}

Cartesian coordinates:

O	3.37017834268050	5.22175736343241	1.13372185116080
C	3.02258434649571	4.04623956085272	0.57448662394895
C	3.45254375673798	2.91006340298608	1.27040264572037
H	4.01860262480036	3.03411923602832	2.18322173118716
C	3.12432288202021	1.66172369896618	0.74492247957013
H	3.43783208647130	0.75888230631501	1.25338059050006
C	2.39104745482899	1.57509011062205	-0.43795475545301
H	2.14290932651011	0.59737594966733	-0.83535919060251
C	1.97049721680163	2.71575795472005	-1.11980498648823
H	1.40142842919668	2.63548759211741	-2.03769114709237
C	2.28582295906801	3.99070395688294	-0.61376067973746
C	1.85874166996442	5.22175947837038	-1.30422916871619
H	0.75577129775090	5.22175955983454	-1.43876221255701
H	2.23049161581033	5.22176048053872	-2.35140742301736
C	3.02258540016087	6.39727590703842	0.57448881983697
C	3.45254621438483	7.53345072427187	1.27040690371568
H	4.01860525661202	7.40939310580664	2.18322560157010
C	3.12432682454940	8.78179164468376	0.74492758065174
H	3.43783700207019	9.68463237375698	1.25338619934480
C	2.39105219169842	8.86842689792141	-0.43795016210508
H	2.14291421585674	9.84614183213420	-0.83535288701794
C	1.97050072265767	7.72776059755036	-1.11980260716377
H	1.40143363920161	7.80803295350829	-2.03768962083806
C	2.28582452367109	6.45281331199389	-0.61375918641778

X = S

Energy: -898.936764454031 Eh Lowest IR freq: 33.53 cm^{-1}

Cartesian coordinates:

C	0.77221717426526	0.08016890278275	0.83801485886852
C	5.50253433816719	-2.14189628194712	-0.04772092887474
C	5.62146069751320	-1.60369087427904	1.26269986255904
C	4.56388220473236	-0.94605896694935	1.82153333829952
C	3.35364218684907	-0.79767378104402	1.10594814153370
C	-0.38737787441931	0.73812289861893	1.30838648575058
C	-1.50284400974712	0.81763598771578	0.52567684189466
C	-1.49543423182916	0.23451992770435	-0.77093075618226
C	-0.36493626637656	-0.40744738196246	-1.23025454319396
C	0.79521793354315	-0.51397474760447	-0.46793918589170
C	1.97733600869452	-1.21471026972702	-1.01171793718396
C	3.21760106451634	-1.33632097147374	-0.21707567243268
C	4.32246083064145	-1.99790673068189	-0.74611193491933
H	6.33770408862310	-2.66430723855960	-0.49707835832168
H	6.54509596405446	-1.71369083716136	1.81678088403697
H	4.64013016804645	-0.52961038648386	2.82067850327804
H	-0.37776716921775	1.17864281535537	2.30003488882563
H	-2.38750936226088	1.32265820674202	0.89243007926959
H	-2.37662277191996	0.29424192409129	-1.39721527103660
H	-0.36876820137338	-0.85052920547307	-2.22226662796611
H	2.23730959852867	-0.74244482730426	-1.97320662642704
H	1.66358584556204	-2.22948597665146	-1.30583706831350
H	4.24031678835030	-2.41299215448002	-1.74679029822885
S	2.10366499505647	0.04254996877228	1.89376132465614

X = SO

Energy: -973.954321575307 Eh Lowest IR freq: 58.51 cm^{-1}

Cartesian coordinates:

S	5.49701753991482	0.88558234633624	13.40535852135563
O	5.00719859693024	-0.44224382274316	12.94697028563788
C	5.02041298951647	1.40561443856016	14.95658363270600
C	5.82196520288916	1.16671724576281	16.08743662670689
H	6.76229561303805	0.63886287830528	15.98792170483613
C	5.39160847137453	1.61636741291028	17.31514491859652
H	6.00530045058242	1.44003333590783	18.19051239403603
C	4.17445306071476	2.28721159027881	17.43832205645025
H	3.83678192104261	2.62881529307415	18.40837131875283
C	3.38888808791971	2.51552815724034	16.30785781935402
H	2.44880011393544	3.04928293761918	16.40245152026829
C	3.77585370623457	2.07988285674285	15.06010138571351
C	2.97594611045760	2.30007193618134	13.81443460254248
H	2.56875623149806	1.33010932578488	13.47899425064106
H	2.12695614599009	2.95459320357378	14.01216951708771
C	3.83595210311319	2.86197110310492	12.72571060728556
C	3.50001969844289	3.96592776192822	11.97412876764028
H	2.55672232663740	4.46315612741751	12.17563017285774
C	4.34058151692371	4.45147670234079	10.97163686043694
H	4.04230397809479	5.31225878168228	10.38698953574410
C	5.56146271332369	3.82337033097513	10.72321388706138
H	6.21746145281261	4.19936202598657	9.94714074774278
C	5.94196640980335	2.71968336448827	11.45237403056188
H	6.88489904472674	2.22384014982261	11.25800744464835
C	5.08529651408303	2.24262451671889	12.46083739133565

