"Molecular Photochemistry - how to study mechanisms of photochemical reactions ?"

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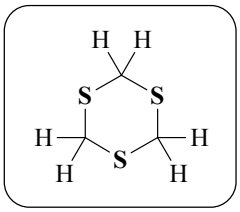
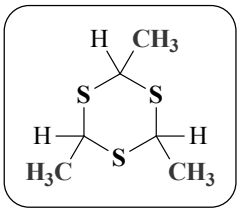
5. Examples illustrating the investigation of photoreaction mechanisms:

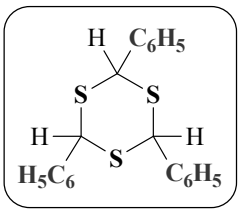
- photochemistry of 1,3,5,-trithianes in solution



TT (1,3,5-trithiane)

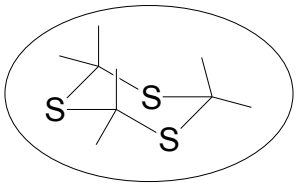


TMT (2,4,6-trimethyl-1,3,5-trithiane)
ISOMER β (cis-cis), ISOMER α (cis–trans)

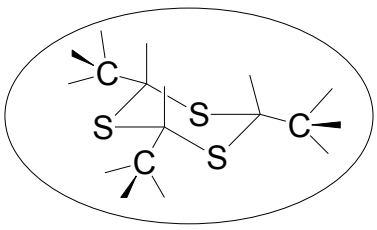


TPT (2,4,6-triphenyl-1,3,5-trithiane)
ISOMER β (cis–cis), ISOMER α (cis–trans)

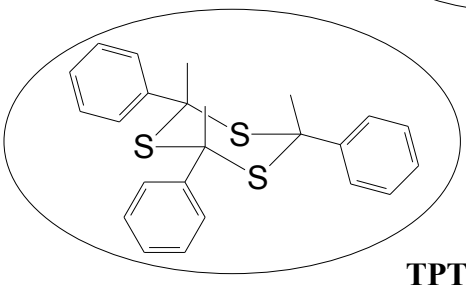
Trithiane structures



TT

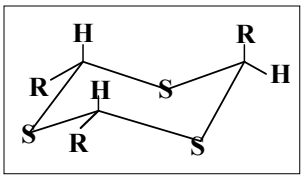


TMT

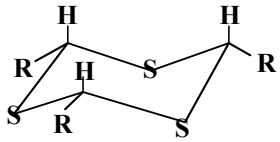


TPT

Isomers of the trithianes



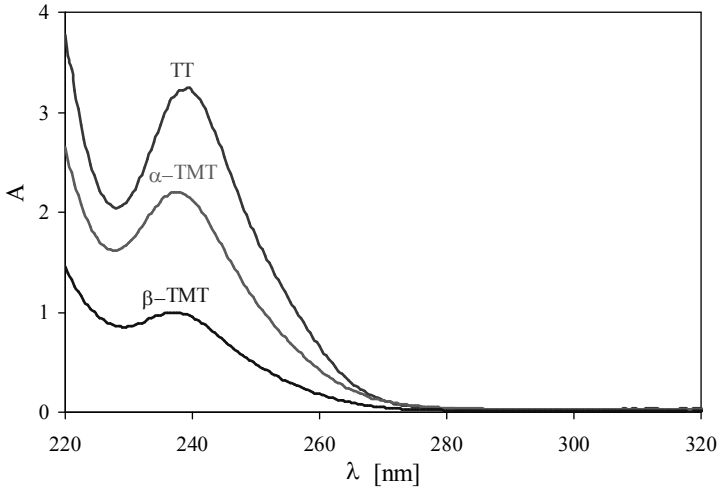
α-form (cis-trans)



