Int. J. Chem. Sci.: 11(4), 2013, 1681-1691
ISSN 0972-768X
www.sadgurupublications.com

STRUCTURAL, VIBRATIONAL AND ELECTRONIC SPECTRAL ANALYSIS OF CHARGE-TRANSFER COMPLEXATION BETWEEN THREE TRIAZINE-STILBENE DERIVATIVES WITH SOME π-ACCEPTORS.

PART FOUR : DDQ

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ABSTRACT

Design and development of triazine-stilbene derivatives have gained extensive attention in the last decade due to their substantially potential applications in textiles and papers industry. In this work, three novel charge-transfer (CT) complexes formed on the reaction between three disodium 4,4′-bis-(1,3,5-triazinylamino)stilbene-2,2′-disulfonate derivatives with dichlorodicyanobenzoquinone (DDQ) were synthesized and characterized by electronic, IR spectroscopy and elemental analysis. The structural investigations exhibit that the CT chelation between donors and DDQ acceptor occurs *via* $\pi \rightarrow \pi^*$ transitions. Based on elemental analyses and photometric titrations, the stoichiometry of the complexes (donor: DDQ molar ratios) was determined to be 1 : 2. The formation constant (K_{CT}), molar extinction coefficient (ε_{CT}) and other spectroscopic data have been determined using the Benesi–Hildebrand method and its modifications.

Key words: Fluorescent brighteners, Triazine-stibene derivatives, Charge-transfer, DDQ.

INTRODUCTION

The term charge transfer complex (CT) was introduced firstly by Mulliken[1,2], and discussed widely by Foster[3]. Mulliken[4,5] showed that the charge transfer interactions within a molecular complex consisting of an electron donor D and an electron acceptor A involved a resonance with a transfer of charge from D to A:

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$$D + A \rightleftarrows D^+A^- \rightleftarrows D^+ + A^-$$

Charge transfer complexation is currently achieving the great importance in biochemical, bioelectrochemical energy transfer process, biological systems, and drug-receptor binding mechanism, for examples, drug action, enzyme catalysis, ion transfers through lipophilic membranes[6]. On the other hand, electron donor-acceptor (EDA) interaction has a worth attention for chemical reactions like addition, substitution and condensation[7]. It shows a great important in many application topics and fields, like in non-liner optical materials and electrical conductivities, second order non-liner optical activity, micro emulsion, surface chemistry, photocatalysts, dendrimers, solar energy storage, organic semiconductors, as well as in studying redox processes[8-14]. Herein, this paper describes the study on the formation of CT complexes which formed between three disodium 4,4′-bis-(1,3,5-triazinylamino) stilbene-2,2′-disulfonate derivatives as donors with dichlorodicyano-benzoquinone (DDQ) as acceptor. The nature and structure of the final products both in solution and solid phase have been characterized to interpret the behavior of interactions using elemental analysis, infrared (IR) and electronic spectra. The spectroscopic, physical data were analyzed in terms of formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy ($\Delta G°$), oscillator strength (f) and transition dipole moment (μ).

