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SPECTROSCOPIC INVESTIGATION ON CHARGE-TRANSFER INTERACTIONS BETWEEN SULFADIAZINE AND DIFFERENT NITRO COMPOUNDS

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ABSTRACT

Charge transfer (CT) complexes formed between sulfadiazine as a donor and different nitro compounds like picric acid (PA), 3,5-dinitrobenzoic acid (DN), 4-nitroaniline (NA), 4-nitrophenol (NP) and 4-nitrobenzaldehyde(NB) as a π-acceptors are studied. Elemental analysis, Infrared, ^{1}H NMR and electronic absorption spectra are used to characterize the complexation behaviors of the resulted CT-complexes. The data obtained indicates that the molar ratio of charge transfer complex formed between donor: acceptor is 1:1.

INTRODUCTION

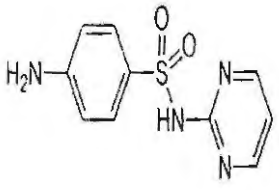
Sulfadiazine is a sulfonamide antibiotic. This drug eliminates bacteria that cause infections by stopping the production of folic acid inside the bacterial cell and it is commonly used to treat urinary tract infections. Charge transfer complexes play an important role in biological systems, Some investigators suggested that the activity of biologically active compounds may depend on their tendencies to form such CT complexes with biological receptors **[Pullman & Pullman (1958); Szent (1960)]**. Many of the electron donor-acceptor (EDA) interactions are widely studied spectrophotometrically in the determination of drugs. The review of literature in the last decade is mainly concentrated on the spectral studies of CT-complexes of drugs **[Sastry et al., (1993); (1997); Amin et al., (1995); Zhao et al., (1999) and Mohamed et al., (2002)]**. A vast number of the charge-transfer complexes formed during the reaction of σ- and π-acceptors with organic compounds containing different sites of donation (nitrogen, oxygen

and/or sulfur atoms) were extensively investigated **[Mourad (1983); Rimmer (1998); Bhowmik & Bhattacharya, (1990); Ramadan et al., (1991) and Rathore et al., (1997)]**. On the other hand, the EDA reactions of certain π -acceptors are successfully been utilized in pharmaceutical analysis **[Abou Attia (2000)]**. For these wide applications, extensive studies on CT-complexes of π-acceptors are performed **[Basavaiah (2004)]**. Charge-transfer complexes of organic species are formed through transfer of an electron from the donor to the acceptor **[Hamed (1993); Jones (1999); Das et al., (2000); Refat et al., (2004)]**. Also, protonation of the donor from acceptors have an acid behavior are generally a route for the formation of ion pair adducts **[Ibrahim (1993); (2001); Smith et al., (1997); (1998); (2000)]**. The formation of molecular CT-complexes between electron acceptors such as dinitro- or trinitrobenzene and electron donors was the subject of a last number of interesting investigations **[Matsunage (1980); Dessouki et al., (1988)]**.

The present work are aimed to investigate spectroscopically the tendency of the CT-complexation between sulfadiazine and some electron acceptors such as 4-nitrophenol (NP), 3,5-dinitrobenzoic acid (DN), picric acid (PA), 4-nitroaniline (NA) and 4-nitro-benzaldehyde (NB) as a π-acceptors. The solid complexes are synthesized and studied by elemental analysis (CHN), electronic absorption, infrared and ^{1}HNMR spectra.

EXPERIMENTAL

Sulfadiazine (4-amino-N-pyrimidin-2-ylbenzene sulfonamide) $C_{10}H_{10}N_4O_2S$ was supplied by Merck.



picric acid, 3,5-dinitrobenzoic acid, 4-nitroaniline, 4- nitro-benzaldehyde and 4-nitrophenol as well as the solvents used are supplied by Aldrich . All chemicals are used as received without further purification.

The solid charge-transfer complexes are prepared in 1:1molar ratio of each donor and acceptors in mixture of CH_3OH and $CHCl_3$. The reaction are stirred for about 2-3 h on water bath. The solid CT complexes formed are filtered immediately and washed several times using $CHCl_3$. The complexes are dried under vacuum and the melting points of the adducts are determined.