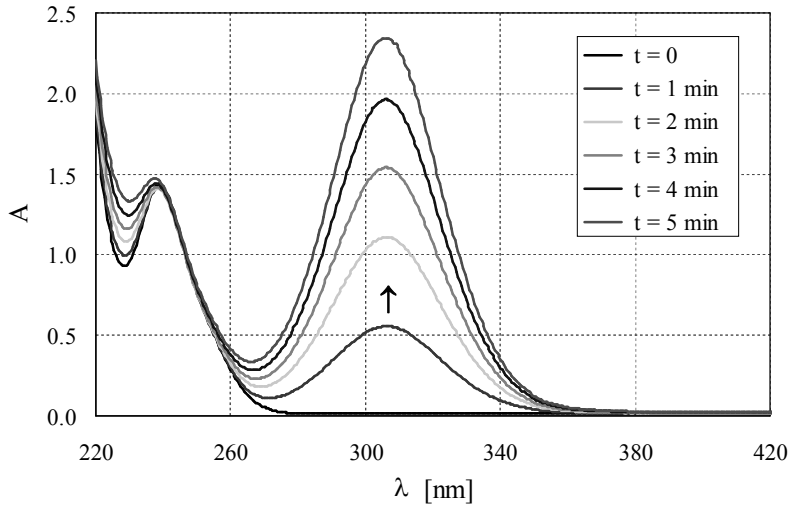
β-form (cis-cis)

R = CH_3, C_6H_5

Ground-state absorptions of trithianes in MeCN

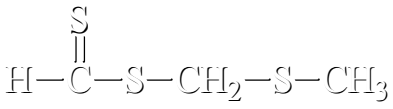


254 nm photolysis of TT in MeCN

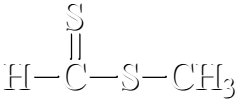


Stable products (GC, GCMS, HPLC, UV)

For TT:

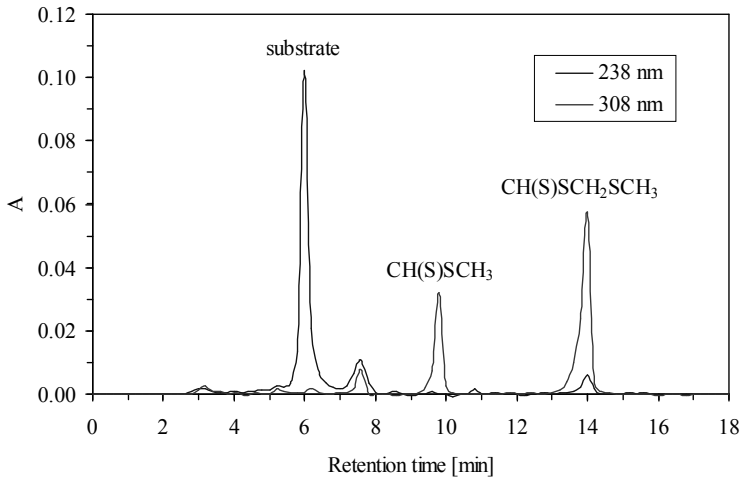


primary product

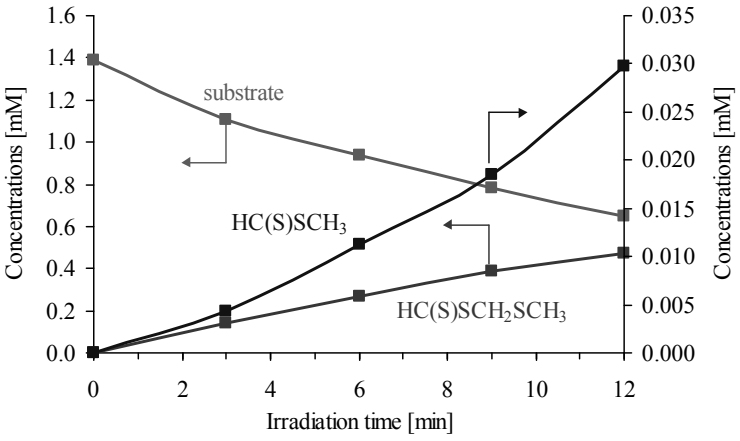


secondary product

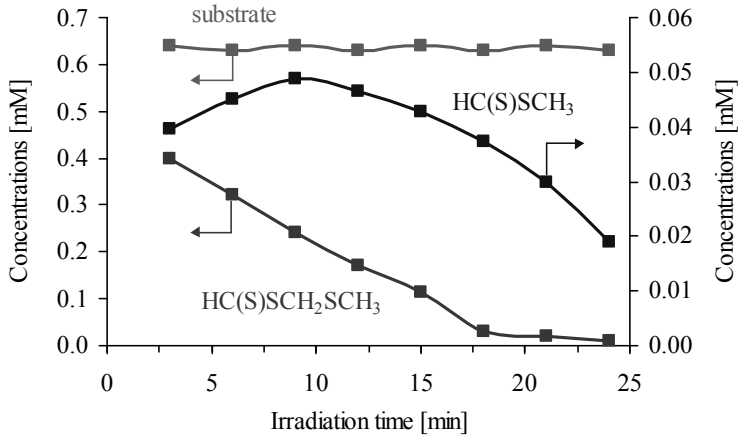
HPLC following 254 nm photolysis of TT in MeCN



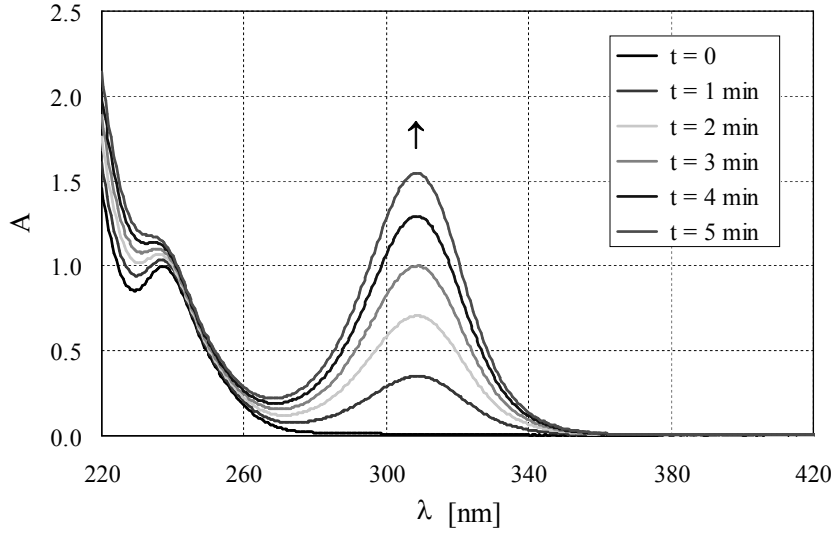
254 nm photolysis of TT in MeCN



313 nm photolysis of TT in MeCN preirradiated at 254 nm for 12 minutes



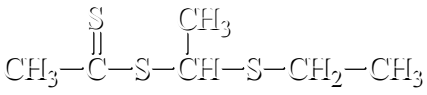
254 nm photolysis of β-TMT in MeCN



Stable products

(GC, GCMS, HPLC, UV)

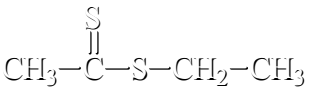
For β-TMT:



