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CHARACTERISATION OF THE CHARGE TRANSFER INTERACTION BETWEEN N-DIMETHYLANILS WITH AROMATIC NITRO-COMPOUNDS. (I-IR, 1NHMR AND ELECTRONIC SPECTRA.)

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M.M. ABOU-SEKKINA; R.M. ISSA AND M. GABER

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By

M.M. ABOU-SEKKINA*; R.M. ISSA AND M. GABER

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt.

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ABSTRACT

The solid complexes of some benzylidene aniline containing the p—$N(CH_3)_2$ substituent are prepared and investigated by ir, electronic absorption and proton magnetic resonance spectroscopy. Molecular compounds with the non-acidic or weak acidic acceptors are formed through $\pi-\pi^*$, transition while those with strong acidic acceptors are formed through proton and electron transfer. The reaction with p-nitrophenol occurs through $\pi—\pi^*$ CT and intermolecular hydrogen bonding.

INTRODUCTION

The donor behaviour of benzylidene aniline derivatives (anils) towards aromatic nitro-compounds was first reported by Weinstein and McInich [1]. These authors investigated the interaction of anils with donor groups in the 4 or 4′ positions with p-nitrophenol. The complex formation was gathered from the change of the intensity of the ν_{OH} band of p-nitrophenol. This change was correlated to the σ-Hammett constant of the substituent and the K_f values were as well determined. Kovacic [2] suggested that complex formation between p-nitrophenol and anils would occur through intermolecular hydrogen bonding involving the azomethine nitrogen of anils and the proton of the phenolic OH-group. In previous studies, $\pi - \pi^*$bonding involving an electron transfer from the HOMO of the donor to the LUMO of the acceptor, was shown to be essential for the complex formation with aromatic

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* Author to whom all correspondence should be addressed.

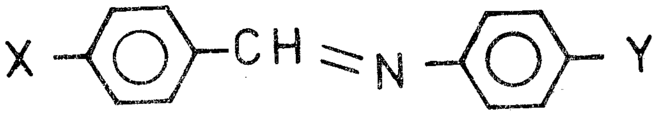
nitro-compounds [3–8]. This was proved to be the case for p-nitrophenol-anil complexes [9]. However, the compounds investigated before [9] contained only weak donor group namely—CH_3 or-OCH_3 in the 4 or 4′ positions.

In the present work, the solid complexes of some 4– and/or 4′ —$N(CH_3)_2$ substituted anils with a series of nitrobenzenes are reported and investigated by IR, ^{1}HNMR electronic absorption spectroscopy. These tools proved to be very helpful in investigating the type of interaction between donor and acceptor molecules. The choice of p—$N(CH_3)_2$ substituents is based on their strong donating properties hence would facilitate the π-donation character in virtue of their obvious lowering of the ionization potential [6].

EXPERIMENTAL

The compounds utilised in the present investigation were of pure laboratory chemicals from BDH (London), Schuchard (Munchen) and Prolabo.

Experimental details for the preparation of the CT complexes and the recording of the spectra were mentioned previously [3,4,8]. The donors used have the following structural formula:



where a(X=H, y=H), b(X=$N(CH_3)_2$, y = H), c(X=H, y=—$N(CH_3)_2$)
d(X=y=$N(CH_3)_2$)

The acceptors encountered in the present study are, picryl chloride (1), trinitirotoluene (2), 1–chloro–2,4–dinitrobenzenes (3) 1–fluoro–2,4–dinitrobenzene (4), 1,5–difluoro–2,4–dinitrobenzene (5), picric acid (6) 3,5–dinitrosalicyclic acid (7), 3–5,dinitrobenzoic acid (8), 2,4–dinitrophenol (9), 2,5–dinitrophenol (10), 2,6–dinitrophenol (11) and p-nitrophenol (12).

