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SUMMARY

Charge transfer complexes of 2,4-dinitrophenol with aniline derivatives are prepared from ethanol or benzene solutions then investigated by ir, ^{1}H nmr and electronic absorption spectroscopy. The type of charge transfer complexes, whether being of the salt or molecular compounds type, was found to depend on the basicity of the amine and solvent used. The spectral changes due to the formation of each type of complexes are given; the results obtained are compared with those of picric acid with aniline derivatives.

INTRODUCTION

The formation of charge transfer (C.T.) complexes of trinitrobenzene derivatives with aromatic compounds was of interest to several workers [1–7]. The interaction between the donor aromatic molecule and the acceptor trinitrobenzene derivative was investigated mainly by infrared spectroscopy while few studies utilised X-ray [6] and e.s.r. [7] methods. The intermolecular charge transfer (C.T.) was assumed to occur under the influence of the high acceptor character of the nitro-compounds due to the existence of the three electron withdrawing nitro-groups around the benzene ring.

In a previous investigation, we reported on charge transfer compounds formed with 3,5-dinitrobenzoic acid [8]. This work revealed that the existence of three nitro groups on the benzene ring is not essential for the occurance of the intermolecular C.T. interaction. Since C.T. compounds with aceptors containing an acidic groups [3–5,8] drew the attention, so for the type of compounds formed (salt or molecular complex) is considered, it seems of interest to investigate the possible formation of C.T. compounds with 2,4-dinitrophenol which is comparable in structure to picric acid where the NO_2—group in position 6 is eliminated.

EXPERIMENTAL

All chemicals used were laboratory pure grade B.D.H. products, few compounds were obtained from Koch-light. The charge transfer compounds involved in the present work were prepared by mixing a hot solution of 2,4-dinitrophenol (0,01 mole) in the least amount of ethanol or benzene with another containing the aromatic amine (0 .01 mole) in the least amount of the solvent. Due to the low solubility of aminobenzoic acids in benzene, they were dissolved in the least amount of acetone then mixed with the acceptor solution in benzene, thereafter acetone was evaporated leaving a clear solution of the molecular complex.

The reaction mixture was boiled for 10 minutes then allowed to cool. The solids separated were filtered off then recrystallised from pure ethanol or benzene and their melting points then determined. The compounds obtained have various colours depending on the nature of the substituent present and the solvent used which recalls the case of the trinitrobenzene derivatives [9]. The determination of nitrogen for all compounds and analysis of some chosen complexes for their C and H content revealed the complexes formed are of the 1:1 type (donor: acceptor).

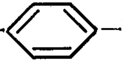
The infrared spectra of charge transfer compounds and their constituents were recorded on a Unicam SP 1000 infrared spectrophotometer as KBr dics. Some spectra were repeated on a Beckman IR4 infrared spectrophotometer.

The ^1H nmr spectra of some compounds were obtained on a varian 60 nmr spectrometer using deuterated chloroform as solvent. The UV spectra of some solid complexes were recorded on the Unicam SP 8000 spectrophotometer using the nujol mull technique.

RESULTS AND DISCUSSION

The results obtained for the compounds under study are collected in Table I, while, representative spectra are given in Fig.1. From these

Table I

Some important bands in the ir-spectra of aniline derivatives (x——NHe) with 2,4-dinitrophenol.

