



CHARGE-TRANSFER COMPLEXES OF THREE TRIAZINE-STILBENE DERIVATIVES WITH SOME π -ACCEPTORS. PART TWO : PICRIC ACID

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ABSTRACT

Three novel charge-transfer complexes formed between three disodium 4,4'-bis-(1,3,5-triazinylamino)stilbene-2,2'-disulfonate derivatives as donors with picric acid as acceptor were reported. Elemental analysis (CHN), electronic absorption spectra, photometric titration and IR spectra show that the interaction between the donors and picric acid was stabilized by hydrogen bonding, via a 1 : 2 stoichiometry. The spectroscopic and physical data were estimated using Benesi-Hildebrand and its modification methods in terms of formation constant (K_{CT}), molar extinction coefficient (ϵ_{CT}), standard free energy (ΔG°), oscillator strength (f) and transition dipole moment (μ).

Key words: Fluorescent brighteners, Triazine-stilbene derivatives, Charge-transfer, Picric acid.

INTRODUCTION

Fluorescent brighteners (FBs) have become a part of everyday life and culture. FBs are primarily applied to textiles to enhance their whiteness and brightness and are commonly added to textile substrates at various manufacturing steps in order to increase their apparent whiteness and to provide an additional layer of protection against UV-A and UV-B radiation¹⁻³. One important class of FBs is based on triazine-stilbene derivatives, which are widely used to create intense and bright white shades in textiles, pulps and papers⁴. Many triazine-stilbene derivatives, involving linear and nonlinear optical materials, photovoltaic materials, light emitting diodes, photoinduced electron transfer sensors, fluorescent switchers, chemosensors, pH chemosensing materials, biofunctional materials and new medicine have been prepared⁵⁻¹⁵. Nowadays, these compounds are also used as ultraviolet

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absorbing agents (UVAs) to the textile material. In some areas of the world, e.g. Australia and America where people enjoy especially sunny climates, there has been a great increase in the awareness of the potential hazards of undue exposure to sunlight. One aspect of the desire to increase the sun protection factor (SPF), they are used on the most natural and synthetic textile materials, especially lightweight summer fabrics, to provide skin beneath clothing protection against Ultraviolet A (UV-A or Long Wave or Black Light) and Ultraviolet B (UV-B or Medium Wave) ranges radiation. It is possible to improve the chemical and physical properties of triazine-stilbene derivatives by studying their complexation behavior with different organic π -acceptors. Therefore, we report in this paper the synthesis and spectral properties of three charge-transfer complexes formed between three disodium 4,4'-bis-(1,3,5-triazinylamino)stilbene-2,2'-disulfonate derivatives as donors with picric acid as acceptor.

EXPERIMENTAL

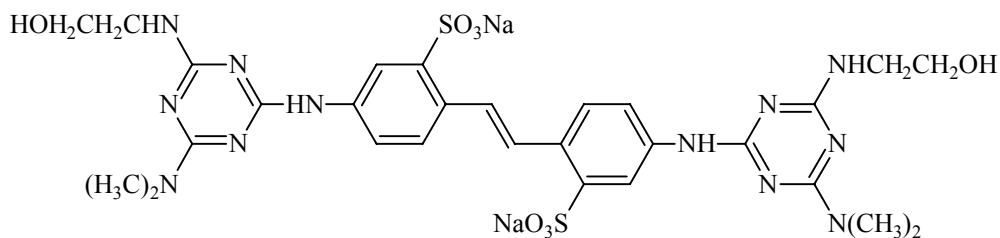
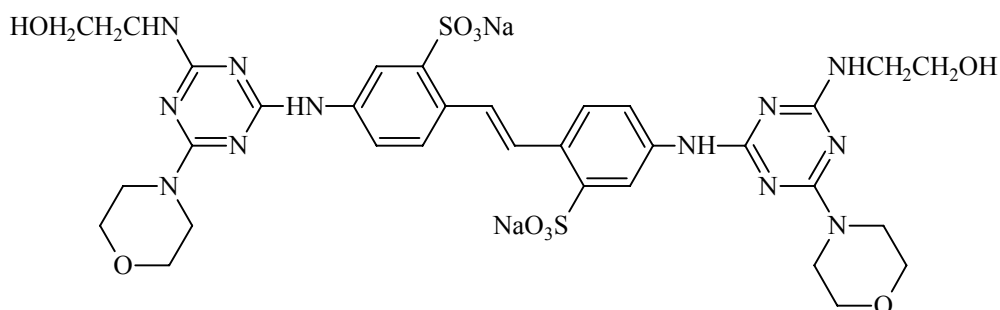
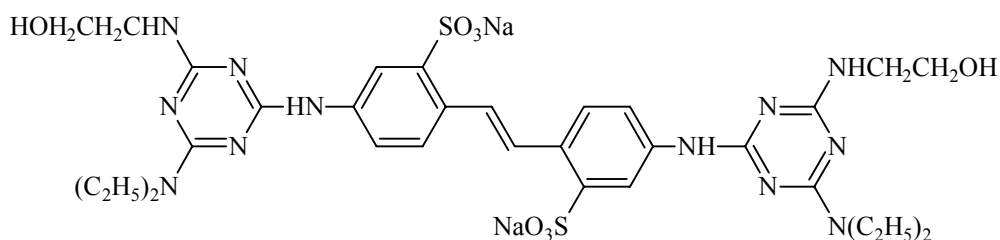
Equipment