primary product

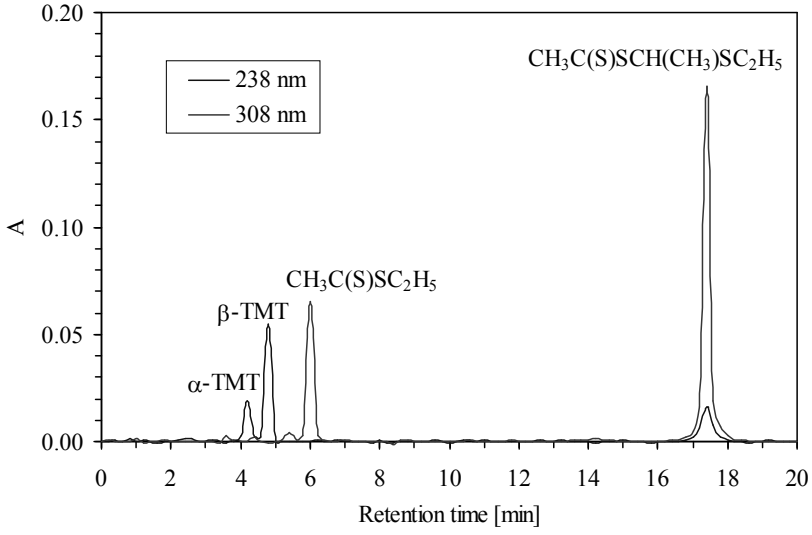
α-TMT

primary product

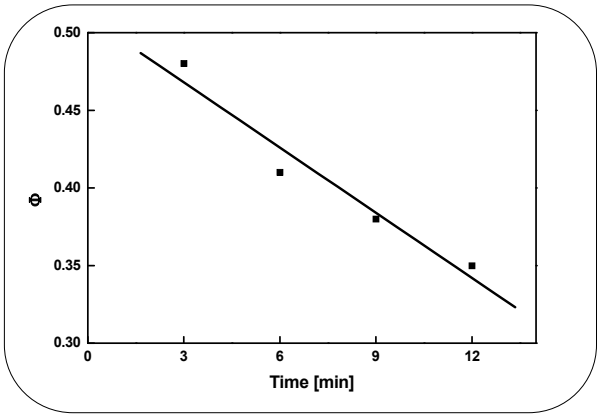


secondary product

HPLC following 254 nm photolysis of β-TMT in MeCN



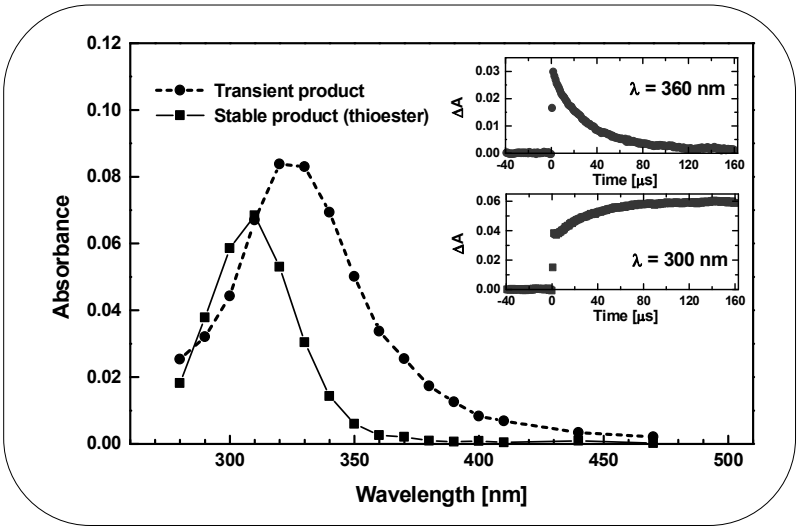
Extrapolation of Φ to zero time



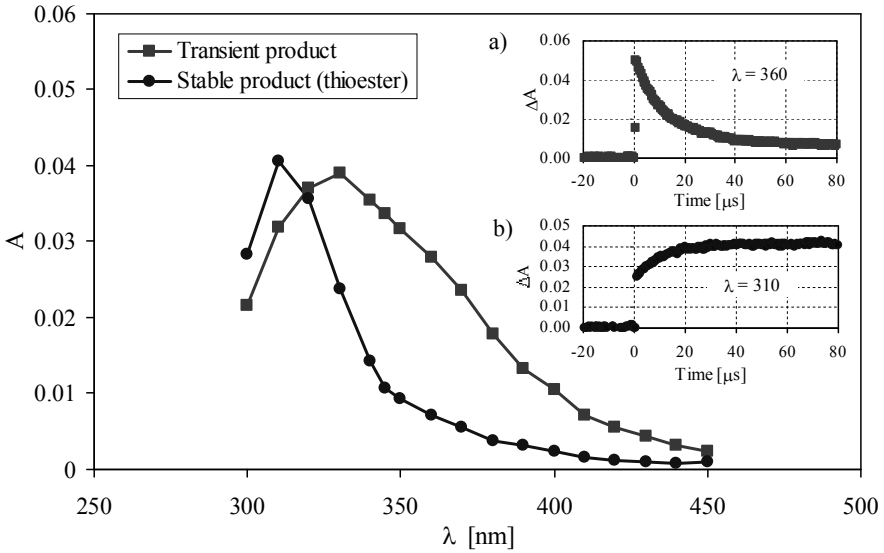
Steady-state photolysis at 254 nm
Laser flash photolysis at 266 nm