Electronic absorption spectra are measured on a Unicam UV2-300 Uv-vis spectrophotometer using 10 mm quartz cells. IR spectra as KBr discs are recorded on Gensis II FT-IR spectrophotometer (400-4000 cm^{-1}). ^1H NMR spectra in dmso-d_6 are measured on a Varian Gemini 200 MHz Spectrometer using TMS as an internal standard. Microanalysis for carbon, hydrogen, nitrogen is carried out at the Micro analytical centers, Cairo, Egypt using a Perkin-Elmer CHN 2400.

RESULT AND DISCUSSION

The electronic absorption spectra of sulfadiazine (S) as donor with picric acid (PA), 3,5-dinitrobenzoic acid (DN), 4-nitroaniline (NA), 4-nitrophenol (NP) and 4-nitrobenzaldhyde (NB) as π – acceptors in amyl alcohol show an extra absorption band not due to any one of the components alone Fig.1. Furthermore, neither electron donor (< 250 nm) nor electron acceptors is absorbed in the region of absorption of molecular complexes formed. These bands have been attributed to the formation of donor-acceptor molecular complexes in solution. The absorption bands in the spectra of sulfadiazine with picric acid as a result of CT-complex formation were appeared at 273 nm. In addition, the picric acid band located at 355 nm suffers an increase in its absorbance due to proton transfer from OH group of picric acid to the nitrogen atom of sulfadiazine (S). Also, the picric acid (PA), 3,5-dinitrobenzoic acid (DN), 4-nitroaniline (NA), 4-nitrophenol (NP), and 4-nitrobenzaldhyde (NB) have the same characteristic bands.

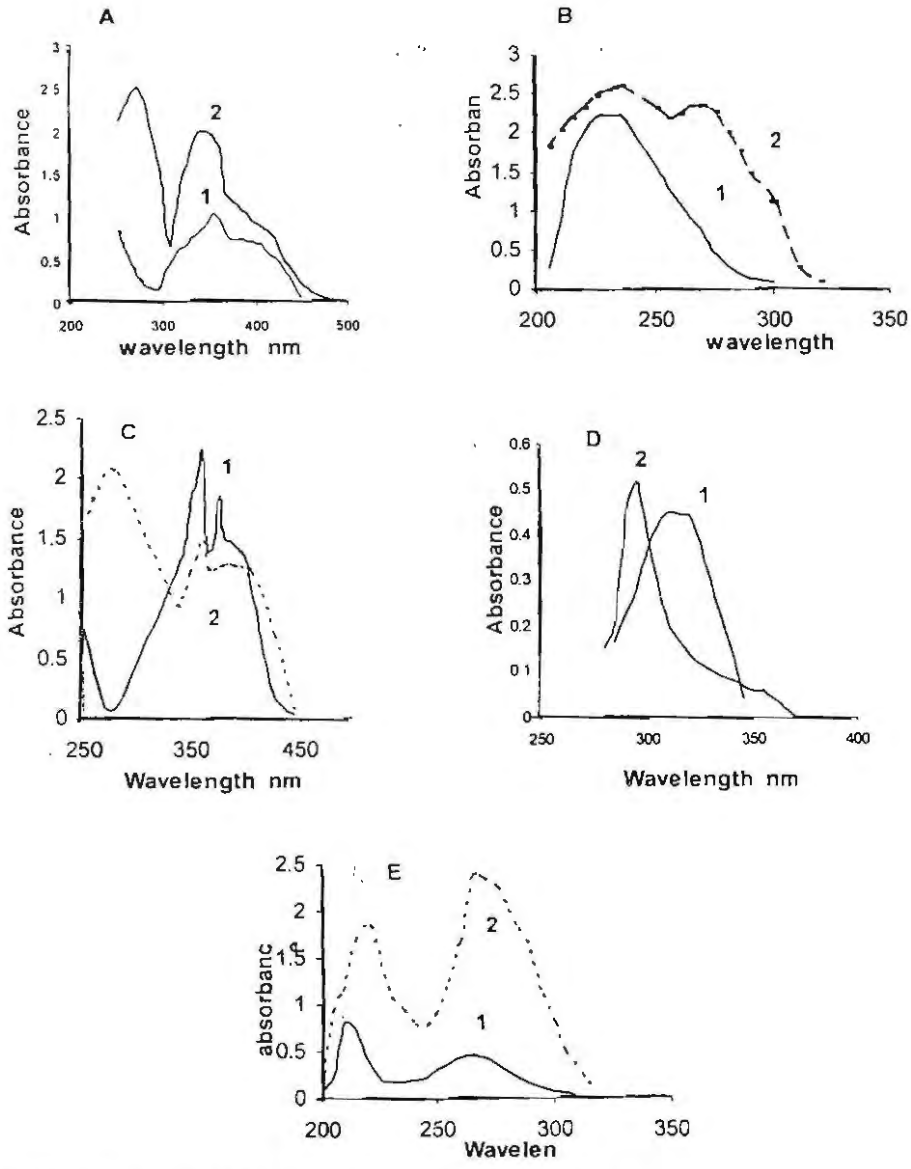
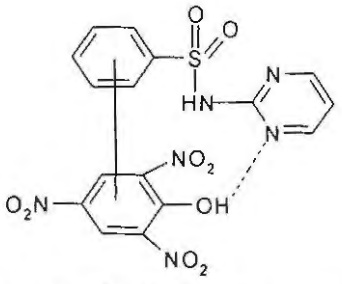