The elemental analyses of the carbon, hydrogen and nitrogen content were performed using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra of the donors, the acceptor and the synthesized complexes were recorded in methanol over a wavelength range of 200-800 nm using a Perkin-Elmer Lambda 25 UV/Vis double-beam spectrophotometer. The instrument was fitted with a quartz cell that had a path length of 1.0 cm. The infrared (IR) spectra using KBr discs within the range of 4000-400 cm^{-1} for the complexes were recorded on a Shimadzu FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution.

Synthesis of complexes

The three triazine-stilbene derivatives used in this work are sodium(E)-6, 6'-(ethene-1, 2-diyl)bis(3-(4-(dimethyl-amino)-6-(2-hydroxyethylamino)-1, 3, 5 triazin-2-ylamino) benzenesulfonate (**TS1**), sodium (E)-6,6'-(ethene-1,2-diyl) bis(3-(4-(2-hydroxyethyl-amino)-6-morpholino-1,3,5-triazin-2-yl-amino)benzene-sulfonate (**TS2**) and sodium (E)-6, 6'-(ethene-1, 2-diyl) bis(3-(4-(diethylamino)-6-(2-hydroxyethyl amino)-1,3,5-triazin-2-yl-amino) benzene-sulfonate (**TS3**) (Formula I). These derivatives were obtained by synthesis according to the literature methods. The charge-transfer complexes of the **TS1**, **TS2** and **TS3** donor with the picric acid (PA) acceptor were prepared by mixing 1 mmol of each donor in pure-grade methanol (20 mL) with 1 mmol of PA acceptor in methanol (20 mL). The mixtures were stirred for approximately 30 min and allowed to evaporate slowly at room temperature resulting in the precipitation of the solid complexes. The resultant complexes

were filtered and washed well with methanol. Then, the synthesized complexes were collected and dried under vacuum over anhydrous calcium chloride for 24 h.

**TS1****TS2****TS3****Formula I: Chemical structure of triazine-stilbene derivatives; TS1, TS2 and TS3**

RESULTS AND DISCUSSION

Elemental analysis results

The elemental analysis data for the prepared complexes (Table 1) are in agreement with the molar ratio obtained from the spectrophotometric titrations. The resulting elemental analysis values are in good agreement with the calculated values. The stoichiometry of the prepared complexes with the PA acceptor was found to have a 1 : 2 ratio. The prepared

complexes were formulated as [(TS)(PA)₂] (TS : **TS1**, **TS2** or **TS3**). The formation of 1 : 2 complexes was strongly supported by IR spectra. All the complexes are insoluble in cold and hot water, but easily soluble in DMSO and DMF.

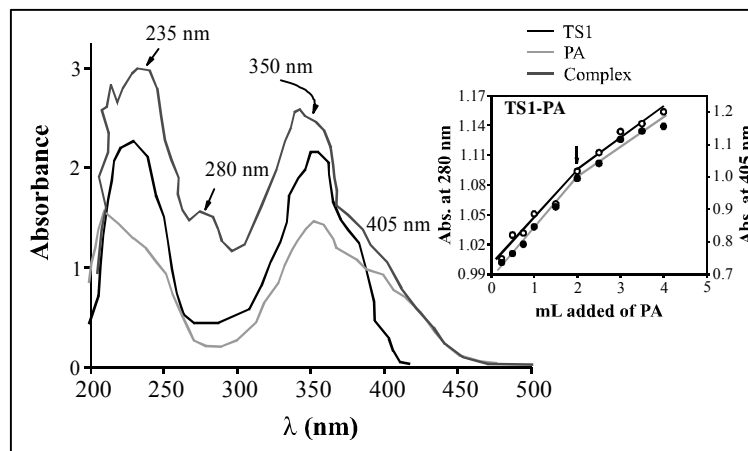
Table 1: Elemental analysis data of the obtained complexes