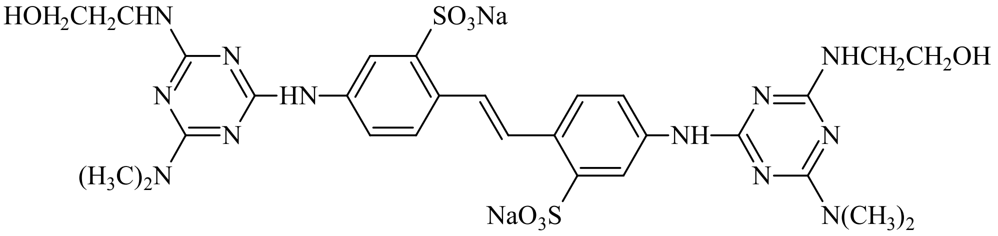
EXPERIMENTAL

General

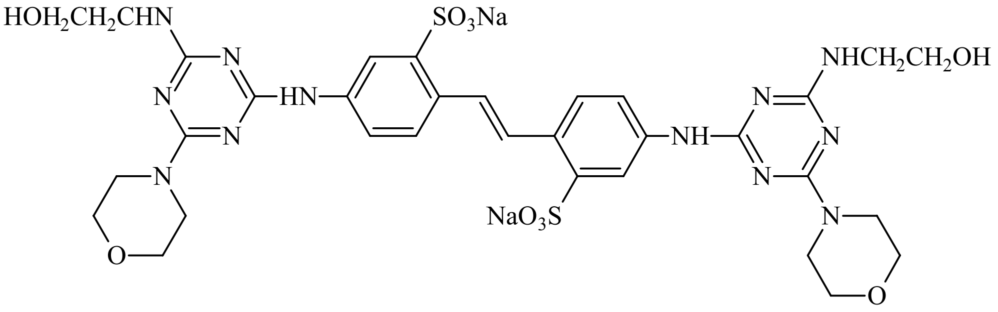
All chemicals used through this work were of analytical grade. The three disodium triazine-stilbene derivatives used in this work, are sodium (E)-6,6′-(ethene-1,2-diyl)bis(3-(4-(dimethyl-amino)-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino) benzenesulfonate (**TS1**), sodium (E)-6,6′-(ethene-1,2-diyl) 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-(diethyl-amino)-6-(2-hydroxyethylamino)-1,3,5-triazin-2-yl-amino) benzenesulfonate (**TS3**) (Formula I). The donors were obtained by synthesis according to the literature methods[15]. The dichlorodicyanobenzoquinone (DDQ) acceptor was purchased from the Sigma-Aldrich Chemical Company and was used without further purification. 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.

Methodology

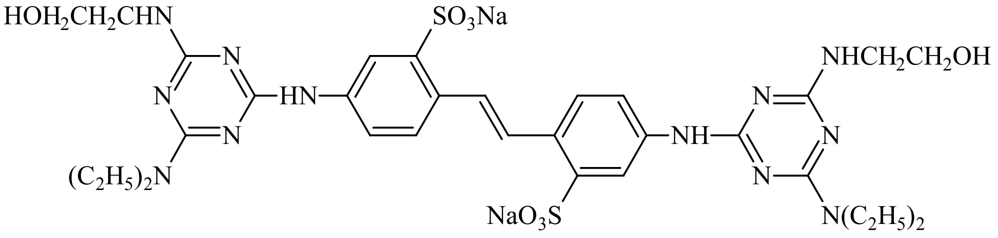
CT complexes of the disodium triazine-stilbene derivatives with the DDQ acceptor were prepared by mixing 1 mmol of each donor in pure–grade methanol (20 mL) with 1 mmol of DDQ acceptor in methanol (20 mL). The mixtures were stirred for approximately 30 min and allowed to evaporate slowly at room temperature 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 disodium triazine-stilbene derivatives.

RESULTS AND DISCUSSION

Elemental analysis

Elemental analyses (C, H, and N) of the CT complexes were performed. The obtained values are in good agreement with the calculated values, and the suggested values are in agreement with the molar ratios determined from the spectrophotometric titration curves. The obtained elemental analysis results are as follows:

(i) [(**TS1**)(DDQ)$_2$]: $C_{44}H_{34}N_{16}O_{12}Cl_4Na_2S_2$; Mol. wt. = 1230.02; Calc.: %C, 42.92; %H, 2.76; %N, 18.21, Found: %C, 42.88; %H, 2.73; %N, 18.25

(ii) [(**TS2**)(DDQ)$_2$]: $C_{48}H_{38}N_{16}O_{14}Cl_4Na_2S_2$; Mol. wt. = 1314.26; Calc.: %C, 43.82; %H, 2.89; %N, 17.04, Found: %C, 53.05; %H, 3.59; %N, 21.94

(iii) [(**TS3**)(DDQ)$_2$]: $C_{48}H_{42}N_{16}O_{12}Cl_4Na_2S_2$; Mol. wt. = 1286.02; Calc.: %C, 44.79; %H, 3.26; %N, 17.42, Found: %C, 44.83; %H, 3.30; %N, 17.39

Stoichiometry of the interaction

The stoichiometry of the CT complexes formed was determined by applying the spectrophotometric molar ratio[16]. Fig. 1 shows the electronic absorption spectra of the CT complexes. These spectra revealed the presence of the absorption bands that correspond to the CT interactions. These bands are observed at 480, 465 and 470 nm for the [(**TS1**)(DDQ)$_2$], [(**TS2**)(DDQ)$_2$] and [(**TS3**)(DDQ)$_2$] complexes, respectively. These detected absorption bands well know to be characteristic of the formation of new CT complexes. Spectrophotometric titration plots based on these characterized absorption bands are shown in FiG. 2. Based on the obtained results, the stoichiometry of the complexes with the DDQ acceptor was found to have a 1 : 2 ratio. The formed CT complexes were formulated as [(**TS1**)(DDQ)$_2$], [(**TS2**)(DDQ)$_2$] and [(**TS3**)(DDQ)$_2$]. These stoichiometry values are consistent with the elemental analyses