x	Comp-ound	Col-our	Sol-vent	Yield %	No	νOH	NO_2 asym.	NO_2 sym.	γCH Acceptor	νNH donor	m.p.°	pK_a
Values of 2,4–dinitrophenol					-	3270	1550,1540	1350,1335	928,825		113	4.00
p—OCH_3	P.T.	B.Y.	EB	90	1	—	1518	1335	922,—	2900–2500	110	5.34
m—OCH_3	P.T.	G.Y.	EB	85	2	—	1518	1335	920,820	2920–2500	89	4.23
o—OCH_3	P.T.	Y.	EB	85	3	—	1535	1337	922,802	2850–2500	86	4.51
p—CH_3	”	Or.Y.	”	70	4	—	1520	1338	925,805	2950–2600	102	5.08
m—CH_3	”	Y.	”	85	5	–	1520	1335	922,820	2900–2600	87	4.73
o—CH_3	”	Y.	B	80	6	—	1540	1340	925,819		92	4.45
p—OH	”	Y.	E	85	7	—	1540	1338	918,—	2980–2500	99	5.50
m—OH	”	O.G.	E	70	8	—	1539	1338	915,—	2400–2500	102	4.17
”	M.C.	M.C.	B	55	9	3250	1540,1530	1358,1345	918,820	3380–3290	88	
o—OH	”	Bn.	EB	45	10	3250	1545,1538	1347,1335	922,—	3360–3290	104	4.72
p—Br	”	Bn.R.	B	40	11	3260	1545,1535	1348,1333	923,819	3390	64	3.86
o—COOH	”	Or.	EB	75	12	3180	1540	1332	925,815	3380	72	2.11
m—COOH	P.T.	Y.	E	85	13	—	1538	1336	925,820	2950–2500	125	2.04
”	M.C.	P.Bn.	B	75	14	3210	1545,1535	1355,1335	925,830	3430–3280	100	
p—COOH	P.T.	Y.	E	80	15	—	1540	1333	925,820	2450–2500	122	2.50
”	M.C.	Or.Y.	B	85	16	3260	1560,1540	1350,1330	922,820	3480–3370	113	
p—$COCH_3$	”	Y.	B	45	17	3230	1550,1540	1350,1332	923,822	3400–3330	96	—
p—NO_2	”	Cr.	EB	90	17	3240	1540,1518	1345,1330	920,822	3390–3360	96	2.03
m-No_3	”	Bn.Y.	EB	80	19	3265	1540,1530	1345,1330	925,818	3390–3350	82	2.45
o—NO_2	”	Or.Y.	EB	75	20	3240	1540,1525	1350,1318	921,815	3380(b)	64	0.06

P.T. = proton transfer compound M.C. = molecular complex

Colours: B.Y. = Bright yellow, G.Y. Greenish yellow, Or.Y. = Orange yellow, O.G. = Olive green, Bn. = Brown
P.Bn. = Pale brown Or. = Orange, BnR. = Brownish red (b) Broad

Solvents: E = Ethanol B = Benzene ——— Masked by neighbouring bands.

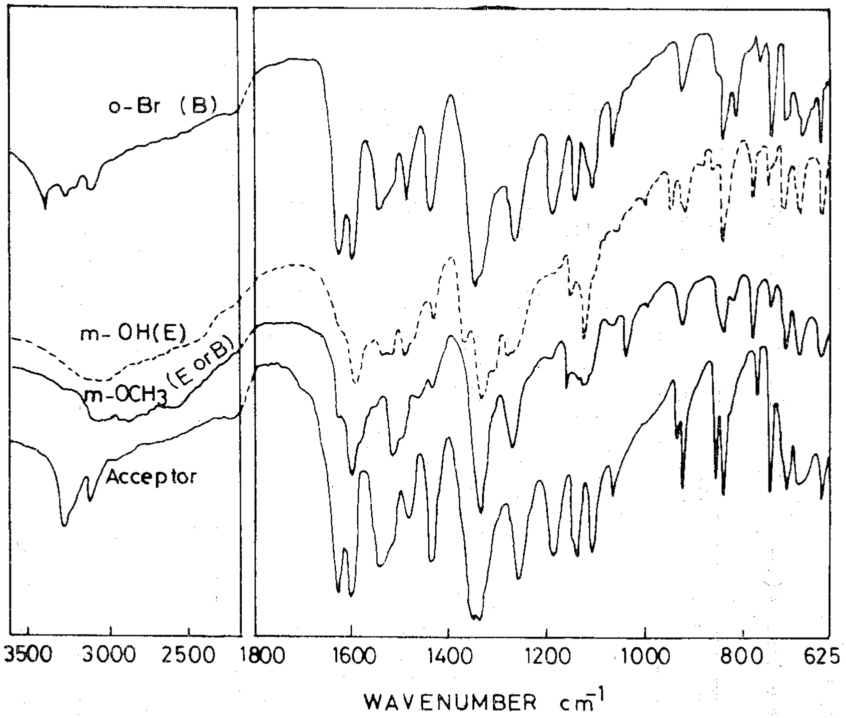


FIG 1

results, the aniline derivatives investigated can be classified into four categories:

a) Aniline derivatives which failed to react with the 2,4-dinitrophenol including aniline and its o—Cl, m—Cl, p—Cl or p—Br aniline derivatives. The p—Br aniline failed to react in ethanol.

