

INFRARED SPECTROSCOPIC CHARACTERISATION OF DONOR-ACCEPTOR COMPLEXES OF DINITROBENZENES WITH *N*-SUBSTITUTED ANILINES

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The donor-acceptor complexes of eight *N*-substituted anilines with five dinitrobenzenes are prepared and their IR spectra are recorded in the solid state as KBr discs. Based on the spectral shifts due to complex formation, four types of charge transfer interactions are pointed out. The spectral characterisation of each class is given.

INTRODUCTION

Donor-acceptor complexes (D-A) of *N*-substituted anilines with aromatic nitro-compounds were the subject of some interesting studies [1-3]. These investigations utilised mainly UV-absorption spectrophotometry and NMR spectroscopy with a view of determining some of their physical constants (K , $-\Delta H$ and $-\Delta S$).

It seems that no previous studies have been carried out on solid charge transfer (C.T.) complexes of *N*-substituted aniline. In the present investigation, the solid D-A complexes of some *N*-substituted anilines with dinitrobenzenes are prepared and investigated by IR spectroscopy.

EXPERIMENTAL

All chemicals used were laboratory grade pure chemicals from BDH. The donors are, *N*-methylaniline (a), *N*-ethylaniline (b), *N*-dimethylaniline (c), diphenylamine (d), *N*-methylantranilic acid (e), *N*-acetylaniline (f), *p*-*N*-dimethylaminobenzaldehyde (g), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (h). The acceptors are 2,5-dinitrophenol (1), 2,6-dinitrophenol (2), 1-fluoro, 2,4-dinitrobenzene (3), 1-chloro, 2,4-dinitrobenzene (4) and 1,5-difluoro-2,4-dinitrobenzene (5).

The preparation of the solid complexes and KBr discs for recording the IR spectra are the same as given before [4]. The IR spectra were recorded on Unicam SP 1000 IR spectrophotometer; some spectra were checked on the Unicam SP 2000 and Beckman IR4 spectrophotometers.

RESULTS AND DISCUSSION

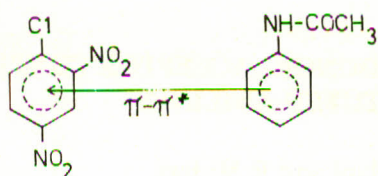
The IR spectra of the D-A complexes under investigation (main bands depicted in Tables 1&2) reveal a more or less common behaviour for donors *a-g* with most accep-

tors while donor *h* displays a different behaviour with the acid acceptors 1 and 2. The changes in the IR spectra of the D-A complexes in comparison to those of their constituents reveal four different types of intermolecular interactions between the donor and acceptor molecules in the complex. The main IR spectroscopic characterisation of these four types are summarised as follows:

Complexes Involving $\pi-\pi^$ Interaction Only.* This class of compounds comprises aniline derivatives of very low basicity, where the *N*-lone pair on the nitrogen atom is not available to intermolecular interactions. This is the case where the *n*-electrons are contributing to intramolecular hydrogen bonding (donor *e*) or in the presence of an acceptor group attached to the *N*-atom (donors *d* and *f*).

The spectra of the C.T. complexes compared to those of their constituents indicate a shift of the γ_{CH} bands of the acceptors to lower wave-numbers whereas those of the donors shift in the opposite direction. Such shifts indicate an increased electron density on the ring of the acceptor molecule and its decrease on that of the donor on complex formation, which results from an intermolecular $\pi-\pi^*$ charge transfer interaction [4,5]. The increased charge density on the ring of the acceptor favours the polarisation of the NO_2 -groups and hence the NO_2 -bands are shifted to lower wave numbers. The same holds for the ν_{OH} bands of acceptors 1 and 2. On the contrary, ν_{NH} and C=O bands of the donors included in this class of compounds display a shift to higher values; this substantiates the decrease of electron density on the donor ring.

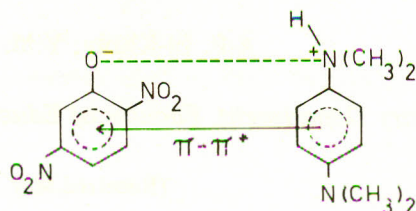
The intermolecular interactions in these complexes take place through $\pi-\pi^*$ bonding only which involves the transfer of an electron from the highest filled π -level on the donating molecule to the lowest vacant level on the acceptor one. The complex can be formulated as follows:



The bonding in complexes of this class involves $\pi-\pi^*$ charge transfer and electrostatic forces between the formed ions [4,7].