X = SO2

Energy: -1049.127888789644 Eh Lowest IR freq: 55.61 cm^{-1}

Cartesian coordinates:

C	3.84678165995569	-2.22094585627194	1.85788659861757
C	3.83479384171946	-3.31941706580473	0.98991499846469
C	3.40398493211146	-4.60874112319971	1.50990594118484
C	2.08084944185730	-4.69341367437047	-0.60042937874665
C	2.69025325789271	-3.39325344605357	-0.83724854615406
C	3.56898219215493	-2.37997780618251	3.19438947860857
C	3.18967279501715	-3.65207892343712	3.69379645442091
C	3.09620279760552	-4.74548427940324	2.86356740249948
C	0.73532225152227	-4.89819664096984	-0.90481879796377
C	-0.00903269797868	-3.86009534866219	-1.41643644943260
C	0.55979141428121	-2.57619538084860	-1.61535104015752
C	1.87588568349318	-2.34894702047041	-1.29171303442631
C	4.12149694790536	-3.19888287237921	-0.46812038790857
H	4.13132294827691	-1.25038018536932	1.46674399173344
H	3.64276096418414	-1.53724631923495	3.86974472206939
H	2.95110187456089	-3.75795358986203	4.74564261678532
H	2.76046260745093	-5.70712950164226	3.23074712302426
H	0.29418351440312	-5.86664845981778	-0.70564724477273
H	-1.05422095225475	-4.01903055402229	-1.65454111542644
H	-0.04522645396042	-1.77835115632286	-2.02655503605218
H	2.31661484849961	-1.36861719098721	-1.43545696701075
H	4.48049710097311	-2.20637939541932	-0.73319990708050
H	4.77904518375677	-3.98246550858412	-0.84816923706093
O	4.20118491574096	-6.18440106871441	-0.40127592048271
O	2.17988967306401	-6.82942127886359	0.89324640765706
S	3.01569925776712	-5.80304635310622	0.32917732761018

DFT Computations Orca 5.0.3, UHF def2-SVP – T_1 of 1 – 4.

X = O

Energy: -572.933311490208 Eh Lowest IR freq: 49.39cm^{-1}

Cartesian coordinates:

O	3.48322478657204	5.22310669580206	1.03889964076132
C	3.08068672784722	4.03289047637432	0.53148005776116
C	3.45834140680124	2.88870684359439	1.24238859734677
H	4.04377311222539	3.00768325997182	2.14321454614147
C	3.07322539438520	1.63320727483257	0.78204763260012
H	3.36262681586478	0.74722243202173	1.33139535394530
C	2.31066028807691	1.52225879018237	-0.38588919477260
H	2.00679979210277	0.54926702029436	-0.74818458243005
C	1.94300131053089	2.67289120966680	-1.08214832954446
H	1.35191108768518	2.58715034171270	-1.98577794086380
C	2.32251876241687	3.94931007843658	-0.63933661254453
C	1.94063987948738	5.19601956753682	-1.40631890589117
H	0.86707327860456	5.18923109366991	-1.60799215474499
H	2.43495069849273	5.19001539953655	-2.38225700785597
C	3.07038723307127	6.37667583972767	0.48580818555190
C	3.50028225588986	7.59692053639507	1.26044228559312
H	4.10498694535242	7.45296914389372	2.14257399514206
C	3.09356752274039	8.84925794027843	0.80397626747566
H	3.38484429468446	9.73725771664197	1.35062168485659
C	2.32334140198655	8.96900287286721	-0.34304728955584
H	2.00568289023045	9.93728299619672	-0.70316841451339
C	1.91466166527680	7.72485924071402	-1.11784644963073
H	1.32071313273798	7.83117741462338	-2.01445183792367
C	2.31249931693661	6.45783581502868	-0.66102952690426

X = S

Energy: -895.506286049398 Eh Lowest IR freq: 36.24 cm^{-1}

Cartesian coordinates:

C	0.99643582969118	0.72882421362837	0.48576009882343
C	5.35333897898474	-2.34595889575582	-0.00694966988156
C	5.33240620321686	-2.02515665238811	1.35379166783631
C	4.30248741719046	-1.23676745209159	1.86193509380707
C	3.28192781257853	-0.75831327616667	1.02006996995197
C	-0.30479757172435	1.32379160983792	0.93490573590093
C	-1.47153115527677	0.67306233785476	0.63152511479797
C	-1.47452675982484	-0.46253422692910	-0.23313288307021
C	-0.27655712439993	-0.87668145435735	-0.88903291694767
C	0.92402322981085	-0.26253126660476	-0.63796090549963
C	2.21641397296760	-0.59512121764227	-1.31431328686240
C	3.28717707252118	-1.08328908133731	-0.35202378559723
C	4.33852689502531	-1.87586760409540	-0.84095813101850
H	6.14687989380616	-2.95937173933335	-0.41241802032076
H	6.10962022488938	-2.38592503528105	2.01430242236727
H	4.28446891631813	-0.98537489956661	2.91436802228603
H	-0.29831031227347	2.24140300110677	1.50879555633068
H	-2.41488471169892	1.05708251337907	0.99986425216687
H	-2.40643823077028	-0.96373756480744	-0.45638206012814
H	-0.33218824731760	-1.66025679202844	-1.63562031929050
H	2.58989635524063	0.30312775387656	-1.82165956122522
H	2.05543268916434	-1.34901068253735	-2.08498592079555
H	4.35139523360403	-2.13304945418870	-1.89302118410241
S	2.04170338827672	0.23745586542788	1.80494071047122

DFT Computations Orca 5.0.3, UHF def2-SVP – T_1

X = SO

Energy: -970.482066348404 Eh Lowest IR freq: 25.90 cm^{-1}

Cartesian coordinates:

S	4.13848954349066	0.12864850916401	11.06304500284040
O	4.38593751855745	-0.07083823238365	9.60822500621710
C	5.36017705516242	1.60419017865185	15.93898901157399
C	5.65563963586887	1.99260281279456	17.23843752961738
H	6.62397554303363	1.80002546693687	17.68144083854082
C	4.64173663437809	2.64546610384546	17.95849780594622
H	4.81960842582316	2.96784969559069	18.97618524091199
C	3.39704862484351	2.87454645735428	17.35471333283562
H	2.61458802392410	3.37331212448849	17.91110341243117
C	3.15004847833897	2.46211403757731	16.03600981601099
H	2.18026530011807	2.64926543662005	15.59131547890057
C	4.14446314710593	1.80641589973001	15.28627208026519
C	3.91336688637652	1.34422322002913	13.86475501359894
H	4.36596224241951	0.35815707166069	13.75384333729885
H	2.84067120471589	1.20327766820793	13.70853401659456
C	4.44856516128837	2.26389860782420	12.77341491591179
C	4.79926625359669	3.59641451114543	13.02507291640150
H	4.72035190549974	3.98438393346999	14.02991753305538
C	5.25567290549568	4.43821185617333	12.00269748302321
H	5.51796705726868	5.46275655240808	12.23128067697973
C	5.36888901657279	3.95771787146022	10.69431067215910
H	5.71811779132470	4.60521468786796	9.90136839860114
C	5.02812656557333	2.63559707445065	10.41062779927919
H	5.10913955618553	2.24272448651232	9.40814694343443
C	4.57082552303720	1.79392396841989	11.44009573756921

X = SO_2

Energy: -1045.06208630477 Eh Lowest IR freq: 55.09 cm^{-1}

Cartesian coordinates:

C	4.28388720597091	-2.25775313596628	2.18692198826777
C	3.78487189187384	-3.13400709631887	1.22537098840942
C	3.20735806785251	-4.45867968503400	1.71573040585510
C	1.86083269837176	-4.53801538282544	-0.58248834469544
C	2.41309473711625	-3.27273581526271	-0.86996691637883
C	4.22105736785192	-2.55262445157975	3.54323139452091
C	3.55292083781286	-3.83428773336701	4.00534152858596
C	3.07941119334398	-4.74312127319914	3.07213937095995
C	0.62666198498614	-4.94610683851635	-1.08992348013154
C	-0.07704403145274	-4.08413588233389	-1.93452789930131
C	0.45533485988670	-2.83020812596999	-2.24485717961492
C	1.68444392829473	-2.42650667785003	-1.71148527414650
C	3.74163321156105	-2.86219171028641	-0.25821106629089
H	4.72228976725250	-1.32030510840473	1.86711967015416
H	4.62797646509678	-1.87843649481092	4.28238260491806
H	3.45523454974549	-4.02523095416485	5.06447970925991
H	2.61993147225011	-5.67257152083102	3.37917529622780
H	0.23172058177572	-5.91451424253250	-0.81846069679744
H	-1.03294436527446	-4.38619290282060	-2.34048369769587
H	-0.08872840964438	-2.15846595524540	-2.89564860587785
H	2.07549151737177	-1.44588771683672	-1.94991208465585
H	3.92365019539597	-1.80582034826846	-0.44547647088444
H	4.54019443192503	-3.42500187747955	-0.75269938462058
O	4.00323192734929	-5.97292834577465	-0.21153714152519
O	1.94272748110450	-6.63265976026718	1.00032043045813
S	2.79306043218170	-5.60831096405347	0.46926485499949

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