Complex	Molecular formula	Mwt. g/mol	Elemental analyses					
			C%		H%		N%	
			Found	Calc.	Found	Calc.	Found	Calc.
[(TS1)(PA) ₂]	C ₄₀ H ₄₀ N ₁₈ O ₂₂ Na ₂ S ₂	1234.22	38.80	38.89	3.21	3.24	20.39	20.41
[(TS2)(PA) ₂]	C ₄₄ H ₄₄ N ₁₈ O ₂₄ Na ₂ S ₂	1318.46	40.20	40.04	3.36	3.33	19.09	19.11
[(TS3)(PA) ₂]	C ₄₄ H ₄₈ N ₁₈ O ₂₂ Na ₂ S ₂	1290.22	40.95	40.92	3.69	3.72	19.57	19.53

Structure characterization

Electronic absorption spectra

The electronic absorption spectra of the reactants, donors (**TS1**, **TS2** or **TS3**) (5.0×10^{-4} M) and PA acceptor (5.0×10^{-4} M), along with those of the prepared complexes are shown in Fig. 1. These spectra revealed the presence of the absorption bands that correspond to the CT interactions. These bands are observed at 405 nm for all the complexes. These absorption bands well know to be characteristic of the formation of new charge-transfer complexes.



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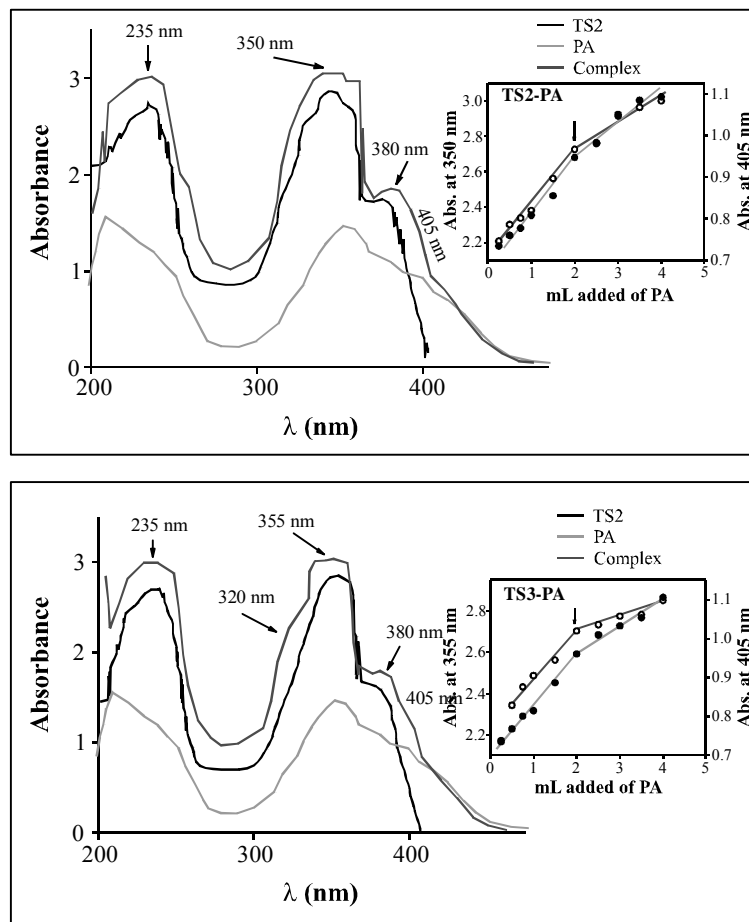


Fig. 1: Electronic spectra of the donors, PA acceptor and the synthesized complexes coupled with spectrophotometric titration spectra