Quantum yields Φ					
	TT	α-TMT	β-TMT	α-TPT	β-TPT
Trithiane disappearance	0.54	0.38	0.43	0.19	0.48
Thioester formation	0.49	0.22	0.32	0.14	0.44
Isomer formation	–	0.01	0.10	< 0.01	< 0.01
Thioester formation from laser flash photolysis	0.52	0.25	0.32	0.17	0.52

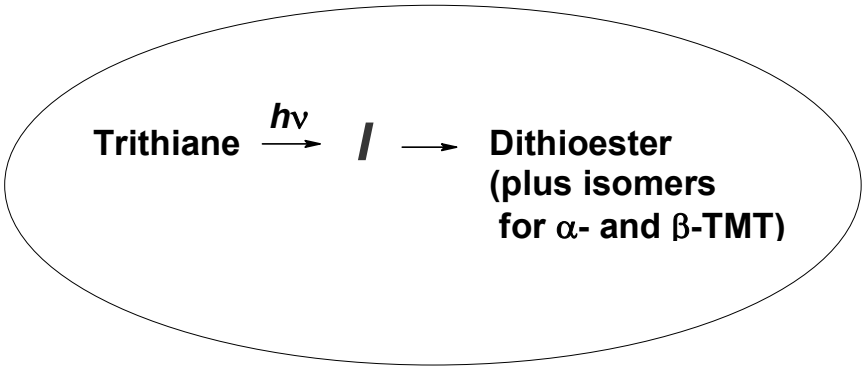
266 nm laser flash of TT in MeCN



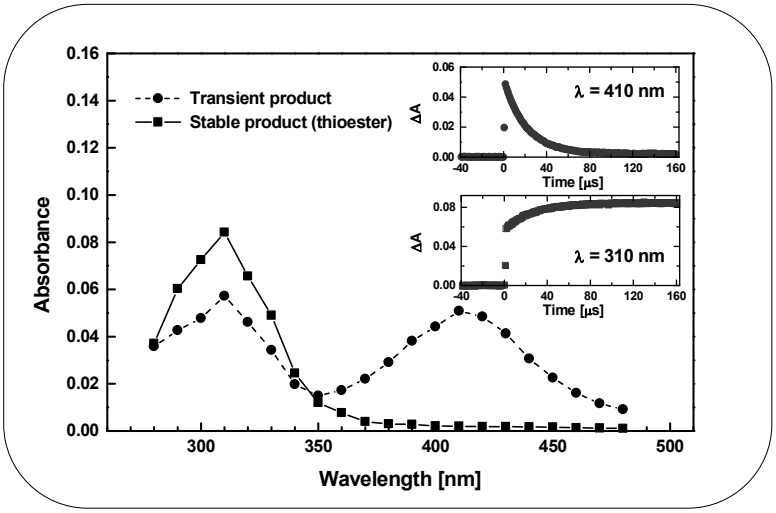
266 nm laser flash of β-TMT in MeCN



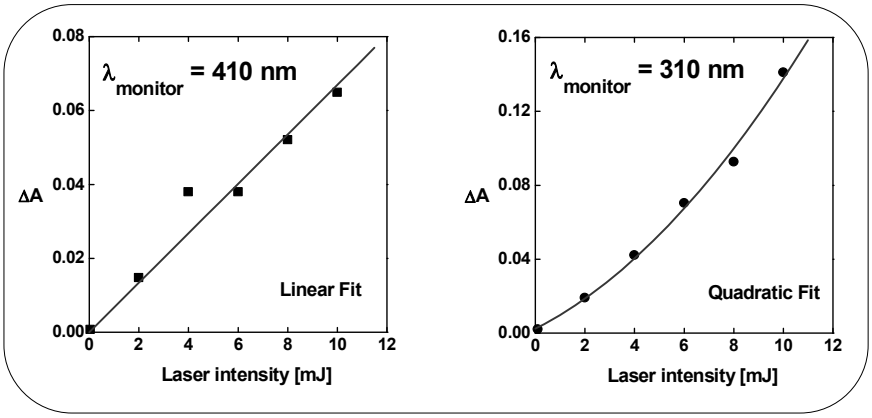
Mechanism for Trithiane = TT, α-TMT, or β-TMT