Complexes Involving $\pi-\pi^*$ and Proton Transfer. This class comprises the complexes of *h* with 1 and 2. The OH-bands of the acceptors are no more observed in the spectra of the C.T. complexes, while a new group of bands appears within $2800-2400\text{ cm}^{-1}$. These bands correspond to the stretching modes of structure $=\text{N}^+-\text{H}$ [6]. Thus the D-A complex is formed through the proton transfer from the OH-group of the acceptors 1 or 2 to the basic nitrogen atom of donor *h*.

The γ_{CH} bands of the acceptors and donor display shifts identical to those for complexes formed through $\pi-\pi^*$ interaction indicating the existence of such a type of bonding in proton transfer complexes. The occurrence of the $\pi-\pi^*$ interaction is further supported by the shift of the NO_2 -bands of the acceptors to lower wavenumbers.



Complexes Involving $\pi-\pi^*$ and $n-\pi^*$ Interactions. This class of compounds comprises aniline derivatives with apparent basicity. The spectra of the C.T. complexes exhibit the shifts of the ν_{NH} and γ_{CH} bands similar to those of class 1 though the magnitude of the shifts is different. Of interest is the shifts observed with the NO_2 -bands in the spectra of the C.T. compounds. Both asym. and sym. NO_2 -bands of the acceptors usually appear as doubled peaks for each series or display two obvious bands. This denotes a difference in the energy states of the NO_2 -groups of each acceptor molecule. In the spectra of the C.T. complexes,

Table 1. Main bands in the IR spectra of molecular complexes of N-substituted anilines with dinitrophenols.

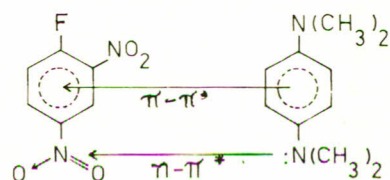
Donor	Colour	M.p. (°C)	ν_{OH}	NO_2 asym.	NO_2 sym.	γ_{CH} acceptor	Class of complex
1. Complexes with 2,5-Dinitrophenol							
	Bands of acceptor		3280	1552,1535	1355	850,837,818	
a	Blue	92	3270	1558,1530	1358,1345	848,833,816	(3)
b	Blue	68-81	3270	1558,1530	1360,1345	848,835,816	(3)
c	Green	98	3260	1555,1525	1358,1335	845,833,813	(3)
d	Green	74	3270	1550,1530	1350	847,834,815	(1)
e	Yellow	81-97	3270	1550,1530	1355	848,835,815	(1)
f	Magenta red	75	3270	1550,1533	1350	848,835,816	(1)
g	Orange	70	3260	1555,1532	1357,1340	842,830,815	(3)
h	Blue	72	-	1548,1540	1350	842,830,815	(2)
2. Complexes with 2,6-Dinitrophenol							
	Bands of acceptor			1543,1537	1354	828,765	
a	Golden yellow	55	*	1556,1531	1358,1346	821,760 sh	(3)
b	Brown	52	*	1555sh,1530	1365,1343	824,762	(3)
c	Olive green	58	*	1548,1525	1365,1340	822,760	(3)
d	Dark red	Oil	*	1545,1530	1340,1325	822,744	(1)
e	Yellow	57	*	1540,1532	1340	825,762	(1)
f	Orange red	48	*	1535	1350,1320	825,761	(1)
g	Red	47	*	1548,1532	1360,1333	823,760	(3)
h	Red	55	*	1545,1538	1345	818,757	(2)

* not apparent.

Table 2. Main bands in the IR spectra of molecular complexes with halogenated dinitrobenzenes.

