

Donor-Acceptor Complexes of N-Substituted Anilines with Aromatic Nitro Compounds : Preparation & Infrared Spectroscopic Investigation

A. M. HINDAWAY, A. M. G. NASSAR* & R. M. ISSA
Chemistry Department, Faculty of Science, Alexandria University, Egypt

and

Y. M. ISSA
Chemistry Department, Faculty of Science, Cairo University, Egypt

Received 26 March 1979; revised and accepted 11 December 1979

Donor-acceptor complexes of some N-substituted anilines with some aromatic di- and tri-nitro compounds have been prepared and investigated by IR spectroscopy. With nonacidic acceptors, π - π^* bonding takes place with amines of low basicity while strong basic amines form complexes by π - π^* and n - π^* interactions. With acidic acceptors, strong basic donors interact through π - π^* CT and also through proton transfer from the acidic centre of the acceptor to the basic centre on the donor molecule. Weak basic compounds form D...A complexes of the π - π^* type only. Generally, the formation of proton transfer complexes occurs with amines of higher basicity.

THOUGH many reports¹⁻³ have appeared about donor-acceptor complexes (D...A) of N-substituted anilines with aromatic nitro compounds utilising UV spectroscopy, these studies are confined to the determination of their stability constant K , $-\Delta H$ and $-\Delta S$.

In this paper, the results of IR spectroscopic investigations on some (D...A) complexes of N-substituted anilines with di- and tri-nitro aromatic compounds in the solid state are reported.

Materials and Methods

The chemicals used in the present investigation were of AR (BDH) grade.

The following N-substituted anilines were used as donors: N-CH₃ (a), N-C₂H₅ (b), N-(CH₃)₂ (c), N- ϕ (d), N-CH₃, *o*-COOH (e), N-COCH₃ (f), N-(CH₃)₂-*p*-CHO (g) and N-(CH₃)₂-*p*-N-(CH₃)₂ (h). The acceptor molecules used were: picryl chloride (1), trinitrotoluene (2), picric acid (3), 3,5-dinitrosalicylic acid (4), 3,5-dinitrobenzoic acid (5) and 2,4-dinitrophenol (6).

The solid complexes were prepared by mixing hot saturated solutions of the donor and the acceptor (0.01 mol each) in absolute ethanol.

The complexes separated out readily with acceptors 1,3,4 and 5 while with 2 and 6 the complexes were obtained on standing. The solids obtained were purified by either boiling with ethanol or crystallisation.

The IR spectra were recorded in KBr matrix on a Unicam SP 1000 instrument. Some spectra were checked on a Unicam SP 2000 or Beckman IR-4 instrument.

Results and Discussion

The acceptors under investigation are either nonacidic compounds (1 and 2) or acidic ones (3-6). The former type can only form D...A complexes involving electron transfer while the acidic compounds are capable of forming both the electron transfer complexes and those comprising proton donation to the amino compounds. The complexes of each class are discussed separately.

Donor-acceptor complexes of (1) and (2)—Complexes of these acceptors display the general spectral shifts of π - π^* complexes⁴⁻⁶. The δ CH bands of the acceptor are shifted to lower wavenumbers whereas those of the donors displays an opposite shift (see Table 1). The ν NH band of the donors with one substituent on the N-atom displays a general shift to higher value indicating a decrease in the charge density on the aromatic ring of the donor molecule.

The NO₂ bands of the acceptor molecules display a peculiar behaviour. The ν_{as} NO₂ is shifted to higher wave numbers in most compounds, resulting from the increased polarisation of the NO₂ groups. The higher ν_{as} NO₂ splits into two bands denoting differentiation of the energy states of the NO₂ groups in the D...A complex. The two new bands are observed at lower values for donors *d*, *e* and *f*; for the other donors, one band lies at lower wavenumber in comparison to the original band of the acceptor while the other band lies at higher wavenumber. The shift of ν_{as} NO₂ to lower values is in accordance with the increased charge density on the ring of the acceptor molecule. The shift in ν_{as} NO₂ to higher wave numbers in the case of complexes with donors *a*, *b*, *c*, *g* and *h* can be explained by involving the occurrence of an n - π^* interaction between an electron on the N-

TABLE 1 — CHARACTERISTIC IR BANDS OF D...A COMPLEXES OF COMPOUNDS 1, 2 AND 6 WITH ACCEPTORS (a-h)