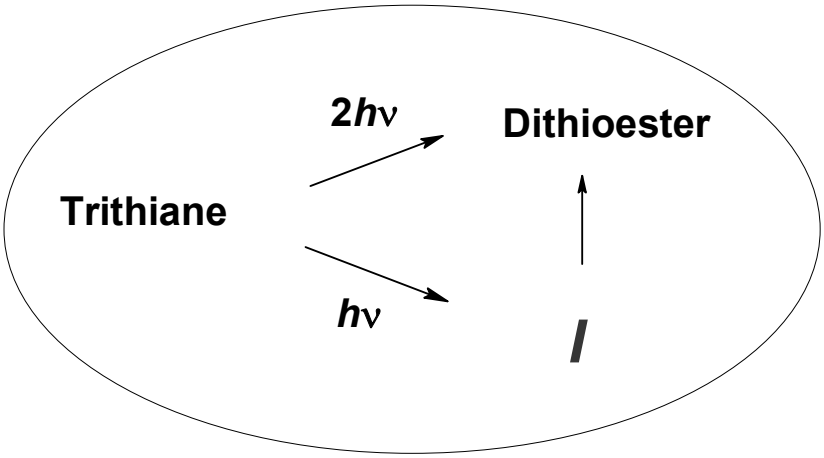
266 nm laser photolysis of β-TPT in MeCN

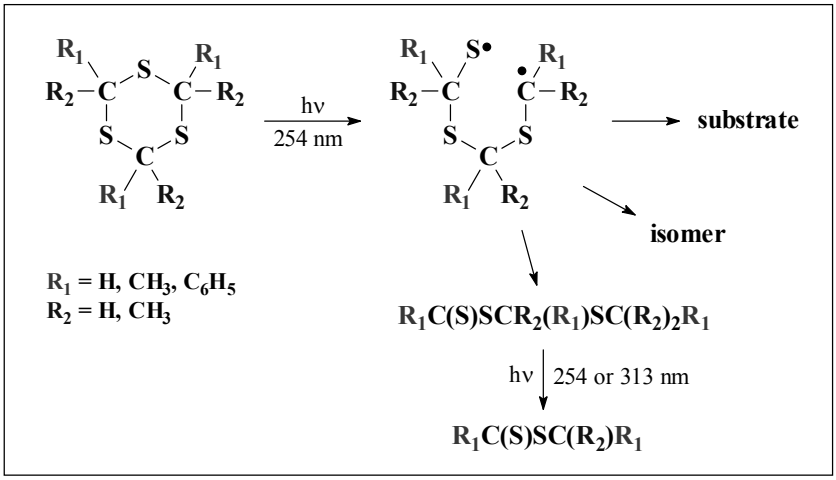


Laser-intensity dependence α-TPT in MeCN



Mechanism for Trithane = α-TPT or β-TPT




R1
S
R1
R2 C C R2
S S
C
R1 R2
hν
254 nm
R1 S•
R2 C
C R1
R2
S S
C
R1 R2
substrate
isomer
R1 = H, CH3, C6H5
R2 = H, CH3
R1C(S)SCR2(R1)SC(R2)2R1
hν
254 or 313 nm
R1C(S)SC(R2)R1

Solvent effect

Table: Quantum yields[a] of trithiane disappearance (ϕ_{dis}) and dithioester formation (ϕ_{prod}) in various solvents

Trithianes	Solvent	ϕ_{dis}	ϕ_{prod}
TT	CH_3CN	0.54	0.51
	CH_3OH	0.51	0.085
α-TMT	CH_3CN	0.39	0.22
	CH_3OH	0.26	0.01
β-TMT	CH_3CN	0.43	0.32
	CH_3OH	0.20	0.04
β-TPT	CH_3CN	0.48	0.46[b]
	CH_3OH	0.24	0.03

[a] All quantum yields were extrapolated to zero irradiation times; estimated error is equal to 10 %.