Donor	Colour	M.p. (°C)	NO ₂ asym.	NO ₂ sym.	γ_{CH} acceptor	Class of complex
3. <i>Complexes with 1-Fluoro-2,4-dinitrobenzene</i>						
	Bands of acceptor		1550,1545	1357,1348	850,840,745	
a	Orange	159	1542,1535	1360,1328	829,777	(4)
b	Orange	71	1555,1530	1350,1325	833,770	(3)
e	Pale yellow	89	1542,1533	1348,1322	835, —	(1)
f	Orange yellow	49	1548,1540	1348,1335	838,775	(1)
g	Dark red	Oil	1555,1540	1355,1348	825, —	(3)
h	Brown red	96	1552,1540	1355,1350	820,765	(3)
4. <i>Complexes with 1-Chloro-2,4-dinitrobenzene</i>						
	Bands of acceptor		1550,1533	1353,1335	852,836,758	
a	Orange	50–80	1552,1530	1357,1325	850,832,750	(4)
b	Orange	48	1553,1527	1354,1326	850,833,753	(3)
c	Brown	45	1555,1530	1355,1332	850,833,750	(3)
d	Buff	45	1552,1530	1351,1336	852,834,753	(4)
e	White	79	1547,1530	1345,1325	848,833, —	(1)
f	Orange yellow	47	1545,1530	1348,1335	848,833,754	(1)
g	Orange	60	1553,1530	1356,1333	845,830, —	(3)
h	Blue	51–68	1555,1530	1355,1331	849,831,755	(3)
5. <i>Complexes with 1,5-Difluoro-2,4-dinitrobenzene</i>						
	Bands of acceptor		1548,1533	1350	840,775	
b	Orange	110–122	1555,1525	1355,1335	822,770	(3)
c	Brown	35	1555,1525	1335	825,760	(3)
d	Blue	Oil	1552,1530	1342	832, —	(4)
e	Yellow	79–107	1550,1530	1330	833, —	(1)
f	Yellow	181	1530	1337	831,768	(1)
g	Red	Oil	1555,1530	1348,1338	820,765sh	(3)
h	Golden yellow	76	1555,1530	1355,1340,	825,770sh	(3)

the lower wavenumber band of each series (asym. or sym.) shifts, in a magnitude that depends on the nature of both donor and acceptor molecules in the complex, to lower values whereas the other band is shifted to higher ones. The shift of the first band is in accordance with the increased electron density on the acceptor molecule. The shift of the other band to higher wavenumbers can be explained by the occurrence of an $n-\pi^*$ interaction. This involves the location of an n -electron from the amino-group of the donor molecule in a vacant π -level on the NO₂-group of the acceptor [4,6]. The interaction in these C.T. complexes can be represented as follows:



Complexes Involving $\pi-\pi^*$ and Weak $n-\pi^*$ Interactions.

This class comprises complexes formed with anilines of moderate basicity. The shifts of the γ_{CH} and ν_{NH} and the low energy NO₂-bands are more or less comparable to classes 1–3. The behaviour of the higher wavenumber NO₂-band is somewhat different; this band shifts to a small

extent to lower or higher values and even may retain its position in the spectra of the C.T. complexes belonging to this class. Nevertheless, at least one of the asym. or sym.

bands displays a shift to higher values. The shifts observed for the high energy NO_2 -band is the resultant of its lowering as a result of the $\pi-\pi^*$ interaction and the increase due to

the $n-\pi^*$ bonding. The direction of the shift will thus depend on which type of these interactions overcomes the

effect of the other. The $n-\pi^*$ interaction tends to be of lower contribution as the n -ionisation potential of the

donor increases and the electron affinity of the acceptor decreases [7].

REFERENCES

1. R. Foster *et al.*, J. Chem. Soc., 3986 (1954); Trans. Faraday Soc., **59**, 2287 (1963).
2. S.D. Ross and M.M. Labes, J. Am. Chem. Soc., **79**, 76 (1957).
3. S. Iwata, H. Tsumbura and S. Nagakura, Bull. Chem. Soc. Japan, **37**, 1506 (1964).
4. R.M. Issa *et al.*, Z. Physik. Chem. (Leipzig), **253**, 96 (1973); Monatsh. Chem. (1980).
5. R.D. Kross and V.A. Fassel, J. Am. Chem. Soc., **79**, 38 (1957).
6. J. Bellanato *et al.*, Spectrochim. Acta, **16**, 1344 (1960).
7. G. Briegleb *et al.*, Z. Elektrochem., **64**, 347 (1960).