Supplementary Material (ESI) for Photochemical & Photobiological Sciences
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Electronic supplementary information (ESI)

Title: Competitive radiative and reactive relaxation channels in the excited state decay of some thio-analogues of *EE*-distyrylbenzene

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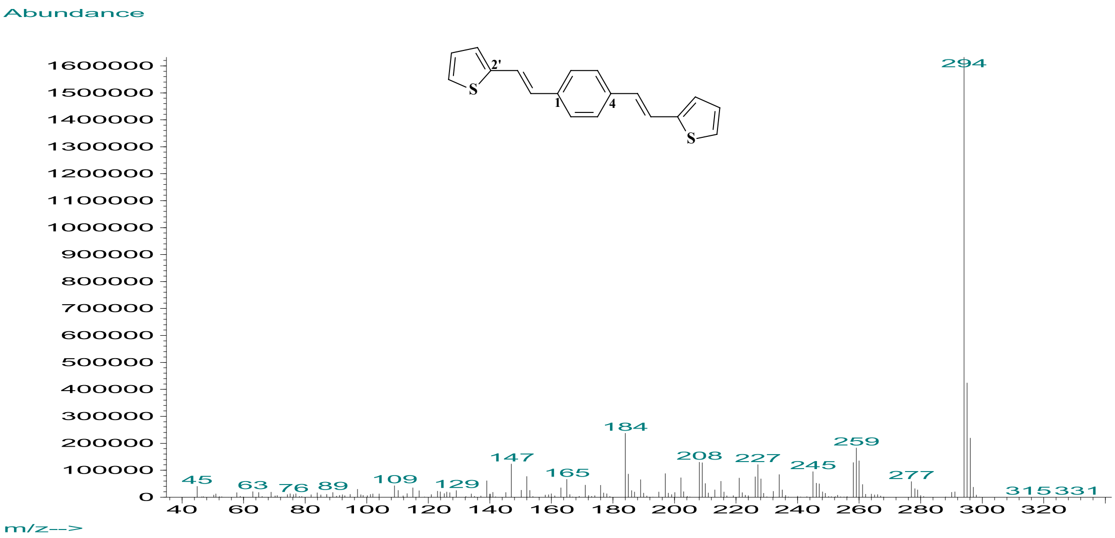
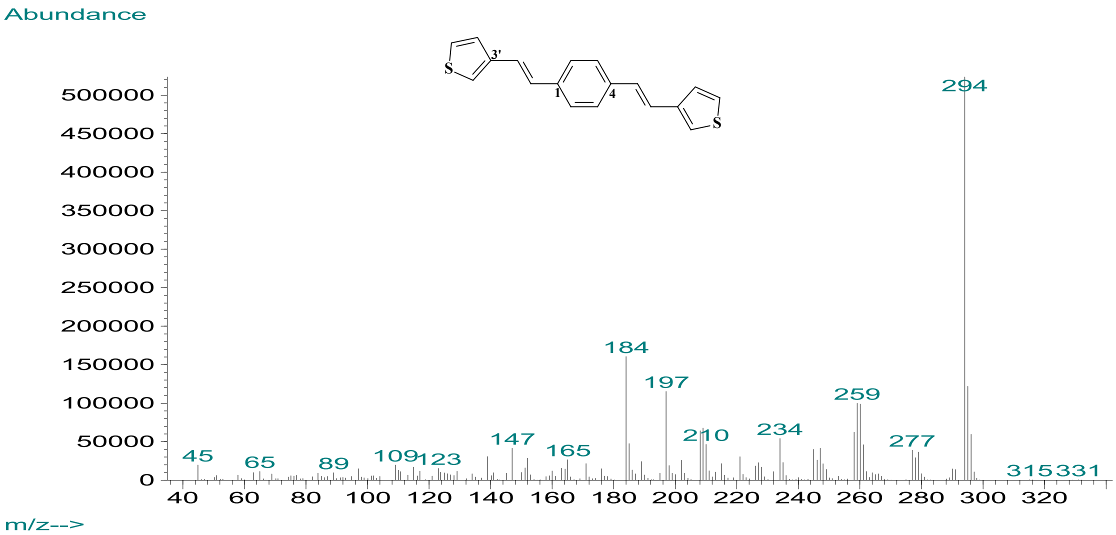
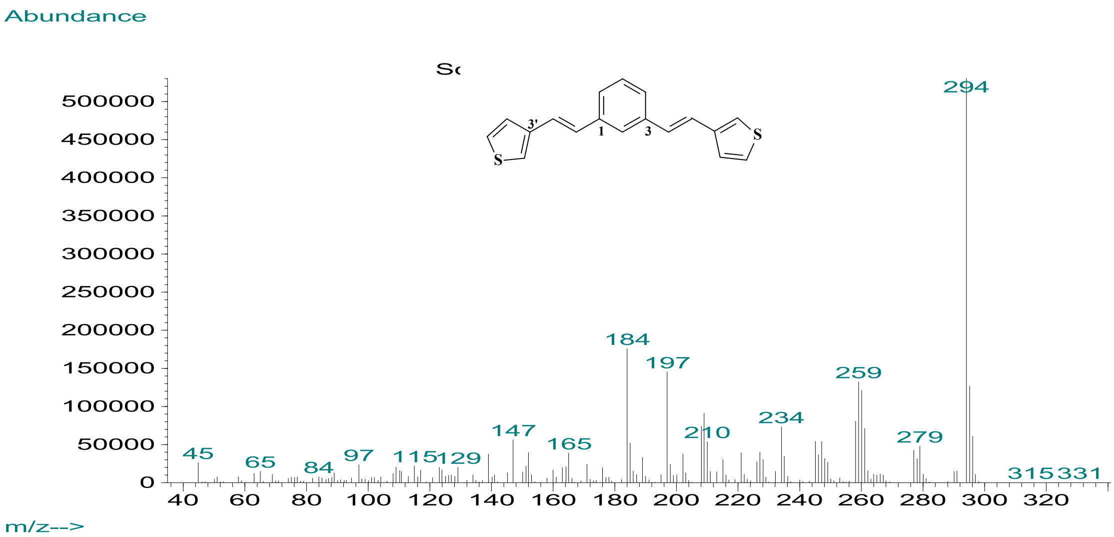
GC-MS measurements.