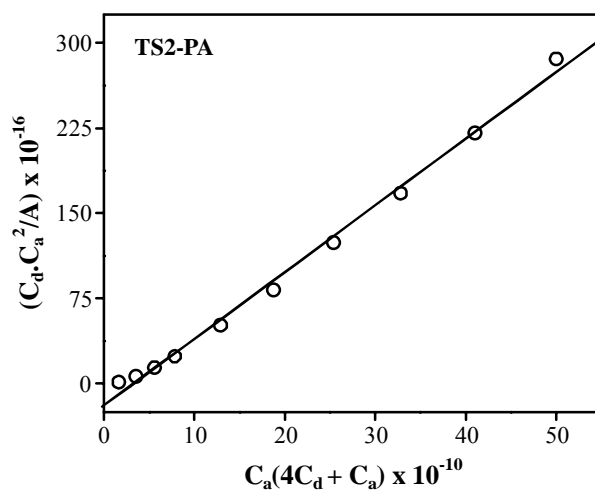
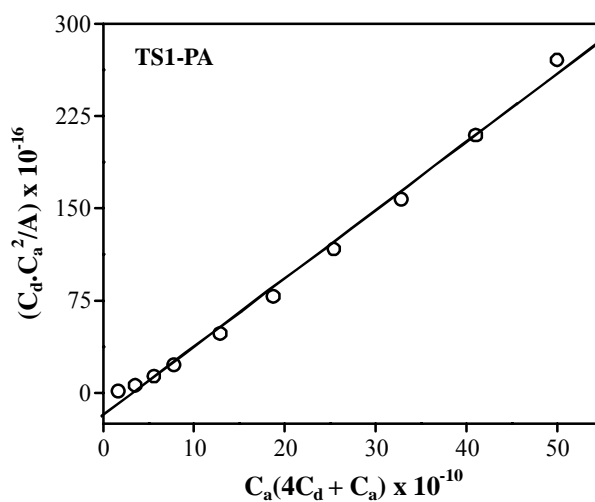
The stoichiometry of the synthesized charge-transfer complexes formed between the donors and the PA acceptor was obtained from the determination of the conventional spectrophotometric molar ratio according to previously published protocols¹⁶. Fig. 1 shows the spectrophotometric titration plots. Based on this figure, the complex formation occurred with a ratio of 1 : 2.

The 1 : 2 modified Benesi–Hildebrand plots are shown in Fig. 2^{17,18}. These plots were used to calculate the formation constant (K_{CT}) and the extinction coefficient (ϵ_{CT}) for each complex. The obtained K_{CT} and ϵ values associated with the synthesized complexes are given in Table 2. The energy of the complex (E_{CT}), the oscillator strength (f), the transition dipole moment (μ) and the standard free energy (ΔG°), were calculated for the formed

complexes as described elsewhere¹⁹⁻²². The calculated values of these spectroscopic data for the complexes are listed in Table 2.

Table 2: Spectroscopic data of the obtained complexes at (25°C)

Complex	λ_{max} (nm)	K (Lmol ⁻¹)	ϵ_{max} (Lmol ⁻¹ cm ⁻¹)	E_{CT} (eV)	f	μ	ΔG° (KJ mol ⁻¹)
[(TS1)(PA) ₂]		30.81×10^8	18.02×10^4		0.779	8.185	-42.729
[(TS2)(PA) ₂]	405	30.54×10^8	17.03×10^4	3.07	0.736	7.956	-42.707
[(TS3)(PA) ₂]		29.57×10^8	16.93×10^4		0.731	7.933	-42.628



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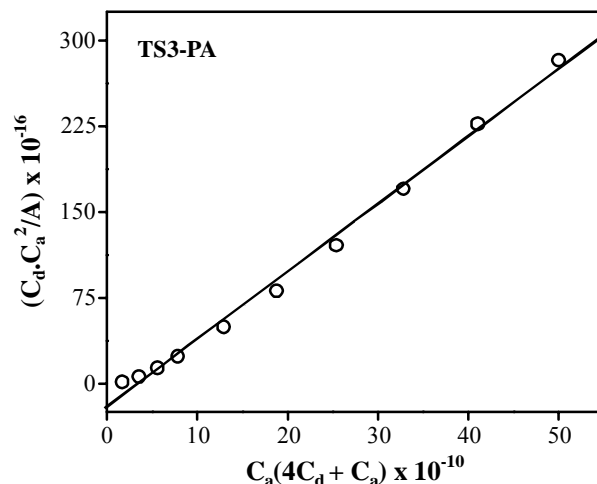