Fig.(1): Electronic absorption spectra of sulfadiazine with:
A-PA, B-DN, C-NA, D-NP and E-NB
1-acceptors($1X10^{-4}$M/L) and 2-donor-acceptors ($1X10^{-4}$M/L)
in amyl alcohol.

IR spectra

The characteristic infrared spectra data of charge transfer complex of sulfadiazine with picric acid are given in Table 2a. The IR peaks of the donor have shifted to the lower or higher wavenumbers. It is observe also that the peak of CT-complex have decreased in intensity relative to that of the donor. This supported the complexation between the donor and acceptor. The IR spectra of the complex is characterized by a group of bands appearing in the region 2300-3000 cm^{-1}. Also, the NO_2 band at 1340-1350 cm^{-1} are shifted to lower frequencies due to the increased polarization of the nitro group. On the other hand, the ν_{CH} and γ_{CH} of the acceptors are shifted to higher frequencies, supporting the intermolecular $\pi - \pi^*$ interaction between the free donor and acceptor. The data show new broad bands around 2600 cm^{-1}region which are not present in the IR spectra of both free donor and acceptors. These bands are attributed to the stretching mode of a proton transfer from the acceptor to a donor group **[Bellamy (1975)]**. This results from the protonation of the NH^+ group of the donor through intermolecular hydrogen bond occurs in the acceptors from the OH or COOH groups to the basic central nitrogen atom. This is further supported by the disappearance or decrease in the stretching of the OH or COOH group of acceptors as a result of intermolecular hydrogen bond formation. The shift of the IR bands of the acceptor to lower wavenumbers and those of the donor part to higher values confirms a donor to acceptor charge transfer of π-π^* interaction of the $D_{HOMO} \rightarrow D_{LUMO}$ transition **[Kross & Fassel (1957)]**.

Accordingly, the bonding between the donor and the acceptor can be formulated as:



Structre of sulfadiazine with picric acid.

^{1}H-NMR spectra

^{1}H-NMR spectra of the charge transfer complex formed between sulfadiazine with picric acid in DMSO were measured and given in Table 2b. The chemical shifts of proton NMR for the defined peaks are analyzed. Evidently, the results obtained from the elemental analysis, infrared spectra and photometric titrations met at the same point with ^{1}H-NMR Spectra. To interpret the mode of interaction between the donor and acceptor it is following that:

(i)There are a decrease in intensity for the peaks that distinguish the-NH_2 group (the donation site for sulfadiazine) and also there was shifting for the peaks towards the down field which indicate that the donation process has been carried out by-NH_2 group.

