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Ionisation Potentials and Electron Affinities of Organic Molecules from Electronic Charge Transfer Spectra

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Summary: Molecular complexes of N-dimethyl benzylidene aniline derivatives (as electron donors) with some aromatic nitro compounds (as acceptors) have been prepared and investigated by electronic absorption spectra. The ionization potentials of the donors are determined from the electronic absorption spectra of the solid CT complexes. The electron affinity of some acceptors are also evaluated.

Introduction

The transfer of an electron from a donor molecule to an acceptor one is mainly governed by the electronic character of those two interacting molecules. This type of interaction lies between two extremes from simple electrostatic attraction till complete separation of charge

$$D + A == D...A == D^{+}...A^{-} == D^{+}...A^{-}$$

The final state acquired in a charge transfer complex is mainly dependent on the ability of the donor to release the electron i.e. its ionization potential and its electron affinity of the acceptor to take up the electron.

The energy of the CT interaction $(HOMO_D----LUMO_A)=E_{CT}$ is related to both the ionization potential of the donor (I_p) and electron affinity of the acceptor (E_A) by the relation.

$$E_{CT} = I_P - (E_A + C)$$

where C is the energy of the coulombic attraction between the electron transferred to the acceptor molecule and the positive hole left behind it on the donor one. The value of C depends to a large extent on the system under consideration essentially the geometry of the two interacting molecules.

Though the ionization potentials of a large number of electron donors have been determined from their electronic CT spectra, yet no investigation dealt with benzylidene aniline derivatives. In recent years, a variety of solid CT complexes of benzylidene aniline derivatives with nitrobenzene have been prepared and investigated by IR, ^{1}H-NMR and electronic spectra [1-3]. However, the I_P of these compounds have not been determined from such spectral studies.

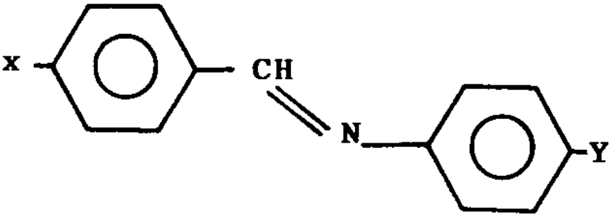
In the present investigation, the electronic CT spectra of four benzylidene aniline derivatives with ten di- and trinitrobenzenes were studied aiming to determine their ionization potentials as well as the electron affinity of the acceptors used.

Experimental

The compounds utilised in the present investigation were purest grade chemicals available from BDH. The benzylidene aniline derivatives were prepared by the condensation of aniline and benzaldehyde derivatives in the usual way [4].

The electronic absorption spectra were recorded on the Unicam SP 8000 spectrophotometer using the Nujol mull technique for the isolated solid complexes.

The donors involved in the present work have the general structure



in which

[X=Y=H] a, [X=H, Y= $-N(CH_3)_2$]b, [X = $-N(CH_3)_2$, Y = H] C, and [X = Y = $-N(CH_3)_2$]d

The acceptors used include strong acids, picric acid (I), 3,5-dinitrobenzoic acid (II) and 3,5-dinitrosalicylic acid (III); weaker acids 2,6-dinitrophenol (IV) and 2,5-dinitrophenol (V) ; and nonacidic compounds, trinitrobenzene (VI), 1-flouro-2,4-dinitrobenzene (VII), 1,5-diflouro-2, 4-dinitrobenzene (VIII), 1-chloro-2, 4-dinitrobenzene (IX) and m-dinitrobenzene (X)

Results and Discussion

The electronic absorption bands of the solid molecular complexes as Nujol mull reveal marked shifts from those of the donors and acceptors. The electronic absorption spectra of most complexes exhibit one CT band within the 400-500 nm range i.e. on the longer wavelength side of the ϕ---NO_2 bands of the acceptor. This band is assigned to the $\pi-\pi^*$ CT interaction of the type (D_{HOMO}) ----- (A_{LUMO}).

For some compounds the spectra display a shallow broad band on the lower energy side of the main CT band indicating an n ----- π^* contribution. The spectra show a higher E_{CT} for complexes involving proton transfer i.e. for complexes with strong acid character of the acceptor. The high E_{CT} energy results from the lower affinity of the anion relative to the neutral molecule. Also the positive centre on the protonated donor would increase ionization potential hence the rise of E_{CT}.

The E_{CT} values can be calculated experimentally from λ_{max} CT in the electronic spectra of the complexes applying the following equation:

$$E_{CT} = \frac{1243.667}{\lambda\ CT}\ \text{eV}.$$

the value thus determined are given table I.

The energy of the $\pi-\pi^*$ CT band (E_{CT}) is used to estimate the electron affinity (E_A) of the acceptor as well as the ionization potentials (I_P) of the donors under investigation using the relation given by Briegleb [5,6].

$$E_{CT} = I_P - (E_A + C)$$

in which I_P = ionization potential of the donor.

E_A = electron affinity of the acceptor

Table-1: The values of the wavelength, energy of CT and calculated E_A of the acceptors used.