RESULTS AND DICCUSSION

Based on the type of interaction, liable to occur between the donor anils and acceptors under investigation, the CT complexes prepared can be classified into the following categories:

I. Complexes involving electron transfer only (compounds formed with acceptors 1–5):

The ir-spectra of the charge transfer (CT) complexes belonging to this group display only shifts in the position of the various bands. Most obvious shifts are observed with the γ_{CH} bands of both donors and acceptors. The γ_{CH} bands of the donors shift to higher wavenumbers while those of the acceptors exhibit a counter shift. The NO_2– bands of the acceptors show varied shifts to lower wavenumbers. Also the bands of acceptors (1) and (2) show more obvious splitting in the spectra of the CT complexes indicating a higher difference in the energy states of the three NO_2–groups in the CT complexes.

The shift of the ir bands of the donor and acceptor components of the CT complexes is in accordance with the increased π–electron density on the acceptor and its decrease on the donor one. This results from the intermolecular $\pi - \pi^*$ CT interaction between the donor and acceptor involving the electron transfer process ($HOMO_D \rightarrow LUMO_A$) [3,8,10]. The shift of the γ_{CH} bands of the donor molecules are higher for the bands of the aniline ring for donors (a), (b) and (d) while for donor (c), the shift is more apparent with bands of the benzol ring. It seems thus that the existence of the strong donor —$N(CH_3)_2$ group on the benzal ring would lower its ionization potential [11] to such an extent that it will be profitable the donor centre.

The C=N band of the donors within the range 1605–1627 cm^{-1} are apparently shifted to lower wavenumbers. The bands would actually exhibit a shift to higher values due to decreased electron density on the donor group. However, the existence of the positive hole left in the donor ring after the electron transfer to the acceptor increases the resonance between two rings of the anil molecule. This causes and apparent lowering of the C=N bond order which is reflected in the shift to lower wavenumbers (see Table I).

The ^{1}HNMR spectra of the CT complexes related to this category show that the signals due to the donor molecules are shifted towards lower fields due to the decreased shielding effect on their protons as a result of the electron donation to the acceptors. The signals of the acceptor molecules are shifted to higher fields denoting increased shielding of the protons which originates from the higher electron density on the acceptor ring after the electron transfer. For donors (b) and (c), the shift of the N—$(CH_3)_2$ signals within the 2 .97 – 3 .10 ppm range

Table (1): Main bands in the ir-spectra of CT complexes involving electron transfer.

Donor	Colour	m.p. °C	$\overset{+}{=N—H}$			νOH	NO_2 — asym.			NO_2—sym.		γ_{CH}acceptor	
Complexes with picryl chrloride													
Bands of free accepteor					—		1540	1520	—	1350	—	928	825
a	orange	178			—		1543	1535	1518	—	1332	910	820
b	dark brown	170			—		1550	1335	1513	1342	—	921	—
c	deep green	179			—		1550	1530	1515	1352	1330	922	808
d	brown	164			—		1555	1535	1515	1355	1330	923	810
Complexes with trinitrotoluene													
Bands of free acceptor							1550	1520	—	1360	—	—	800
a	reddish brown	72			—		1554	1540	1515	1353	—	—	792
b	brown	59			—		1555	1540	1515	1345	—	—	790
c	dark brown	72			—		1557	1535	1515	1360	1345	910	792
d	dark brown	183			—		1555	1535	1515	1362	1345	908	497
Complexes with p-nitrophenol													
Bands of free acceptor					—	3320	1520			1350		855	760
a	green	59				3170	1515			1338		848	755
b	dark brown	47	2750	2590	2400	—	1518			1335		840	755
c	brown yellow	77	2000	2620	2480	—	1517			1346		848	752
d	dark brown	204	2860	2700	2470	—	1520			1335		858	753

* shoulder (d) decomposed

shows obvious shifts while for donor (d) the signals appear either broadened or splitted.