Donor	Colour	m.p. °C	ν NH	ν OH	ν NO ₂		δ CH
					Asym.	Sym.	
D...A COMPLEXES OF PICRYL CHLORIDE (1)							
Free acceptor					1553, 1540	1348	788
a	Magenta red	56	3350	—	1558, 1550, 1538	1345	782
b	Magenta red	41	3360	—	1558, 1550, 1535	1345	785
c	Brown	68	—	—	1557, 1550, 1538	1352	786
d	Magenta red	59	3430	—	1552, 1545, 1535	1345	782
e	Yellow	65	3300	—	1550, 1540, 1535	1348	—
f	Orange yellow	169	3350	—	1545, 1540, 1520	1342	—
g	Magenta red	Oil	—	—	1558, 1540, 1530	1350	790
h	Dark brown	58	—	—	1565, 1550, 1538	1350	785
D...A COMPLEXES OF TRINITROTOLUENE (2)							
Free acceptor					1553, 1540	1348	778
a	Pale violet	74	3330	—	1550, 1530	1360	800
b	Pale violet	75	3350	—	1552, 1540, 1530	1355	793
c	Pale grey	75	..	—	1553, 1545, 1530	1352	792
d	Buff	78	3330	—	1545, 1535, 1525	1355	795
e	White	79	3340	—	1548, 1530, 1525	1350	791
f	Orange yellow	68	3350	—	1545, 1535, 1528	1352	793
g	Red	61	—	—	1550, 1545, 1525	1340	791
h	Dark blue	83	—	—	1555, 1535, 1525	1347	790
D...A COMPLEXES OF 2,4-DINITROPHENOL (6)							
Free acceptor				3280	1540, 1520	1350	928, 825
a	Pale brown	113	3320	3270	1550, 1515	1352, 1335	918, 810
b	Pale yellow	111	3380	3270	1545, 1517	1350, 1335	920, 812
c	Pale olive-green	110	—	3260	1535, 1518	1348, 1335	920, 820
d	Pale brown	107	3330	3270	1538, 1518	1348, 1333	918, 812
e	Pale yellow	97-106	3340	3260	1538, 1520	1347, 1336	910, 818
f	Orange	108	3370	3230	1535, 1515	1350, 1335	917, 820
g	Red	88	—	3270	1545, 1515	1348, 1332	920, 815
h	Green	108	—	—	1530	1340	920, 817

lone pair with a vacant π -level on the nitro group facing it. The ν_s NO₂ of the acceptor is broadened and generally shifts to lower wavenumbers in D...A complexes but in a few cases, especially where $n-\pi^*$ bonding takes place, these bands are shifted though slightly to higher wavenumbers. In a few cases these bands undergo splitting into two bands at lower and higher frequencies relative to those of the free acceptors.

The donor molecules *d* and *e* are not capable of undergoing $n-\pi^*$ transition due to the low charge density on the N-atom of *d* and *e* resulting from the substitution at the N-atom by the acceptor groups. In the case of donor *f*, the intramolecular hydrogen

bonding with the *o*-COOH group blocks the N-lone pair hence the $n-\pi^*$ transition is not possible. The donor-acceptor complexes of *d*, *e* and *f* can be represented by structure (I).

Donor-acceptor complexes of acceptors (3-5)—The acceptors (3-5) contain an acidic centre hence can form donor-acceptor complexes involving a proton transfer from the acceptor to the basic centre on the donor. The blocking of the lone pair on the nitrogen atom of the donor by the proton from the acceptor prevents $n-\pi^*$ transition. Accordingly, in complexes of the proton transfer type, the charge transfer (CT) interaction would be of the $\pi-\pi^*$ type only.

A comparison of the spectra of the CT complexes and of their components reveals that complexes involving proton transfer are formed by acceptors *a, b, c, h* and *g* with 3 or 4 only, i.e. with more basic donors. The spectral changes (Table 2) in this case can be summarised as follows :

(i) The ν OH of the phenolic group in 3 or 4 and the ν OH band of the COOH group in 5 dis-

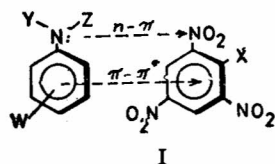


TABLE 2 — CHARACTERISTIC IR BANDS OF D...A COMPLEXES OF COMPOUNDS 3,4 AND 5 WITH ACCEPTORS (a-h)

