On The formation of 1:2 (Donor:Acceptor) CT Complexes Between Hydroxy Aromatic Schiff Base Donors and Nitrobenzenes Acceptors

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Summary: The molecular complexes of some hydroxy aromatic Schiff base with aromatic tri- and dinitrobenzenes are prepared and investigated using element analysis, ir, ^{1}H-nmr and electronic absorption spectra. Elemental analysis showed the possible formation of 1:1 and 1:2 (donor:acceptor) complexes. The ir, ^{1}H-nmr spectra showed that the CT interaction in the 1:1 complexes originates from the anilino ring while for the 1:2 complexes both anilino and benzal rings contributes to CT complex formation. The spectral changes revealed that complexes with non acidic or weak acidic acceptors are formed through charge transfer while those with acidic acceptors are formed through proton and electron transfer.

Introduction

The formation of molecular complexes of the charge transfer (CT) type between electron acceptors such as dinitro or trinitro benzenes and π-electron donors was the subject of a vast number of interesting investigations [1-6].

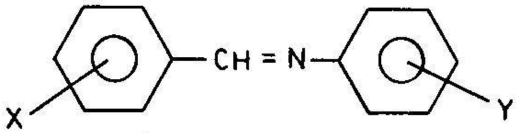
Previous studies [7-10] on CT complexes of aromatic compounds containing more than one π-donor system showed that these compounds can form 1:1 and 1:2 (donor:acceptor) CT complexes. However, with Schiff bases only 1:1 compounds have been reported and in that case the aniline ring was the donor part of the molecule.

In the present investigation the formation of 1:2 (donor:acceptor) complexes of some hydroxy Schiff bases and nitrobenzene derivatives is reported. The composition of the compounds is tested by element analysis and the bonding is examined by ir, nmr and electronic absorption spectra.

Experimental

All compounds used in the present investigation were pure grade BDH chemicals.

The working procedures for the preparation of CT complexes are the same as given before [3]. The donors used in the present investigation have the general structural formula:



In which X and Y are (o-OH, H)A, (p-OH,H)B, (H, o-OH); C (H,m-OH)D, and (H,p-OH)E.

The acceptors used are non-acidic acceptors such as picryl chloride (I), trinitrotoluene (II), acceptors with weakly acidic properties such as 2,4-dinitrophenol (III) or acceptors with strong acidic acceptors such as picric acid (IV), 3,5-dinitrosalicylic acid (V) and 3,5-dinitrobenzoic acid (VI).

The ir spectra of the CT complexes were recorded with KBr discs using the Perkin Elmer 683 infrared spectrophotometer. The ^{1}H-nmr spectra were obtained in d^6-DMSO as solvent using the Varian T 60 nmr spectrometer. The electronic absorption spectra were recorded by the aid of the Unicam SP 8000 spectrophotometer applying the Nujol mull technique.

Results and Discussion

The intermolecular interaction between the donors and acceptors used, as gathered from the result if ir, ^{1}H-nmr and electronic absorption spectra, depends to a large extent on the nature of the acceptor rather than that of the donor. The spectral characteristics of the CT complexes are discussed as follows:

(A) *Charge transfer complexes involving electron transfer only:*

This class of compounds is formed when the donors react with non-acidic acceptors (I) and (II) or the weakly acidic acceptor (III).

The ir spectra:

The ir spectra of these complexes compared to that of the free components reveal that the various vibrations of the acceptor part are shifted to lower wavenumbers while those of the donor part acquire a counter shift. This shift is characteristic to charge transfer of the - type [11] which originates from the aniline ring for 1:1 complexes as gathered from the higher shift of the CH bands of the anilino part rather than those of the benzal part.

The NO_2 bands of the acceptor molecules display a shift to lower wavenumbers. The asymmetric and symmetric bands of (I) and (II) display in many cases a higher splitting in the spectra of the CT complexes indicating increased differentiation in the energy of the NO_2-group. For compounds formed with donor (E) containing the OH-group in p-position of the anilino ring, the highest shifts to lower values are observed as a result of the possible hydrogen bonding between the p-OH and the p-NO_2 groups.

The ^{1}H-nmr spectra:

The ^{1}H-nmr spectra of the CT complexes compared to those of the free components reveal a shift of the signals due to the protons of the acceptors towards higher fields, whereas those corresponding to protons of the donor are shifted down field. The magnitude of the shift varies according to the donor and acceptor used; also the shift is higher with the signals due to aniline ring protons which is in accordance with the results of the ir-spectra. The shifts of the acceptor signals are higher for the 1:1 complexes than for the 1:2 type which can be due to stronger interaction in the 1:1 complexes since the donation power is concentrated on one acceptor molecule in the former case and distributed between two in the latter. For the donor signals the shifts are contrary to those for the acceptors i.e. they are higher for 1:2 complexes.