The electronic absorption spectra of the CT complexes exhibit the CT band within the 400–500 nm region i.e. on the longer wavelength side of the $\varnothing \rightarrow NO_2$ bands of the acceptors. This band is assigned to the $\pi - \pi^*$ CT interaction. This is supported by calculating the energy for this CT interaction using the relations given by Briegleb [12,13].

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

where I_P is taken as that for anilin (7 .7 eV); E_A is the electron affinity taken for TNT (—0 .6 eV) [8] and C is the coulombic factor between the electron transferred and the positive hole left behind (5 .2 – 5 .6 eV).

The value of E_{CT} obtained amounts to 2 .7 – 3 .1 eV for CT complexes of TNT which corresponds to λ_{max} 400–460 nm which is in good agreement with the experimental results.

The spectra of some compounds exhibit also a shallow or broad band within the 520–550 nm range which can be assigned to n– π^* interaction involving the nitrogen lone pair of the —$N(CH_3)_2$ groups and a Vacant π –level on a nitrogroups [3,4,9,10] faceing it.

II. Complexes involving proton and electron transfer

This class of compounds is obtained when the donors are allowed to react with acidic acceptors except p-nitrophenol.

1 . The main spectral changes in the ir spectra are:

a) The γ_{CH} bands of the donors are shifted to higher wavenumbers while those of the acceptors shift to lower values.

b) The bands due to the various vibrations of the phenolic OH–groups of acceptors [6,7,9,01 and 11] as well as those for the OH of the COOH of acceptor [8] are no more observed in the spectra of the CT complexes. This behaviour can be explained by the transfer of a proton from the OH–groups to a basic centre on the donor molecule. This assumption is supported by the appearance of a new group of new intense broad bands as observed within the 2900–2400 cm^{-1} region. These bands can be assigned to the stretching mode of a proton attached to a positively charged quaternary nitrogen [14]. In case of donor (a), the basic centre liable to accept the proton is the azomethine nitrogen, for other donors, the centre capable of accepting the proton would either be the azomethine nitrogen or that of the $—N(CH_3)_2$ group. However, it is not possible to judge this point from the ir-spectra with certainity. However, since the $—N(CH_3)_2$ group is more basic, then this centre would be the proton acceptor.

c) The asym NO_2 — bands show varied behaviour from one compound to the other. The bands corresponding to the NO_2 — group contributing to hydrogen bonding with the —OH or —COOH groups exhibit different shifts to higher or lower values or even appear unaffected. The shift of these bands would be the resultant of a shift to higher values due to the destruction of the hydrogen bond and a shift to lower values resulting from the increased π –electron density on the ring of acceptor. The other bands are essentially shifted to lower values. The spectra of many complexes show the sym. NO_2— bands splitted into two bands indicating an increased differentiation of the energy states of the nitrogroups in the CT complexes (see Tables I and II).

2- The ^{1}HNMR spectra of the complexes related to this class vary much from those of the free components. The signals due to protons of the acceptor ring shift towards higher fields while those of the donor are shifted down fields.

These shifts are characteristics of CT interaction of the $\pi - \pi^*$ type, leading to higher shielding of the acceptor protons and increased deshielding of the donor protons.

The spectra of the CT complexes of (a) with picric acid exhibit a new broad signal at 6 .83 ppm with an integration equivalent to one proton which can be assigned to the proton of the $(—CH{=}N^+—H)$ centre. The spectra of the other donors with picric acid display all sharp signals denoting that no protons are bonded to the azomethine nitrogen. The spectra however display a splitting of the $N—(CH_3)_2$ signal as a result of the presence of the protons on the dimethyl amino-nitrogen. The proton bonded to the positive nitrogen leads to the signal within the 3 .0 – 3 .6 ppm range for the compounds investigated. Based on this, the proton transferred from the acceptor to the donor molecule in case of donor (b), (c) and (d) would be bonded to the $—N(CH_3)_2$ group.