Donor		Donor (a)			(b)			(c)			(d)			
accetpor	λ_{nm}	E_{CT}	E_A	λ_{nm}	E_{CT}	E_A	λ	E_{CT}	E_A	λ	E_{CT}	E_A	mean value	literature value*
I	502	2.48	0.82	450	2.76	0.58	450	2.76	0.51	480	2.59	0.65	0.64	0.72
II	450	2.76	0.54	450	2.76	0.58	450	2.76	0.51	490	2.54	0.70	0.58	0.58
III	500	2.44	0.81	480	2.59	0.75	500	2.49	0.78	500	2.49	0.75	0.78	0.59
IV	440	2.83	0.47	455	2.86	0.48	450	2.76	0.51	460	2.71	0.53	0.50	
V	460	2.70	0.6	-	-	-	450	2.76	0.51	472	2.64	0.60	0.56	0.54
VI	480	2.59	0.71	-	-	-	490	2.54	0.73	480	2.59	0.65	0.70	0.69
VII	460	2.70	0.60	480	2.56	0.75	500	2.49	0.78	470	2.65	0.59	0.68	
VIII	450	2.76	0.54	450	2.76	0.58	450	2.76	0.51	465	2.68	0.56	0.65	
IX	-	-	-	450	2.96	0.38	400	3.11	0.28	420	2.96	0.28	0.374	
X	445	2.80	0.50	450	2.76	0.58	-	-	-	-	-	-	0.54	0.58

*Ref.11

Table-2: The values of I_p calculated from electronic spectra of free ligand and CT complexes.

Donor	I_p calculated from electronic spectra*	I_p Calculated from CT complexes accetpor V	VI	X	mean I_p
a	8.61	8.44	8.49	8.58	8.50
b	8.67	-	-	8.54	8.54
c	8.59	8.50	8.44	-	8.47
d	8.69	8.38	8.49	-	8.44

*mean value calculated from the relaction

$$I_p = a + b\,\nu_o$$

where $\nu_o = \frac{10^7}{\lambda CT} \times 1.24 \times 10^{-4}$ eV

C = 5.2 eV, the coulombic force between the electron transfered and the resulting positive hole [7].

The values of ionization potential (I_P) required for estimation of (E_A) are determined from electronic absorption spectra of the free donors applying the relation

$$I_P = a + b\nu_o$$

where ν_o = is the energy of the HOMO -LUMO $\pi - \pi^*$ transition of the free donor in the gas phase, taken for approximately that in solution, since the solvation energy is too low compared to the electronic excitation energy, (a) and (b) are constants amounting to 4.39 and 0.875 [8] or 5.156 and 0.778 [9] or 5.11 and 0.701 [10]. These values of I_P were determined for each case; the mean value was taken to represent the I_P used for calculating the electron affinity. The value of ν_o are calculated from the relation

$$\nu_o = \frac{10^7}{\lambda CT} \times 1.24 \times 10^{-4} \text{ eV}$$

The results are collected in table (1).

The values of electron affinity of most acceptor under investigation, determined using the above relation, agree with those determined previously [11].

A substantial support for the data obtained is gained by considering the experimental values of E_{CT}, the electron affinity for a given accetpor for which E_A is already known and the value of the C = 5.2 and then calculating the I_P of the donors under investigation and comparing the values with those obtained from the electronic spectra of the free donors.

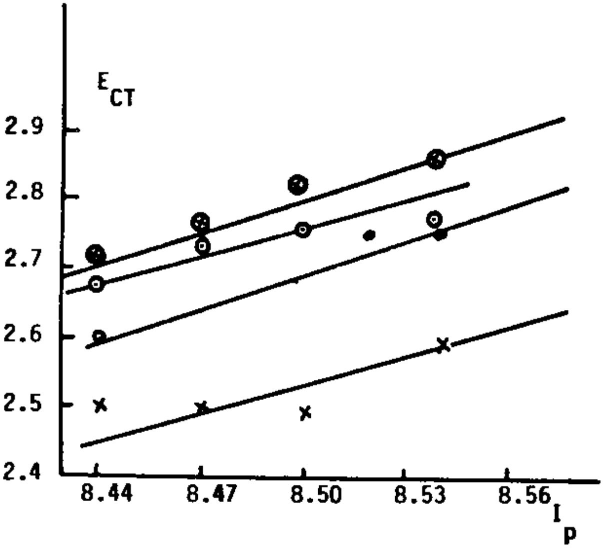


Fig. 1: The correlation between E_{CT} and I_p for complexes of acceptors I, III, IV and VIII.

The values of I_P evaluated from Briegleb equation are comparable to those calculated from the electronic absorption spectra (Table II).

The Briegleb relation requires that the plot of E_{CT} as a function of I_P should be a linear relation. The curves in Fig. (1) show satisfactory linear plots with almost identical slopes but varied intercepts. From the intercepts the values of the electron affinities (E_A) of the acceptors are determined. The values of E_A for some acceptors are comparable to those known in the literature [11].

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