(ii) It is observed noticed also that the interaction between sulfadiazine and 3,5-dinitrobenzoic acid does not result in –COOH group character in addition to the above mentioned change

(i) in the resulting CT-complexes. This justifies the complexation between –NH_2 and –COOH group in 3,5-dinitrobenzoic acid (i.e.intermolecular hydrogen bond formated lead to the absence of the wavenumber of the peak of free carboxylic group of DN at 1704 cm^{-1} which existed before complexation) indicated in IR spectra.

(iii) The shift in the intensity of the aromatic charater peaks for both donor and acceptor, resulted from the $\pi - \pi^*$ CT-complexes which were originally formed via the benzene rings (electron rich group) as sulfadiazine and nitro compounds (electron acceptor) **[Zhao et al., (1999)]**.

Photometric titration

Photometric measurements at the characteristic absorption bands of CT complexes are obtained using the molar ratio method for the studied complexes of sulfadiazine with picric acid. These photometric curves were obtained by the plot of the absorbance against the ratio of the acceptor to the donor **[Skoog (1985)]**. The equivalence points shown in these curves clearly indicate that the formed CT-complexes between sulfadiazine and picric acid is of 1:1 ratio (Fig.2).

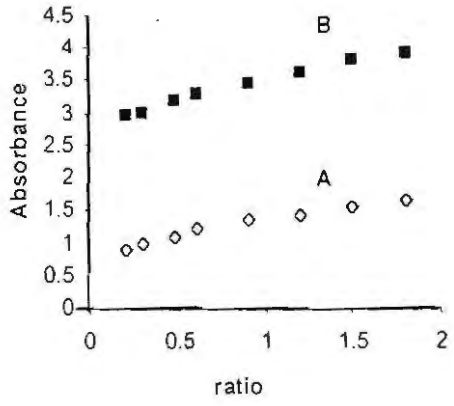


Fig.(2): Photometric titration curve of sulphadiazine with picric acid at A- 420 nm and B-273 nm.

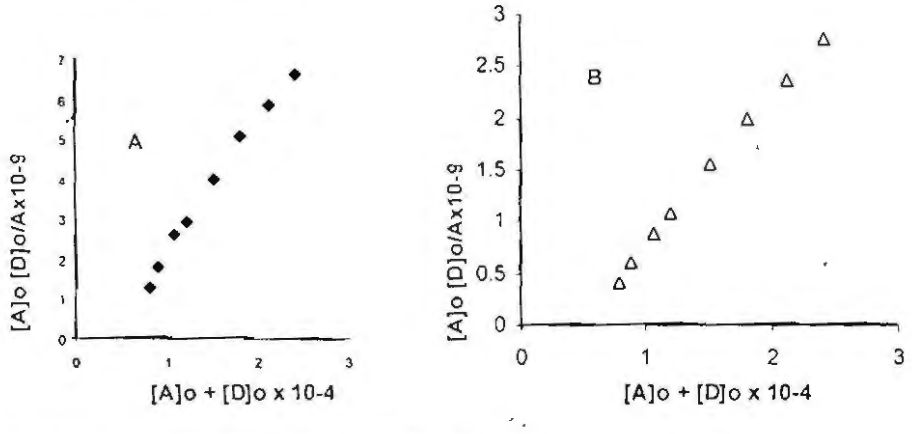


Fig.(3): Relation between $[A]_o\ [D]_o/\ A$ against $[A]_o + [D]_o$ for sulphadiazine with picric acid at : A- 420 nm and B-273 nm.