3 . The electronic absorption spectra of the CT complexes related to this class exhibit one CT band for compounds derived from donor (a), denoting that only $\pi - \pi^*$ electronic interaction is possible with this donor. For other compounds, many spectra display the shallow broad

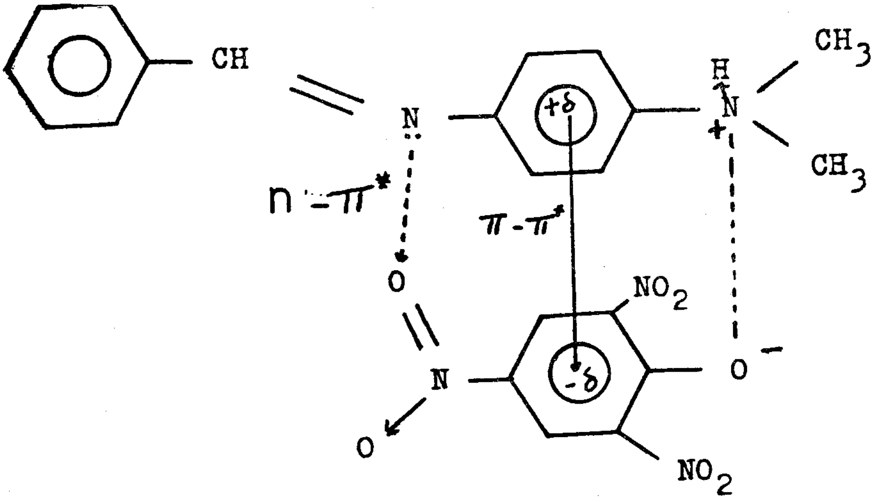
Table (II): Main bands in the ir-spectra of the CT complexes involving proton transfer.

Donor	Colour	m.p. °C	$=\overset{+}{N}-H$			νOH	NO_2 — asym.			NO_2—sym.		γ_{CH}acceptor	
Complexes with picric acid													
Bands of free acceptor						3110	1555	1540	1530	1350		784	
a	greenish yellow	171	2900	2400	—	—	1550	1540	—	1338		775	
b	orange	242 (d)	2850	2630	2500	—	1565	1555	1540	1337		776	
c	dark brown	173	2850	2720	2600	—	1560	1540		1335		780	
d	dark brown	231	2780	2670	2550	—	1555	1535		1360	1335	780	
Complexes with 3,5-dinitro salicylic acid													
Bands of free acceptor						3560 3470 3120				1349		925	825
a	golden yellow	184	2800	2400	—	3460	1540	1532		1348		918	813*
b	orange	254 (d)	2750	2530	—	3480	1550	1538		1325		920	813*
c	brown	217	2750	2560	—	3450	1560	1530		1360	1325		812
d	dark brown	240	2750	2570	2450	3450	1550	1535		1360	1345	920	
Complexes with 3,5-dinitrobenzoic acid													
Bands of free acceptor						3090	1555	1540		1350		923	808
a	dark green	90	2900	2500		—	1552	1535		1345		915	790
b	dark orange	152	2870	2750	2530	—	1553	1535		1345	1330	920	795
c	dark brown	190	2890	2750	2550	—	1552	1538		1345	1335	920	790
d	dark brown	227	2870	2720	2500	—	1552	1535		1345	1335	915	800
Complexes with 2,4-dinitrophenol													
Bands of free acceptor						3280	1540	1520		1350		928	825
a	yellowish green	101				3260	1545	1518		1338		218	820
b	orange	155	2820	2700	2480		1552	1538		1360	1342	920	820
b	brown	79	2800	2630	2550		1555	1528		1360	1335	918	815
d	dark brown	186	2900	2680	2570		1550	1535		1360	1338	920	

* shoulder, (d) decomposed.

band on the lower energy side of the main CT band indicating that n–π^* would also contribute to bonding. The main CT band lies within the 450–570 nm range which denotes a higher E_{CT} for complexes involving proton transfer. The higher 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 lower its ionisation potential, hence the rise of E_{CT}.

Based on the above results the CT interaction can be represented as follows:



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