These analyses were performed on a Hewlett-Packard mode 6890A gas chromatograph (DB 35 MS column, 30m) coupled with a MSD-HP 5973 mass-selective detector (70 eV).







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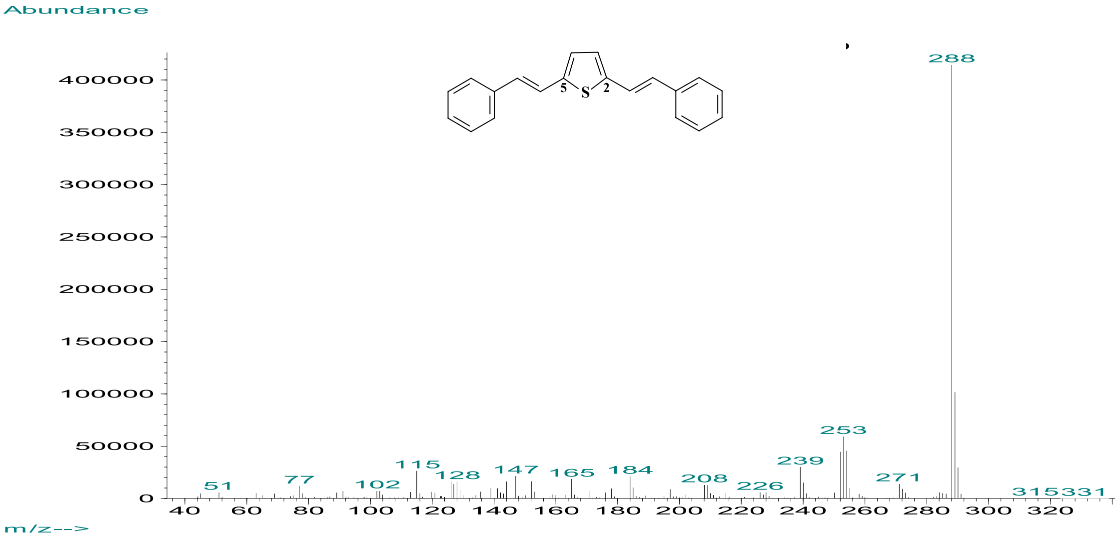