b) Aniline derivatives which yield C.T. complexes of the salt type from either ethanol or benzene, namely, o—, m—, or p-anisidine and o—, m—, or p-toluidine.

c) Aniline derivatives giving C.T. complexes of the molecular complex type from ethanol and or benzene including o—, m—, or p—NO_2, p—Br, o—OH and o—COOH substituents.

d) Aniline derivatives displaying colour or molecular isomerism, these yield C.T. complexes of the salt type from ethanol and molecular complexes from benzene. These are the m—OH, m—COOH, and p—COOH substituents.

In what follows the main spectral behaviour of the two types of compounds are considered.

I- *The ir spectra:*

A- *Compounds of the salt type:*

The formation of these compounds takes place through a proton transfer (P.T.) from the phenolic group to the amino group of the aromatic amines in addition to the intermolecular charge transfer between the aromatic rigns.

These compounds have higher melting points compared to molecular complexes formed with the same aniline derivative and are characterised by intense yellow colours. The infrared spectra of these C.T. complexes display the following changes in comparison to those of their constituents:

1– The υNH_2 bands of the aniline derivative within the 3450–3300 cm^{-1} and the υOH band of the 2,4-dinitrophenol in the spectum of the C.T. complex being replaced by a group of broad bands within the 3100–2800 cm^{-1} due to the strecthing vibration of the ($—NH^+$) [2–4]. Also the δNH_2 band of the aniline derivatives near 1620 cm^{-1} and the δOH band of the phenolic group 1195 cm^{-1} are no more observed in the spectra of the C.T. compounds.

2– The NO_2 - bands at 1550 cm^{-1} and 1540 cm^{-1} (asym) or 1350 and 1335 cm^{-1} (sym.) which appear doubled in the spectrum of the free acceptor appear as a single broad band in the spectra of the C.T. commounds due to the distruction of the intramolecular hydrogen bonding between the OH and the o—NO_2 groups. Also the NO_2 bands are generally shifted to lower frequencies as a results of the increased electron density on the aromatic ring of the 2,4–dinitrophenate ion.

3– The γCH bands of the acceptor part of the C.T. compound at 928 and 825 cm^{-1} are shifted to lower wavenumbers, the lower frequency band becomes merged with the neighbouring band at 820 cm^{-1} in the spectrum of 2,4-dinitrophenol. Contrary to this behaviour, the γCH bands of the aniline derivatives are shifted to higher wavenumbers.

This behaviour denotes increased electron density on the 2,4-dinitrophenate part and its lowering on the aniline ring.

Accordingly, in compounds of the salt type the bonding between the two molecules of the C.T. complex would occur through the π—π^* charge transfer in addition to the electrostatic forces between the positive charges of the anilinium ion and phenate ion of the dinitro component.

B- *Compounds of the molecular complex type:*

Compounds of this type have low m.p.'s and are characterized by orange, red or brown colours. The spectra of these compounds are more or less superposition of the spectra of the simple components but showing obvious shifts in the band position.

The νNH_2 of the donor and νOH of the acceptor are observed though being slightly shifted to lower wavenumbers. The shift can be explained in the light of C.T. from the aniline ring to the dinitrophenol component.

The increased negative charge density on the 2,4-dinitrophenol component facilitates the charge migration to the NO_2 - groups hence favours their shift to lower wavenumbers; also the splitting of the NO_2 — bands is still observed in spectra of the molecular complex. The γCH bands of the dinitrophenol are shifted to lower wavenumbers as a result of the increased electron density on the ring of the acceptor component.