The modified Benesi-Hildebrand equation **[Benesi & Hildebrand (1949)]** was used to determine the value of the equilibrium constant, K_{ct} ($Lmol^{-1}$), and the extinction coefficient, ϵ_{ct} ($Lmol^{-1}cm^{-1}$) for the complex formed in solution. This equation can be written as follows:

$$[A]_o\ [D]_o/\ A = [A]_o + [D]_o\ /\ \epsilon_{ct} + 1/\ K_{ct}\ \epsilon_{ct} \qquad (1)$$

Where, $[A]_o$ and $[D]_o$ are the initial concentrations of picric acid and sulfadiazine, respectively, while A is the absorbance at the mentioned CT bands. The data obtained throughout this calculation are given in Table 3. On plotting the values of $[A]_o\ [D]_o/\ A$ values against the $[A]_o + [D]_o$

values, a straight lines were obtained with a slope of 1/ $\epsilon_{ct}$and intercept of 1/Kϵ_{ct}.

The oscillator strength (f=22.27), which is a dimensionless quantity, is used to express the transition probability of the CT-band [**Lever (1985)**] and the transition dipole moment (μ = 359.386) of the CT complexes [**Tsubomura & Lang (1964)**] are calculated by using the fo.lowing equations:

$$F = 4.42X10^{-9}(\epsilon_{max}\ \Delta\nu_{1}/2) \quad (2)$$

$$\mu = 0.0958(\epsilon_{max}\ \Delta\nu_{1}/2/\nu_{max})^{1/2} \quad (3)$$

where $\Delta\nu_{1}/2$ is the half bandwidth of absorbance and ϵ_{max} , ν_{max} are the extinction coefficient and wavenumber at maximum absorption peak of the CT complex, respectively.

The dissociation energy (W) is calculated from the corresponding CT energy E_{ct} , ionization potential of the donor (I_P) and electron affinity of the acceptor (E_A) using the relationship as follow [**McConnel et al., (1964)**].

$$E_{ct} = I_P - E_A - W \quad (4)$$

The energy of the $\pi - \pi^*$ interaction (E_{ct}) is calculated using the following equation [**Briegleb (1964)**].

$$E_{ct} = 1243.667/\lambda_{ct}\ nm \quad (5)$$

The ionization potential of sulfadizine is estimed from the CT energy of this complex with PA by using equation (6):

$$I_P = a + b\ (h\nu_{max}) \quad (6)$$

Where $h\nu_{max}$ is the $\pi - \pi^*$ transition energy in electron volts eV; a and b are 5.11and 0.701 [**Wheat (1969) – (1970)**], 4.39 and 0.857 [**Mosten (1956)**] or 5.156 and 0.778 [**Becker & Worth (1962-1963)**] respectively. The mean value calculated by this methode is 8.303 eV. The calculated value of W using the defined acceptor is 2.297 eV where the E_A electron affinity of picric acid is 1.45 eV [**Ramadan et al., (1990)**]. The high values of both the equilbrium constant (K = 19.40 $x10^3$ $Lmol^{-1}$) and extinction coefficient (ϵ = 51.55 $x10^3$ $Lmol^{-1}cm^{-1}$), reflects the high stability of the formed CT-complexes as a result of the expected high donation of the sulfadiazine. The equivalent conductance values at $1X10^{-4}$ molar concentration indicated that these complexes have a small limit of conductivity. The conductivity given in Table 1, confirms that these complexes have a positive ($^+NH_2$) and negative charge (O^- of acidic group) which resulted from a CT transition. The low conductivity values for the CT-complexes may be due to intermolecular hydrogen bond formation.

Table (1): Elmental analysis, melting point and CT band λ ct values of Complexes of sulfadiazine with nitro compounds

acceptor	Melting point °C	Elemental analysis	λ ct nm	ϵ_{max} $Lmol^{-1}cm$	Λ_m $(ohm^{-1}cm^{-1}mol^{-1}L)$
Picric acid	160	40.999 3.031 20.779 40.088 2.768 20.453	273	$51.55x10^3$	11.0
3,5-dintrobenzoic acid	180	45.711 3.089 19.411 44.16 3.052 18.180	300	$11.00x10^3$	10.2
4-nitroaniline	120	49.982 4.899 11.094 49.478 4.152 10.818	275	$20.70x10^3$	8.2
4-nitrophenol	135	49.974 4.119 18.542 49.353 3.883 17.986	355	$0.57x10^3$	8.9
4-nitrobenzaldehyde	205	51.321 4.124 17.998 50.869 3.766 17.448	205	$9.30x10^3$	7.1

Table(2): a - IR spectra of sulfadiazine with picric acid.