Benesi-Hildebrand plots

The Benesi-Hildebrand and its modification methods were applied for the determination of the spectroscopic physical data such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), energy of the complex (E_{CT}), standard free energy ($\Delta G°$), oscillator strength (f) and transition dipole moment (μ) for the CT complexes as described elsewhere[17-21]. The calculated values of these spectroscopic data for the complexes are presented in Table 1. The molar extinction coefficient (ε_{CT}) values reflect the molecular planarity and enlargement of π-conjugation. [(**TS1**)(DDQ)$_2$] complex has higher ε value than that of the other complexes which indicates that complex of **TS1** has much more planar and rigid π-conjugation system[22]. The DDQ complexes exhibit high values for the K_{CT}. These high K_{CT} values reflect the high stabilities of the CT complexes due to the strong donation of the triazine-stilbene derivatives. The [(**TS3**)(DDQ)$_2$] complex exhibited higher value for both K_{CT} and $\Delta G°$.

Table 1: Spectroscopic data of the synthesized complexes (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**)(DDQ)$_2$]	480	3.76×10^8	4.19×10^4	2.59	0.453	6.796	-37.519
[(**TS2**)(DDQ)$_2$]	465	7.52×10^8	1.72×10^4	2.67	0.186	4.315	-39.234
[(**TS3**)(DDQ)$_2$]	470	36.58×10^8	99.8	2.64	0.108	3.281	-43.154

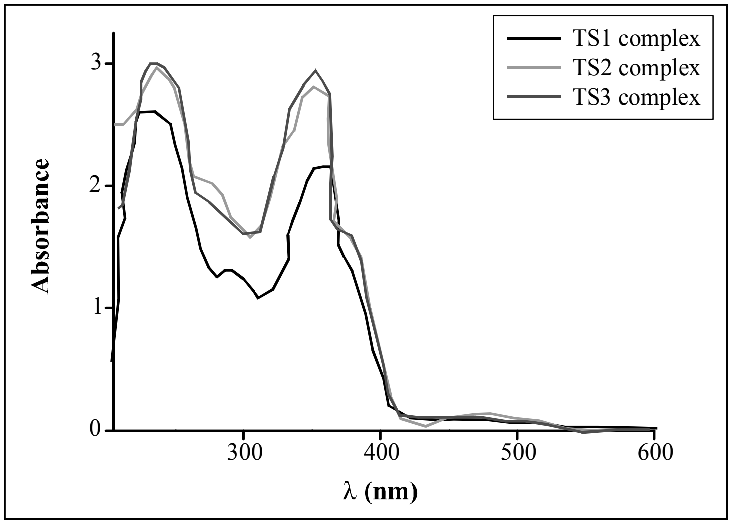


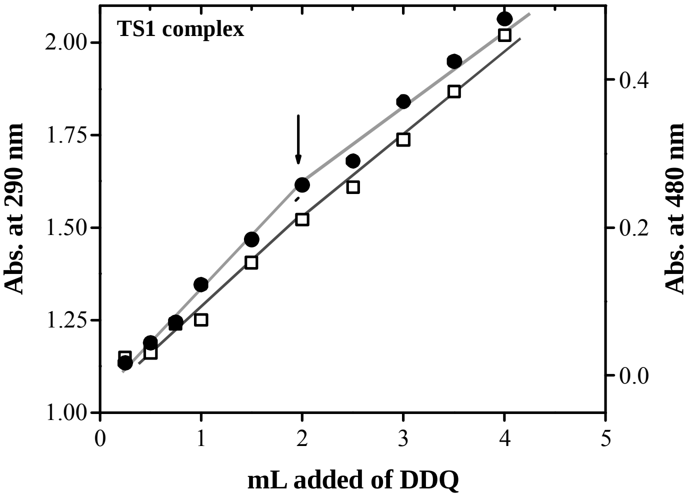
Fig. 1: Electronic absorption spectra of TS1/DDQ, TS2/DDQ and TS3/DDQ complexes