The electronic absorption spectra:

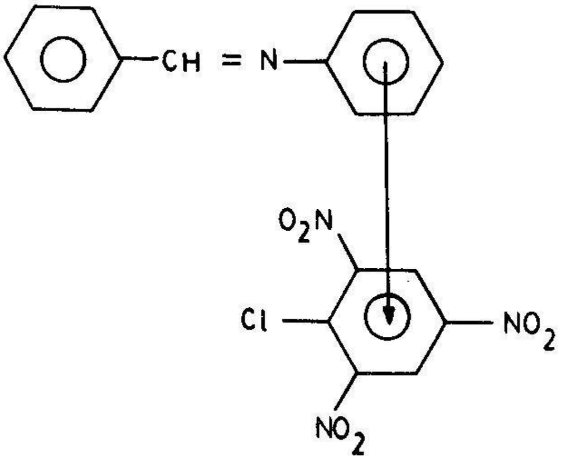
The electronic absorption spectra of the CT complexes under investigation as nujol mull display only one CT band within the 400-470 nm range corresponding to the $\pi - \pi^*$ intermolecular CT interaction. This point of view is supported by the calculation of the energy of the CT band for the complexes and comparing it with the experimental results. The E_{CT} for the CT complexes with trinitrobenzene are calculated using the relation.

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

whereas I_p ionization potentials of the donor, the values of which are determined from the electronic absorption spectra [6] (8.8 - 9.1 eV). E_A is electron affinity of the acceptor amounting to -0.7 eV [12] for trinitrotoluene, C: coulombic force between the electron transferred and the positive hole left behind amounting to -5.7 eV. The values of E_{CT} thus obtained amounts to 2.18 - 2.25 eV which coincides well with that determined from λ_{max}. The existence of a single CT band denotes that only $\pi-\pi^*$ interaction contributes to bonding in these CT complexes; $n-\pi^*$ interaction would be of low contribution to complex formation or even absent.

The interesting observation with the electronic absorption spectra is the blue shift of the Ct band in the spectra of 1:2 complexes relative to the CT bands in the spectra of the 1:1 complexes. This shift denotes a higher CT energy for the 1:2 complexes relative to the 1:1 type. This would result from blocking the resonance between the benzal and aniline rings occuring through C=N linkage, in the 1:2(D:A) complexes.

From the information gained from IR and NMR spectra the CT interaction can be formulated as follows:



(B) Charge transfer complexes with strong acidic acceptors:

This class of compounds is obtained when the donors are allowed to react with acidic acceptors (IV-VI). The ir, nmr and electronic absorption spectra of these complexes display drastic changes compared to those of their components.

The ir spectra:

The ir spectra of these complexes are characterised by a group of bands within the 2400-3000 cm^{-1} range which can be assigned to the stretching mode of the =N - H structure formed through the transfer of a proton from the phenolic groups of (IV) and (V) or the carboxyl group of (VI) [3]. This is supported by the disappearance of the OH bands corresponding to these groups and the shift of the C=N band to lower values in the 1:1 Ct complexes. The ir-spectra of 1:2 (D:A)

Table-1: Main bands in the IR-spectra of some CT complexes

Donor	Ratio D:A	Colour	m.p.	.N-H	OH	NO_2 Asymmetric	NO_2 Symmetric	CH	Acceptor		
		Complexes with picric acid									
		Bands of free acceptor			3110	1555,1540	1530	1350	784		
a	1:1	yellow	161	2900-2400	-	1555	1541	1343	781		
	1:2	pale brown	127	2900-2400	3085	1560	1540	1340	778		
b	1:2	Yellow	211	2900-2400	-	1547	1530	1335	780		
	1:2	Orange	164	2900-2400	3095	1560	1550	1335	782		
c	1:1	olive green	175	2900-2400	-	1560	1538	1339	779		
	1:2	green	170	2900-2400	3105	1550	1530	1342	780		
d	1:1	brown	162	2900-2400		1560	1540	1340	781		
	1:2	Pale brown	159	2900-2400	3096	1550	1534	1388	782		
e	1:1	brownish fellow	175	2900-2400		1550	1545	1342	1335	780	
	pale yellow		185	2900-2400	3095	1550		1534	1330	782	
		Complexes with 3,5-dinidtro salicylic acid									
		Bands of free acceptor			3460	3100	1540	1530	1349	925	825
A	1:1	orange brown	173	2900-2300	3160	1528		1345	913	812	
	1:2	pale green	106	2900-2300	3160	1530	1525	1340	910	812	
B	1:1	pale yellow	240	2900-2300	3130	1515		1320	915	812	
	1:2	yellow	182	2900-2400	3120	1532	1525	1340-1330		912	810
C	1:1	grey	210	2900-2300	3170	1533		1345	920	818	
	1:2	deep grey	176	1900-2500	3150	1530	1520	1340	915	912	
D	1:1	brown	129	2900-2300	3210	1530		1342	922	815	
	1:2	deep brown	123	2900-2500	3120	1530		1330	915	812	
E	1:1	pale brown	212	.2900-2400	3130	1533	1525	1345-1330		912	810
	1:2	brown	148	2950-2500	3250	1532	1525	1340-1328		915	810

Table-1 (Cont'd..)