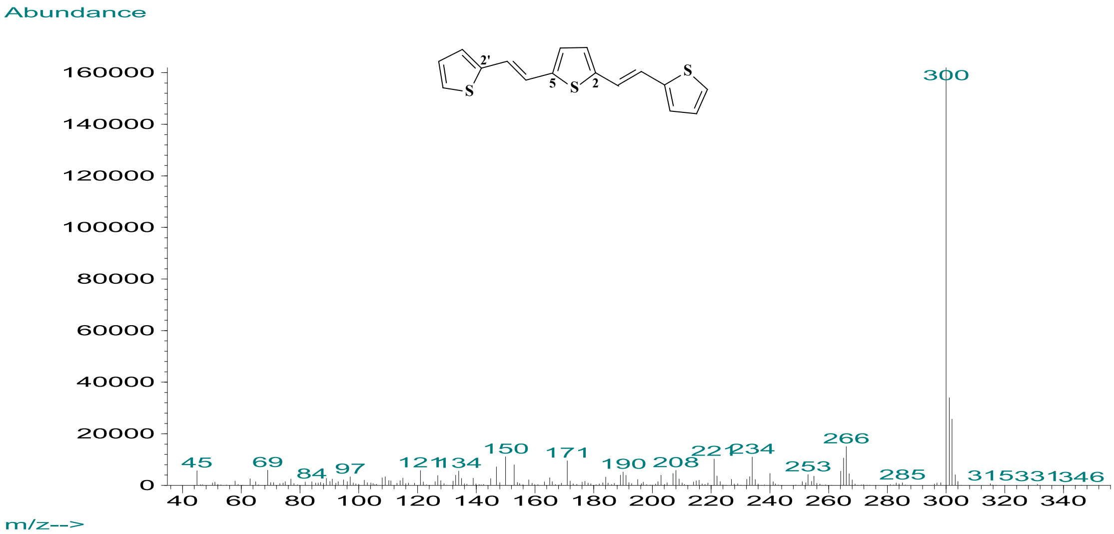

Fig. 1' Mass spectra of the five thio-analogues of distyrylbenzene investigated.

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^{1}H NMR data

The one-dimensional ^{1}H-NMR spectra were measured using a Bruker AC 400 Spectrometer and TMS as reference. The solvents used were deuterated benzene and dimethylsulphoxide (DMSO).