II- *The ^{1}Hnmr spectra:*

To throw more light on the donor-acceptor interaction in the C.T. complexes under investigation, the nmr spectra of some compounds from both classes are investigated.

The nmr spectrum of 2,4-dinitrophenol displays a multiplet signal in the 9 .2 and 7 .3 ppm region for the three aromatic protons. The OH— signal appears as a broad singlet at 10 .8 ppm which remains unchanged on deuteration, a case which is refered to the strong intramolecular hydrogen bonding between the OH— and o—NO_2—group. The OCH_3 and CH_3 signals appear near 3 .8 and 2 .4 ppm respectively; the four aromatic protons of anisidenes and toluidines yield the signals at 7 .1–6 .7 ppm.

In the nmr spectra of all complexes of the salt type the signals due to the OH— and NH—protons disappear and some new signals are observed in the 6 .8–6 .0 and or the 2 .4–2 .2 ppm regions. These signals correspond to the protons of the NH_3^+ group formed through a proton transfer from the OH— group of 2,4-dinitrophenol to the NH_2—group of the aniline derivative. The signals of the aromatic protons of the aniline derivative display a shift to higher field strengths while those of the 2,4-dinitrophenol component exhibit a counter shift. These changes are in accordance with increased charge density on the acceptor and its decrease on the donor ring.

The nmr spectra of C.T. complexes of the molecular type can be considered as a superposition of the various signals of the components with small shifts in their positions. Generally, the signals of the aromatic ring protons of the donor molecule shift to higher fields while those of the acceptor display on opposite shift in virtue of the π—π^* C.T. interaction from the aniline derivative as donor to 2,4-dinitrophenol as acceptor. The signals of the OH— and NH_2—groups shift to lower fields on complex formation; this can be explained by the increased intramolecular hydrogen bonding in the 2,4-dinitrophenol component and the formation of an intermolecular hydrogen bond between the NH_2—group of the donor and p—NO_2 group of the acceptor.

The results of the nmr spectra are in confirmity with those of the ir-spectra.

III- *The electronic absorption spectra:*

The intermolecular charge transfer interaction in the C.T. complexes is visualised from the appearance of a new band in the electronic absorption spectra of the solid complexes within the 380–420 nm for compounds involving proton transfer interaction and 390–460 nm for molecular complexes. Thus the band lies at shorter wavelengths in the former case indicating a higher C.T. energy in P.T. compounds. This results from the formation of the negative charge of the phenate ion on the acceptor which lowers the electron affinity of the acceptor ring, and the NH_3^+— on the donor leading to a higher ionisation potential.

The spectra of some molecular complexes [9,10,11] exhibit a low extinction broad band within the 480–550 nm range which corresponds probably to the π—π^* interaction.

The results of the uv spectra are in good agreement with the conclusions gained from the shifts in the ir- spectra.

On considering the behaviour of the different anilines under investigation in relation to their basic character, it becomes apparent that amines of high basicity ($pK_a \geq 4.5$) form C.T. complexes of the salt type whereas, aniline derivatives with low basicity ($pK_a \leq 2.0$) can only form molecular complexes, aniline derivatives of intermediate basicity are capable of forming both the salty type and molecular complexes i.e. display colour and structural isomerism when ethanol or benzene are used as solvents. The varied behaviour in the two media is due to the high polarity of ethanol favouring the ionisation of 2,4-dinitrophenol hence leading to proton transfer complexes which is not the case for benzene.

On comparing the results obtained in the present work with those of the previous investigation on C.T. compounds of picric acid with aniline derivatives [4], it becomes obvious that the formation of molecular compounds starts with p—NO_2—aniline in case of picric acid ($pK_a = 0.38$) [10] while it starts with m—OH aniline when 2,4-dinitrophenol ($pK_a = 4.0$), is used as the acceptor molecule. Thus the formation of complexes of the salt type shifts to amines of higher basicity as the acid character of the acceptor molecule decreases.

According to the present findings, it can be concluded that the formation of C.T. complexes of the salt type or molecular compound type will depend on the basicity of the amine used as donor molecule, the acidity of the phenolic compounds acting as acceptor as well as the polarity of the solvent in which the C.T. complex is prepared.

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