IR spectral characteristics

The peak assignments for the important characteristic IR spectral bands for the formed CT complexes are shown in Table 2. A comparison of the relevant IR spectral bands of the free donors and DDQ acceptor with the corresponding bands in the IR spectra of the isolated solid CT complexes clearly indicated that the characteristic bands of the donors exhibit small shifts in frequency and changes in their band intensities. This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complexes. In the CT complexes, the ν(C=O), ν(C≡N) and ν(C-Cl) stretching vibrations in the free DDQ appeared at 1673, 2231 and 800 cm^{-1}, respectively, where in the formed CT complexes, these stretching vibrations occurred at 1619, 2210 and 773 cm^{-1} for **TS1** complex; at 1656, 2204 and 775 cm^{-1} for **TS2** complex; at 1623, 224 and 778 cm^{-1} for **TS3** complex, respectively. Because DDQ lacks acidic centers, the molecular complexes can be concluded to form through π→π* and/or n→π* charge migration from the HOMO of the donor to the LUMO of the acceptor. The π→π* CT complex is formed via the benzene ring (electron-rich group) of the donors and the DDQ reagent (electron acceptor). The cyano group (–C≡N) is an electron-withdrawing group that exists in DDQ in a conjugated bonding system. The cyano groups in DDQ withdraw electrons from the aromatic ring, and such a process will make the aromatic ring an electron-accepting region. This behavior will decrease the CN bond order and therefore lower its vibrational wavenumber value upon complexation[23-25].

Structural interpretation

The structures of the [(**TS1**)(DDQ)$_2$], [(**TS2**)(DDQ)$_2$] and [(**TS3**)(DDQ)$_2$] CT complexes are confirmed by elemental analysis, spectrophotometric titration and IR spectra. The proposed structures of these CT complexes are shown in Formulas II-IV.



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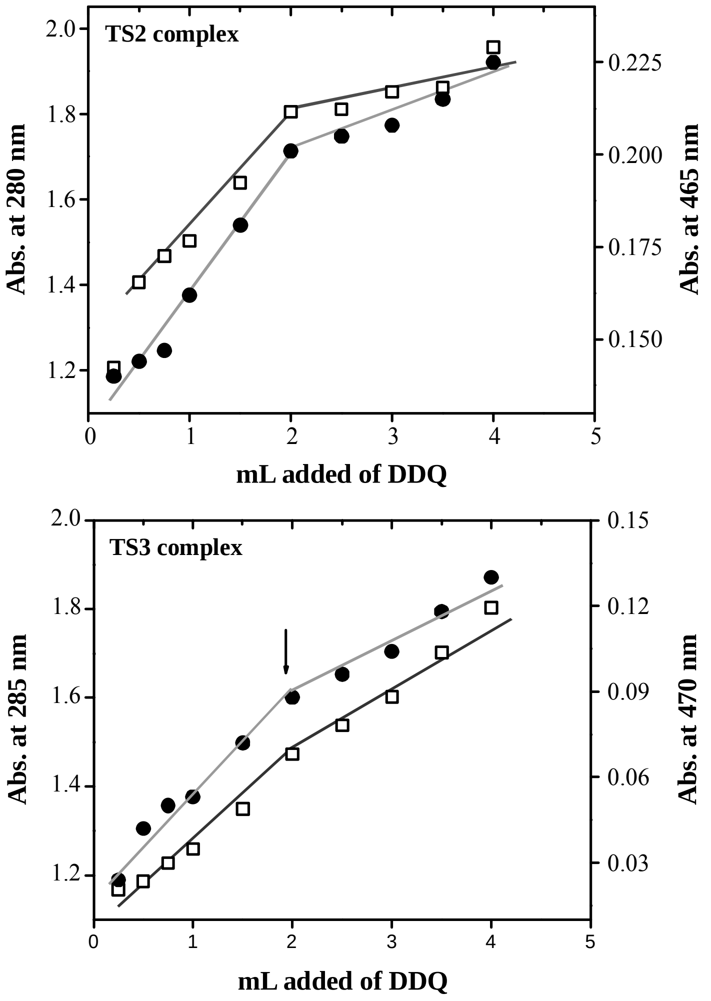


Fig. 2: Spectrophotometric titration curves for TS1/DDQ, TS2/DDQ and TS3/DDQ system