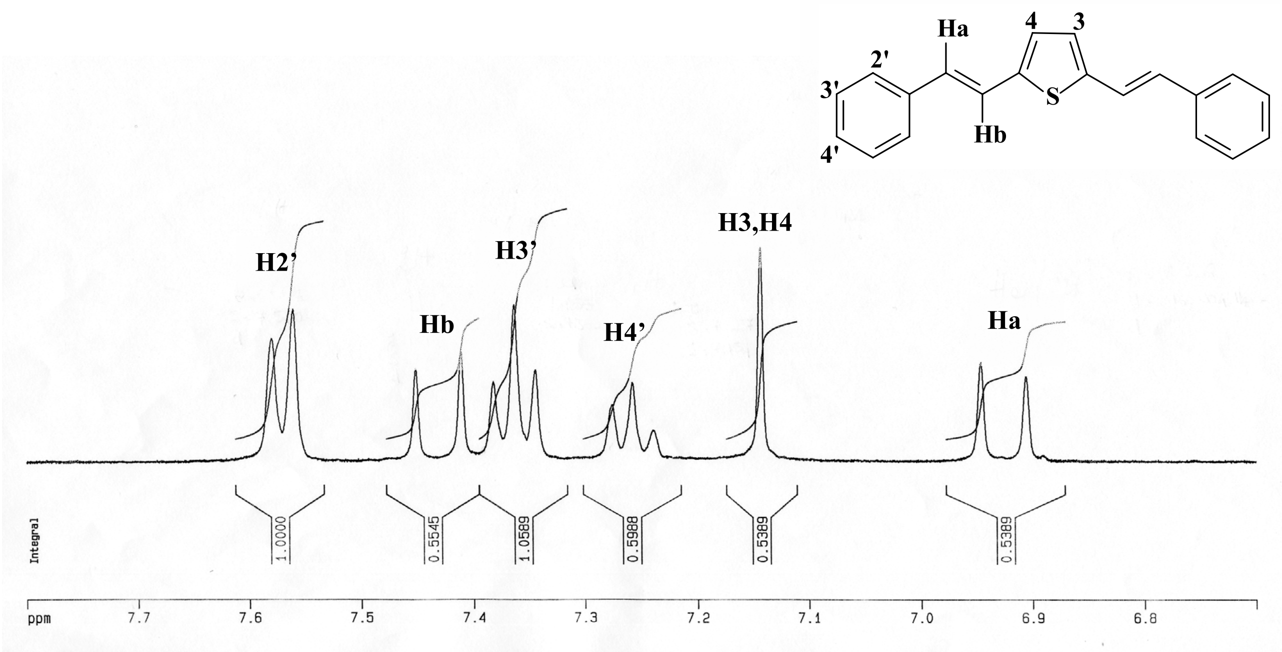

Fig. 2' ^{1}H-NMR spectrum of *EE*-2,5-di(phenylethenyl)thiophene in DMSO as an example.

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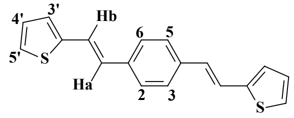
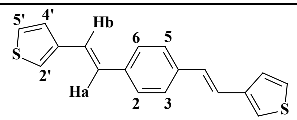
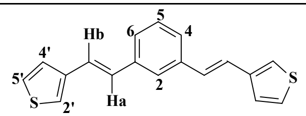
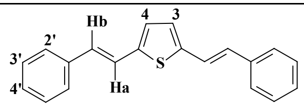
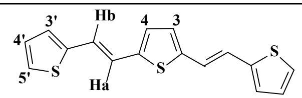
Table 1' Chemical shifts (δ) and coupling constants (J) for olefinic, central ring and side ring protons of the five thio-analogues of *EE*-distyrylbenzene investigated.

Compound	Olefinic protons δ (ppm)	Olefinic J (Hz)	Central ring protons δ (ppm)	Central ring J (Hz)	Side ring protons δ (ppm)	Side ring J (Hz)
 *EE*-1,4-(2TE)$_2$B	Ha 6.93 (d, 2H) Hb 7.48 (d, 2H)	16.2 16.3	H2, H3, H5, H6 7.35 (s, 4H)		H4' 7.07 (m, 2H) H3' 7.21 (d, 2H) H5' 7.56 (d, 2H)	
 *EE*-1,4-(3TE)$_2$B	Ha 7.03 (d, 2H) Hb 7.24 (d, 2H)	16.4 16.4	H2, H3, H5, H6 7.5 (m, 4H)		H2', H4', H5' 7.39-7.42 (m, 6H)	
 *EE*-1,3-(3TE)$_2$B	Ha 7.03 (d, 2H) Hb 7.26 (d, 2H)	16.2 16.2	H2 7.66 (s, 1H) H5 7.28 (t, 1H) H4, H6 7.37 (d, 2H)	 8.5 8.5	H2', H4', H5' 7.35-7.42 (m. 6H)	
 *EE*-2,5-(PhE)$_2$T	Hb 6.93 (d, 2H) Ha 7.43 (d, 2H)	16.0 16.1	H3, H4 7.14 (s, 2H)		H4' 7.26 (t, 2H) H3' 7.36 (dd, 4H) H2' 7.57 (d, 4H)	7.2 7.5 7.7
 *EE*-2,5-(2TE)$_2$T	Hb 7.06 (d, 2H) Ha 7.14 (d, 2H)	15.8 15.8	H3, H4 6.60 (s, 2H)		H4' 6.75 (dd, 2H) H3' 6.79 (d, 2H) H5' 6.82 (d, 2H)	4.9-3.6 2.8 4.9