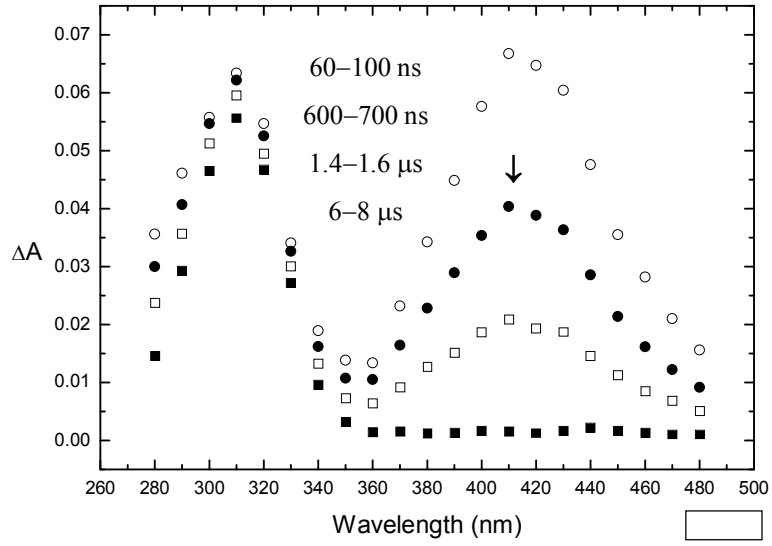
[b] Sum of 0.34 + 0.12 for $RC(=S)SCH(R)SCH_2R$ and $RC(=S)SCH_2R$, respectively.

Decay time (τ_{decay}) of intermediate ***I***, growth time (τ_{growth}) of the dithioesters absorbing at 310 nm, and rate constant (k^{II}) of ***I*** with CH_3OH

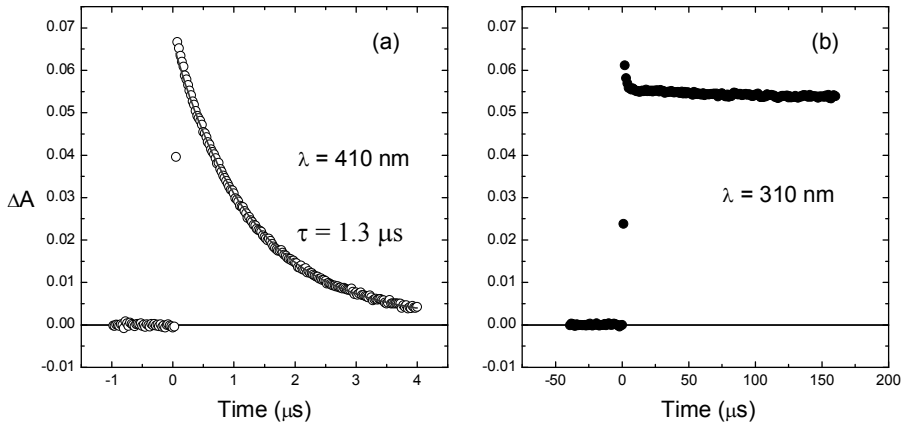
Trithiane	Solvent	τ_{decay} (μs)	τ_{growth} (μs)	k^{II} (M^{-1} s^{-1})
TT	CH_3CN	28	31[a]	
	CH_3OH	3.8	– [b]	
	EtOEt	57	61	
	1-BuOH	20	13[c]	
α-TMT	CH_3CN	14[d]	9[d]	8.4×10^4
	CH_3OH	0.13	– [b]	
	Cyclohexane	17	13	
β-TMT	CH_3CN	13[e]	13[e]	
	CH_3OH	-	-	
β-TPT	CH_3CN	29[a]	30[a]	7.8×10^3
	CH_3OH	1.3	– [a]	
	Cyclohexane	20	23	

[a] Previously measured [9].
[b] No growth observed.
[c] Determined from a growth/decay fitting function
[d] The decay lifetime of the shorter component of a biexponential decay.
[e] Previously measured [6].