S-PA	
3423.0 s	$\gamma(NH_2)$
3654.9 s	
3257.2 w	γ (NH)
3102.1 vs	γ (CH)
3036.6 m	γ_s (CH)
2936.0 m	γ_{as} (CH)
1651.8 w	ν(C=N)
1582.7 s	ν(C=O)
1494.0 s	δ(N-H): $^+NH_2$
	ring breathing bands
1440.6 w	C-H deformation
1406.9 w	ν(C-C)
1324.4 s	ν(S=O)
1154.9 s	
1260.9 vs	ν (C-N)
998.8 vs	(C-H) bend
941.6 s	$\delta_{rock.}$ $^+NH_2$
843.2 m	
824.5 vs	CH_2 rock
797.0 m	skeletal vibrations
721.8 vs	
683.6 s	
571.1 vs	δONO;PA
548.2 vs	CNC deformation
523.3 vs	

s, strong; w, weak; m, medium; sh, shoulder; v, very; br, broad.

b - ^{1}H-NMR spectra of sulfadiazine with picric acid.

Compound		
S-PA	11.2 s	1H, NH
	7.8 – 8.4 m	4H aromatic
	7.0 s	1H, SO_3H
	6.8 m	2H, pyrimidine
	5.6 s	2H, NH_2

S, single; m, multiplet.

Table (3): The values $[A]_o [D]_o/A$ against $[A]_o+[D]_o$ for sulphadiazine with picric acid Complex in amyl alcohol.

Ratio	$[D]_o X10^{-4}$	$[A]_o X10^{-4}$	Absorbance at 420 nm	$[A]_o+[D]_o x10^{-4}$	$[A]_o [D]_o/Ax10^{-9}$
0.3	0.6	0.20	0.880	0.80	1.302
0.5	0.6	0.30	0.90	0.90	1.801
0.75	0.6	0.48	1.097	1.075	2.60
1	0.6	0.60	1.225	1.20	2.90
1.5	0.6	0.90	1.342	1.50	4.01
2.5	0.6	1.50	1.542	2.10	5.84
3	0.6	1.80	1.642	2.40	6.58

Ratio	$[D]_o X10^{-4}$	$[A]_o X10^{-4}$	Absorbance at 295 nm	$[A]_o+[D]_o x10^{-4}$	$[A]_o [D]_o/Ax10^{-9}$
0.3	0.6	0.20	2.954	0.80	0.406
0.5	0.6	0.30	2.984	0.90	0.603
0.75	0.6	0.48	3.203	1.075	0.89
1	0.6	0.60	3.312	1.20	1.09
1.5	0.6	0.90	3.450	1.50	1.565
2	0.6	1.20	3.621	1.80	2.01
2.5	0.6	1.50	3.802	2.10	2.368
3	0.6	1.80	3.931	2.40	2.769

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الملخص العربـــــى

دراسة تكون متراكبات أنتقال الشحنة بين سلفاديزين كمعطي ومركبات نتروبنـزين مثل حمض البكريك و٣،٥ - ثنائي نتروحمض البنزويك و٤- نتـروأنيلين و٤- نتروفينـول و٤- نترو بنزالدهيد كمستقبل. أستخدم التحليل العنصرى واشعة تحـت حمـراء والـرنين المغناطيسى وطيف الامتصاص الالكترونى لأثبات سلوك متراكبات أنتقال الـشحنة. تـدل النتائج علي أن نسبة تكوين المتراكب بين المعطى والمستقبل هى ١: ١ .