Donor	Ratio D:A	Colour	m.p.	.N-H	OH	NO_2 Asymmetric	NO_2 Symmetric	CH	Acceptor	
		Complexes with 2,4-dinitrophenol								
		Band of free acceptor			3270	1540	1520	1350	928	825
A	1:1	pale buff	112		3250	1530	2515	1342	922	818
	1:2	green	98		3255	1532	1512	1342	918	825
B	1:2	orange	132		3252	1530	1510	1342	918	820
C	1:1	dark brown	93		3260	1530	1515	1345	928	820
	1:2	brown	96		32601532		1510	1330-1343	918	820
D	1:1	dark brown	119		3260	1535	1515	1343	923	820
	1:2	brown	121		3260	1530	1512	1330-1345	918	820
E	1:1	pale buff	115		3260	1535	1510	1343	925	818
	1:2	pale yellow	125		3250	1530	1512	1330-1345	915	814

Table-2: The ^1H-nmr spectra of some 1:2 (D:A) CT complexes.

Acceptor	Signal of acceptor part					Signal of anilino part						Signal of benzal part							NH
	H^3	H^4	H^5	H^6	OH	H^2	H^3	H^4	H^5	H^6	OH	H^2	H^3	H^4	H^5	H^6	OH	CH	
	Complexes with donor (B)																		
	Free Donor					7.1	6.8	7.1	6.8	7.1	-	7.7	7.3	-	7.3	7.7	10	6.6	-
IV	8.05(8.46)	-	8.05(8.46)	-	6.2(6.16)	7.18	7.0	7.18	7.0	7.18	-	7.9	7.63	-	7.67	7.9	10.13	8.88	6.15
V	-	8.9(8.78) -	-	8.9(8.7)	6.0(5.6)	7.10	7.0	7.10	7.0	7.10	-	7.9	7.60	-	7.6	7.9	10.44	7.0	6.20
	Complexes with donor (E)																		
	Free Donor					7.05	6.75	-	6.75	7.05	8.8	7.75	7.4	7.55	7.4	7.75	-	6.65	-
IV	7.8(8.46)	-	7.8(8.46)	-	7.0(6.16)	7.18	7.0	-	7.0	7.18	9.2	7.88	7.43	7.6	7.43	7.88	-	6.8	6.8
V	-	8.75(8.7)	-	8.75(8.7)		7.4	7.25	-	7.25	7.4	8.85	8.25	7.6	8.05	7.6	8.25	-	6.83	6.83

Free acceptor

complexes show that with strong or weak acidic acceptors the OH bands of the second acceptor molecule are still observed, as given in Table (1). Thus the second acceptor molecule would behave as an electron acceptor only, while the first one behave as an electron acceptor and proton donor.

The shift of the acceptor bands is identical with the case of CT complexes involving electron transfer only.

The ^{1}H-nmr spectra:

The ^{1}H-nmr spectra of the complexes reveal that the chemical shift of the acceptor signal is the same as in the 1st type, but the shift of the donor part is of higher magnitude due to the positively charged azomethine linkage $(-C^+H=N)$[13] which appears as broad signal at 5.6-9.8 ppm.

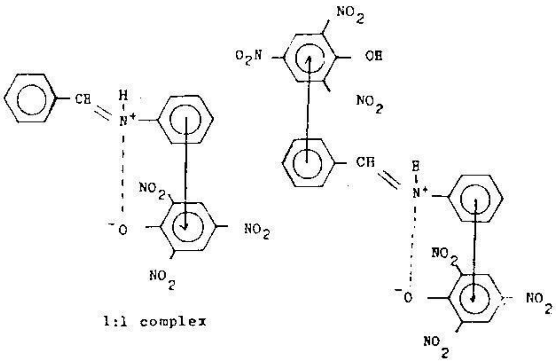
For the 1:2 CT complexes the OH signal of the second acceptor molecule is observed at 5.6-7.0 ppm, hence in this type of complexes one molecule of the acceptor contributes through proton and electron transfer whereas the second molecule displays the electron transfer only.

The magnitude of shift of the acceptor signals are larger for the 1:1 complexes than for 1:2 type which reveals stronger interaction in the 1:1 complexes since the interaction of the donor molecule is concentrated on one acceptor molecule in the 1:1 CT complexes while the charge transferred is distributed between two acceptor molecules in the 1:2 type. For the donor signals the shifts, are higher for 1:2 complexes than 1:1 CT complexes since the donor molecule is falling under the influence of two acceptor molecules.

The electronic absorption spectra:

The electronic spectra of these CT complexes display only one CT band located at 430-570 nm. The band is situated at higher energies compared to those of complexes with non acidic acceptors. This would result from the higher ionization potential of the protonated azomethine molecule and the lower electron affinity of the anion of the acceptor compared to the neutral molecule.

Based on the above results the bonding in the CT complexes with picric acid can be formulated as follows:



1:1 complex

1:2 complex

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