Fig. 2: The 1 : 2 Benesi-Hildebrand plot of TS1, TS2 and TS3 complexes with PA acceptor

All the complexes exhibited high values for the K_{CT} , E_{CT} , f and μ which indicates a strong interaction between the donor-acceptor pairs. The high K_{CT} values reflect the high stabilities of the prepared complexes due to the strong donation of the triazine-stilbene derivatives. The formation constant (K_{CT}) is strongly dependent on the nature of the acceptor including the type of electron withdrawing substituents on it (e.g., nitro and halo groups). The negative values of the standard free energy change (ΔG°) for the complexes indicate that the interaction between the donors and the PA acceptor is spontaneous²³.

IR spectra

The infrared absorption spectra of the synthesized CT complexes were recorded in the frequency range 4000-400 cm^{-1} using a KBr disc. The assignments for the characteristic IR spectral bands for the complexes are shown in Table 3. The formation of the CT complexes during the reaction of the donors with PA acceptor is strongly supported by the observation of main infrared bands of the donors (**TS1**, **TS2** and **TS3**) and PA acceptor in the product spectra. However, the bands of the donors and PA acceptor in the spectra of the complexes reveal small changes in frequency and in their band intensities compared with those of the free donors and acceptor. This result could be attributed to the expected changes in symmetry and electronic structure upon the formation of the CT complexes. The IR spectra of the complexes are characterized by some bands that appear between 2400-2800 cm^{-1} which does not appear in the spectra of the free donors or those of the PA acceptor. The presence of these bands which due to hydrogen bonding in the complex, confirmed that the complexation occurs through the protonation of the donors by the phenolic group of the PA

acceptor²⁴⁻³². According to these observations, the suggested structures for the obtained complexes are illustrated in Formulas II-IV.

Table 3: Infrared frequencies^(a) (cm⁻¹) and tentative assignments for TS1, TS2 and TS3 complexes with PA acceptor

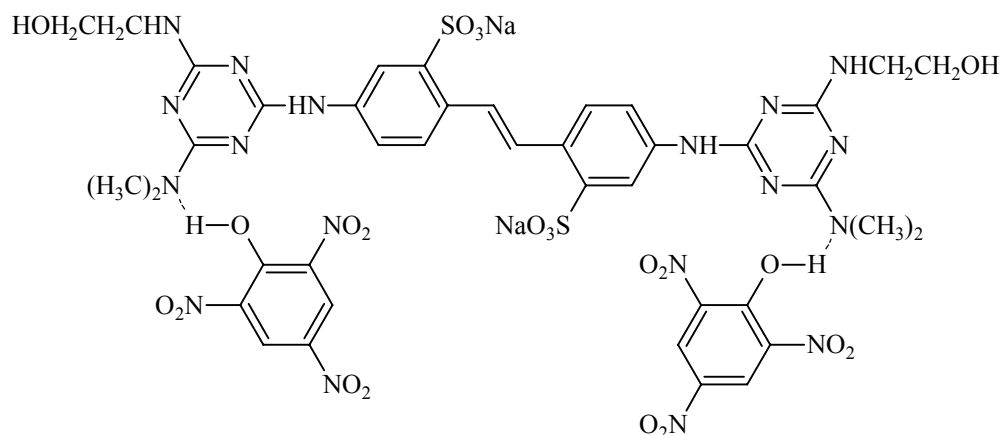
Donors			Acceptor	Complexes			Assignments ^(b)
TS1	TS2	TS3	PA	TS1-PA	TS2-PA	TS3-PA	
3423	3374	3420	3416	3614	3613	3614	ν (O-H)
			3103	3544	3422	3544	ν (N-H)
				3424		3404	ν (C-H); aromatic
2927	2928	2972	2980	3090	3091	3093	ν_s (C-H) + ν_{as} (C-H)
2877	2861	2931	2872	2927	2966	2976	Hydrogen bond
		2872		2833	2824	2834	
1620	1616	1614	1632	1634	1631	1631	ν_{as} (NO ₂); PA complex
1575	1567	1570	1608	1563	1592	1563	δ_{def} (N-H)
			1529		1561		Ring breathing bands
1529	1541	1516	1432	1518	1538	1518	ν (C=C)
1490	1492	1488		1492	1484	1489	δ (C-H) deformation
1402	1442	1412		1428	1425	1414	
	1416						
1286	1357	1358	1343	1373	1341	1372	ν (C-C) + ν (C-O) + ν_{as} (C-N)
1187	1303	1308	1312	1341	1281	1341	
1078	1276	1225	1263	1283	1222	1283	
1021	1226	1180	1150	1225	1173	1229	
	1180	1080	1086	1165	1110	1172	
	1108	1024		1079	1077	1080	
	1078			1022	1020	1023	
	1021						
993	888	983	917	923	933	934	δ_{rock} ; NH
903	832	894	829	790	905	908	δ (CH) in-plane bending
829	805	829	781	745	837	831	
801	699	806	732	709	786	785	
717		782	703		744	744	
		695				710	