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Theoretical Calculations

These were performed using the HyperChem computational package (version 6.1). The calculated electronic spectra (transition energies and oscillator strengths) were obtained by ZINDO/S using optimized geometries (according to PM3 method). Calculations of the configuration interaction included 81 (9x9) single excited configurations. The heats of formation of various conformations of the compounds investigated were also computed.

Table 2' Computed formation enthalpies ($\Delta H_f°$) and spectral parameters (transition energy, λ, and oscillator strength, f) for elongated s-cis,s-cis conformations of the EE isomers of the investigated thio-derivatives.

compound	$\Delta H_f°$ (kcal mol^{-1})	λ (nm)	f
1,4-(2TE)$_2$B	115.65	377	2.01
		307	0.00
1,4-(3TE)$_2$B	112.29	340	1.66
		301	0.01
1,3-(3TE)$_2$B	112.52	310	0.05
		303	1.45
2,5-(PhE)$_2$T	108.39	396	1.81
		299	0.01
2,5-(2TE)$_2$T	126.08	430	1.84
		323	0.01

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Table 3' Computed formation enthalpies and spectral parameters (transition energy, λ, and oscillator strength, f) for conformers of the EE isomer of the investigated 3T-derivatives.

compound	rotamer	ΔH_f° (kcal mol^{-1})	λ (nm)	f
1,4-$(3TE)_2B$	elongated s-cis,s-cis	112.29	340	1.66
			301	0.01
	elongated s-cis, s-trans	112.59	338	1.72
			301	0.02
	elongated s-trans, s-trans	112.90	335	1.89
			301	0.03
1,3-$(3TE)_2B$	compressed s-cis,s-cis	112.55	314	0.22
			306	1.11
	elongated s-cis, s-cis	112.52	310	0.05
			303	1.45
	elongated s-trans, s-trans	113.13	310	0.02
			293	2.52

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Spectral data

The absorption and emission spectra were recorded by a Perkin Elmer Lambda 800 spectrophotometer and a Spex Fluorolog –2 F112AI spectrofluorimeter, respectively.

Table 4' Spectral properties (main maximum in italics, sh = shoulder) of the EE isomer of the investigated compounds in toluene at room temperature.

Compound	λ_{abs}^{max} (nm)	ε_{abs}^{max} (10^4 $M^{-1}cm^{-1}$)	λ_{F}^{max} (nm)
1,4-$(2TE)_2B$	362^{sh}, *379*, 396^{sh}	5.3	417^{sh}, *441*, 467^{sh}
1,4-$(3TE)_2B$	340^{sh}, *352*, 370^{sh}	5.7	386^{sh}, *407*, 427^{sh}
2,5-$(PhE)_2T$	374^{sh}, *392*, 415^{sh}	4.1	435^{sh}, *461*, 489^{sh}
1,3-$(3TE)_2B^{a}$	*301*,314^{sh}	4.7	*373*
2,5-$(2TE)_2T$	393^{sh}, *413*, 436^{sh}	4.9	462^{sh}, *491*, 520^{sh}

^{a} In MCH/3MP.