Table 2: Infrared frequencies[(a)] (cm^{-1}) and tentative assignments for TS1, TS2 and TS3 complexes with DDQ acceptor

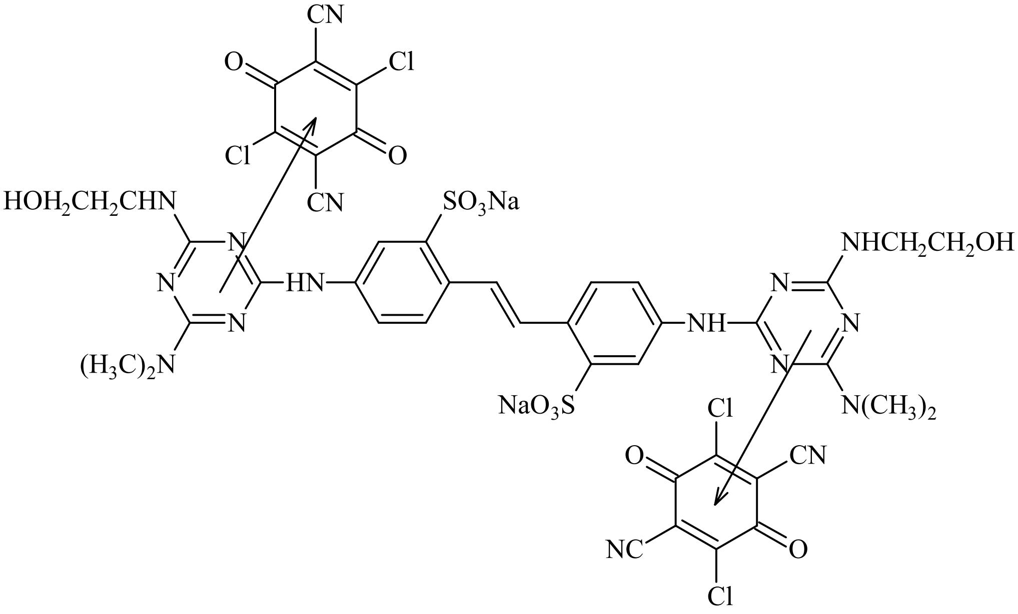
Donors			Acceptor	Complexes			Assignments[(b)]
TS1	TS2	TS3	DDQ	TS1-DDQ	TS2-DDQ	TS3-DDQ	
3423	3374	3420	3325 3218	3421	3419	3407	ν (O-H) ν (N-H) ν (C-H); aromatic