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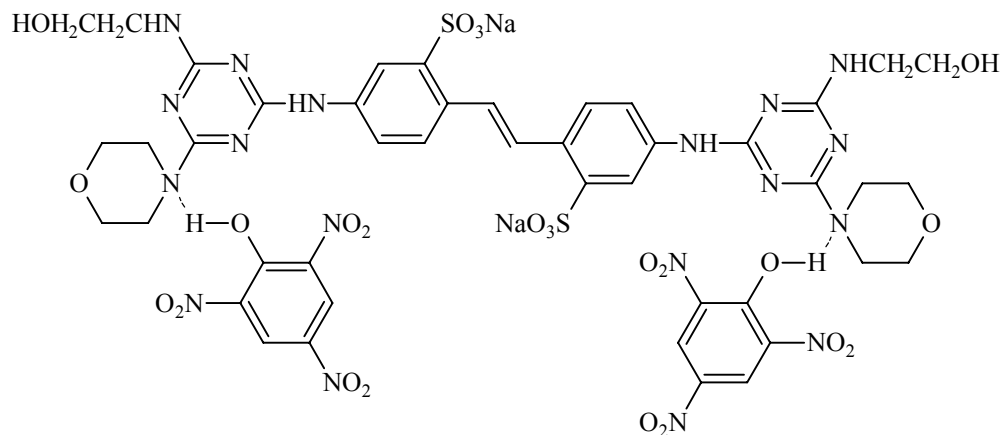
Donors			Acceptor	Complexes			Assignments ^(b)
TS1	TS2	TS3	PA	TS1-PA	TS2-PA	TS3-PA	
625	626	625	652	627	624	625	$\delta(\text{C-N})$ out-of-plane bending
540	543	544	522	547	543	546	skeletal vibration
				519			$\delta(\text{ONO})$; PA complex CNC deformation

(a): s, strong; w, weak; m, medium; sh, shoulder; v, very; vs, very strong; br, broad.

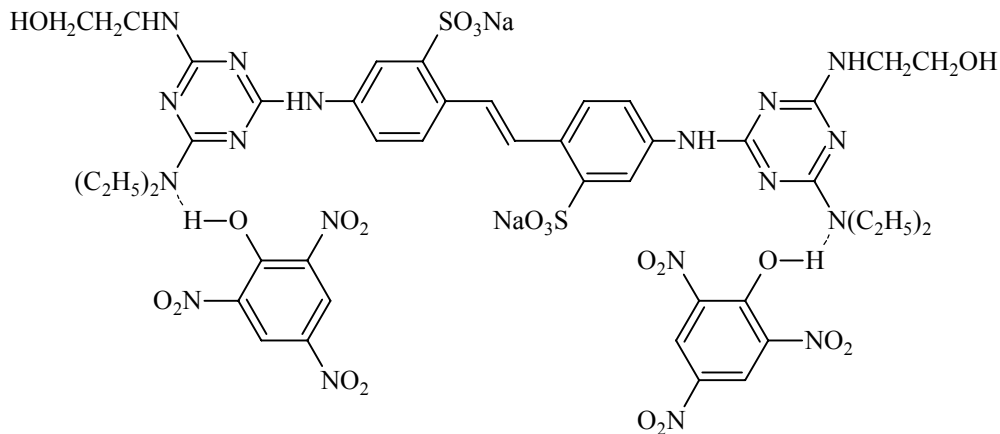
(b): ν , stretching; ν_s , symmetrical stretching; ν_{as} , asymmetrical stretching; δ , bending



Formula II: Suggested structural formula of [(TS1)(PA)₂] complex



Formula III: Suggested structural formula of [(TS2)(PA)₂] complex



Formula IV: Suggested structural formula of [(TS3)(PA)₂] complex

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