266 nm laser flash of β-TPT *in MeOH*

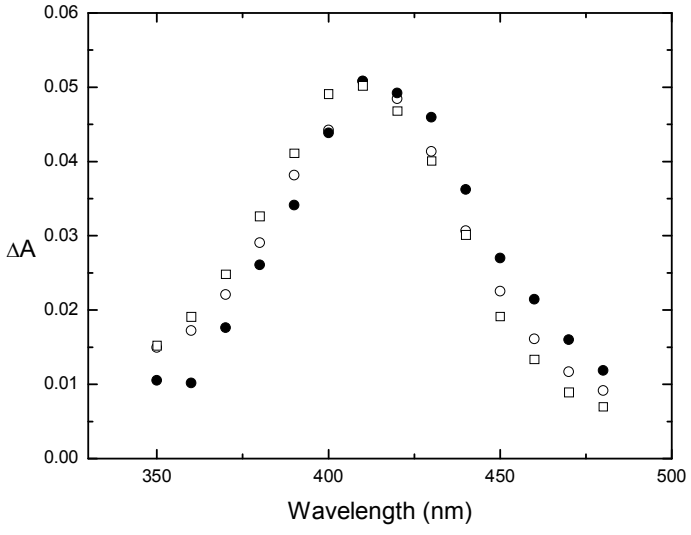


266 nm laser flash of β-TPT *in MeOH*

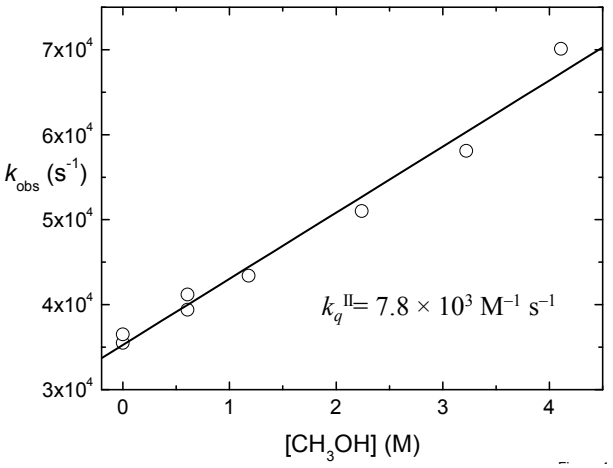


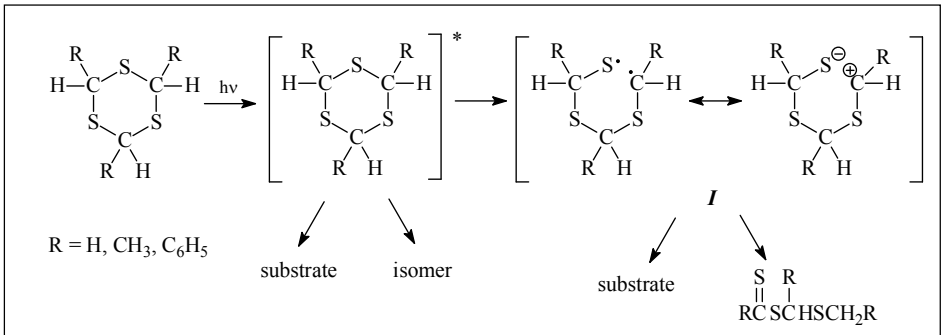
Initial spectra of 266-nm photolysis of β-TPT in various solvents

Open circles: CH_3CN, filled circles: CH_3OH, squares: cyclohexane

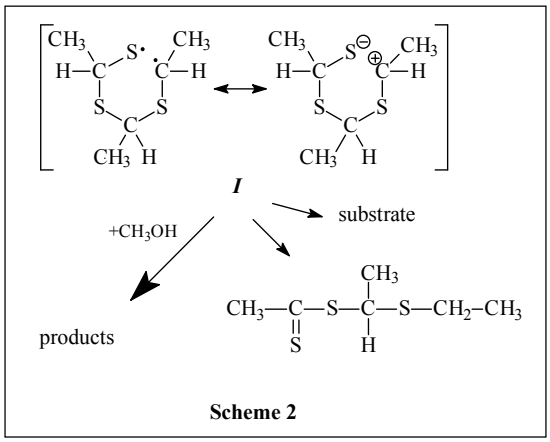


Quenching of intermediate, *I*, by methanol, following 266-nm laser excitation of β-TPT in acetonitrile





Scheme 1



Scheme 2