Cont…

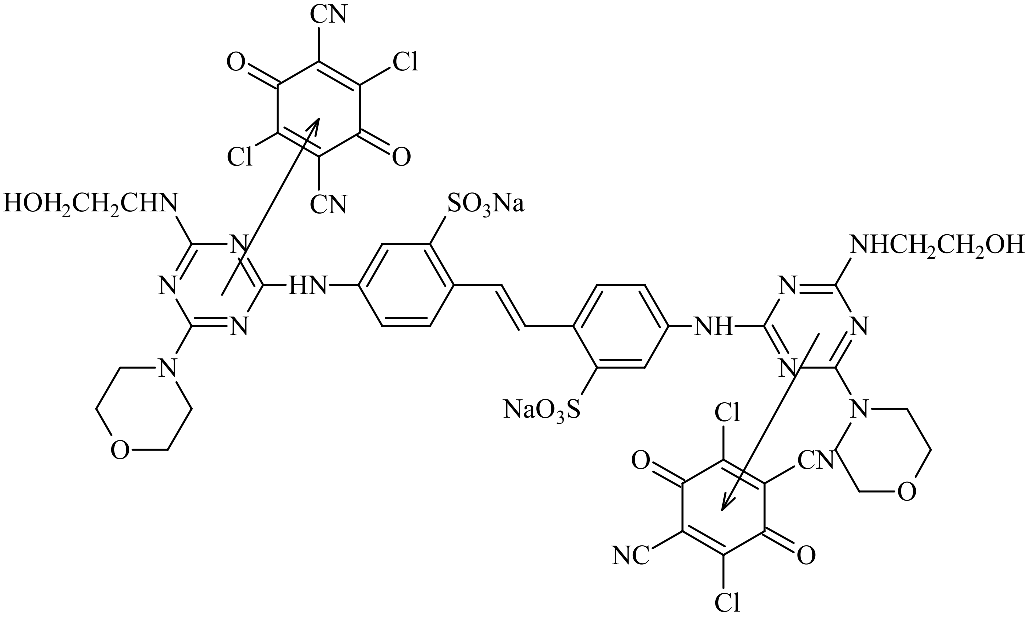
Donors			**Acceptor**	**Complexes**			**Assignments$^{(b)}$**
TS1	**TS2**	**TS3**	**DDQ**	**TS1-DDQ**	**TS2-DDQ**	**TS3-DDQ**	
2927 2877	2928 2861	2972 2931 2872	-	2936	2967 2925	2979	ν(C-H) + ν_{as}(C-H)
-	-	-	2250 2231	2210	2209	2214	ν(C≡N)
1620	1616	1614	1673	1619	1656 1626	1623	ν(C=O)
1575	1567	1570	1552	1591	1590	1591	δ_{def}(N-H) Ring breathing bands
1529 1490 1402	1541 1492 1442 1416	1516 1488 1412	1451	1524 1405	1538 1479 1442 1412	1544 1485 1412	ν(C=C) δ(C-H) deformation
1286 1187 1078 1021	1357 1303 1276 1226 1180 1108 1078 1021	1358 1308 1225 1180 1080 1024	1358 1267 1172 1072 1010	1338 1304 1223 1197 1078 1023	1358 1283 1222 1170 1110 1077 1020	1355 1225 1173 1081 1023	ν(C-C) + ν(C-O) + ν_{as}(C-N)
993 903 829 801 717	888 832 805 699	983 894 829 806 782 695	893 800 720	993 839 773 706	895 840 775 717	894 866 835 778 668	δ_{rock}; NH δ(CH) in-plane bending ν(C-Cl); DDQ, complex
625 540	626 543	625 544	615 527 457	625 544	623 542	609 546	δ(C-N) out-of-plane bending skeletal vibration CNC deformation

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

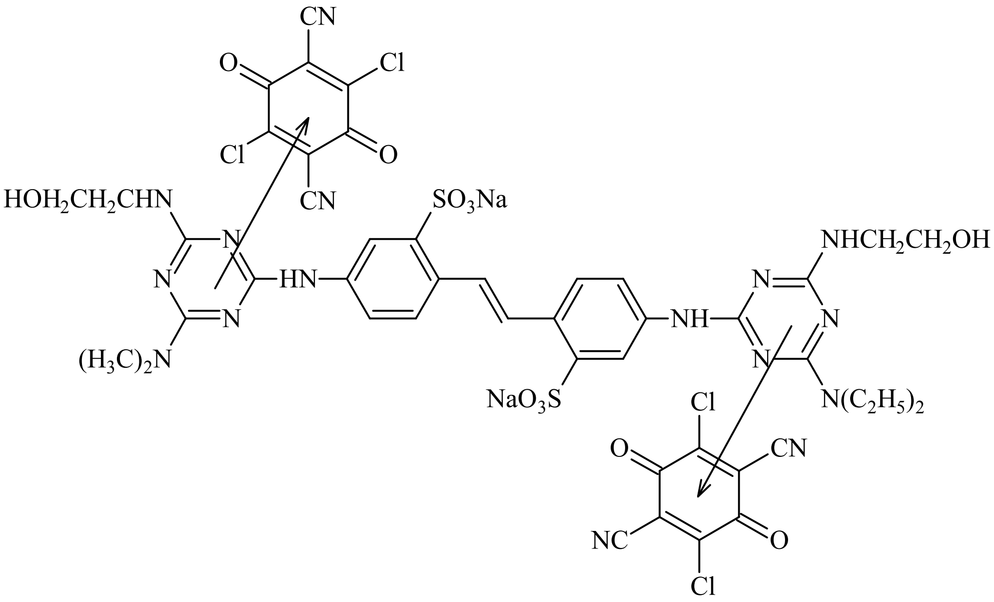
(b): ν, stretching; ν_s, symmetrical stretching; ν_{as}, asymmetrical stretching; δ, bending



Formula II: Suggested structural formula of [(TS1)(DDQ)$_2$] complex



Formula III: Suggested structural formula of [(TS2)(DDQ)$_2$] complex



Formula IV: Suggested structural formula of [(TS3)(DDQ)$_2$] complex

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Accepted : 20.09.2013