Donor	Colour	m.p. °C	ν NH	ν OH	ν NO ₂		δ CH
					Asym.	Sym.	
D...A COMPLEXES OF PICRIC ACID (3)							
Free acceptor				3110	1555, 1540, 1530	1350	784
a	Yellow	119	2900, 2470	—	1563, 1550	1333	783
b	Yellow	136	2820, 2500	—	1563, 1553	1335	785
c	Yellow	165	2730, 2490	—	1563, 1550	1330	788
d	Blue	85	3380	3100	1550, 1535, 1525	1340	780
e	Golden yellow	90	3300	3090	1549, 1535, 1527	1340	782
f	Yellow	105	3240	3080	1554, 1534, 1527	1338	775sh
g	Yellow	98	2700, 2490	—	1550, 1535	1335	masked
h	Orange yellow	187	2720, 2510	—	1550, 1540	1332	masked
D...A COMPLEXES OF 3,5-DINITROSALICYLIC ACID (4)							
Free acceptor				3570, 3460 3100	1540, 1530	1349	925, 825
a	Yellow	201	2760, 2460	3430	1538	1353, 1330	—, 815
b	Yellow	140	2750, 2470	3430	1525	1335	920, 812
c	Yellow	159	2730, 2460	3420	1535	1343	920, 815
d	Green	56	3390	3410, 3090	1535, 1525	1342	917, 810
e	Yellow	126	3370	3420, 3080	1535, 1525	1345	—, 812
f	Yellow	156	3360	3440, 3090	1537, 1520	1340	920, 812
g	Red	150	—	3420	1535	1338	920, 810
h	Orange brown	151	—	3420	1538	1340	921, 814
D...A COMPLEXES OF 3,5-DINITROBENZOIC ACID (5)							
Free acceptor				3190	1555, 1540	1350	923, 808, 727
a	Buff	118	2740, 2330	—	1545, 1532	1346	920, 797, 715
b	Buff	101	2680, 2310	—	1550, 1535	1345	—, 794, 716
c	Pale grey	112	2660, 2460	—	1542, 1532	1346	919, 793, 710
d	White	208	3220	3400	1553, 1548	1355, 1348	—, 805, 715
e	White	140-198	3350	3400	1555, 1550	1358, 1348	915, 803, 700
f	Yellow	120	3210	3450	1553, 1548	1355, 1345	917, 808, 710
g	Orange red	145	—	3420	1540, 1530	1338	922, 815, —
h	Magenta red	135	2730, 2420	—	1535	1340	920, 805, 710

appear in the spectra of the complexes. The two ν OH bands of the carboxylic OH-group appear as a single band at a frequency lower than the H-bonded OH group of the acceptor in the free state. The shift denotes a stronger intramolecular hydrogen bonding in the CT complex. This results from both the intermolecular CT and the bonding of the OH group with the phenate ion which is a stronger proton acceptor than the phenolic OH group.

(ii) The ν NH \sim 3350 cm^{-1} in the spectra of donors *a* and *b* are no more observed in the spectra of the corresponding D...A complexes. The spectra of all CT complexes of the proton transfer type display a group of broad medium intensity bands in the region 3000-2400 cm^{-1} . These bands are reminiscent of the aniline salts⁷ and can be assigned to ν NH in a structure comprising a quaternary positively charged nitrogen atom.

(iii) The number of bands due to ν_{as} NO₂ of the acceptor decreases on complex formation. This results from the destruction of the intramolecular

hydrogen bonding in **3** and **4** and due to intermolecular hydrogen bonding in **5**, a case of proton transfer from the acceptor to the donor. The NO₂ bands are generally shifted to lower wavenumbers indicating increased polarisation of the NO₂ groups in the donor-acceptor complex. This results from the negative charge on the phenate or carboxylate ion as well as from the intermolecular CT interaction.

(iv) The δ CH bands of the donors are shifted to higher wavenumbers while those of the acceptor are shifted to lower values. This indicates a decrease of charge density on the donor molecule and an increase on the acceptor one, as a result of the intermolecular π - π^* charge transfer.

(v) The C=O band of the free acceptor **5** disappears in the spectra of the CT complexes, being replaced by a medium intensity doublet at 1410-1430 and 1490-1520 cm^{-1} ; the latter bands are characteristic of the carboxylate ion. The two C=O bands of acceptor **4** appear as a single band in the spectra of the D...A complexes with a value intermediate

to those of the free dinitrosalicylic acid. The appearance of the $\nu\text{C}=\text{O} \sim 1700\text{ cm}^{-1}$ indicates that the COOH group retains its identity in the CT complex of the proton transfer type. This supports the explanation given above that the phenolic OH group of acceptor **4** is the acidic centre participating in the proton transfer interaction.

The spectra of the D...A complexes of *d*, *e* or *f* and *g* with **5** are actually a superposition of the spectra of their components with apparent shifts in the position of several bands.

(i) The NO_2 bands are shifted to lower wavenumbers. For **3** and **4** the magnitude of shift of the lower $\nu_{\text{as}}\text{NO}_2$ is generally higher as compared to other bands. The shift of this band, corresponding to the hydrogen bonded NO_2 group, reveals strengthening of the intramolecular H-bond in the CT complex. This assumption is supported by the shift of νOH band to lower values. The number of the NO_2 bands remains the same as in the free acceptor. However, $\nu_{\text{as}}\text{NO}_2$ tends to be splitted in the spectra of the D...A complexes.

(ii) The δCH of the donors and acceptors display a behaviour similar to that of the proton transfer complexes, indicating the intermolecular $\pi-\pi^*$ interaction between the two molecules forming the complex.

(iii) The two $\text{C}=\text{O}$ bands in the spectrum of the free acceptor **4** appear as single band at wavenumber lower than the value for the H-bonded COOH group but higher than that of the COOH group not involved in hydrogen bonding. This behaviour has earlier been explained by the disappearance of the rotational isomerism existing in the case of the non-complexed dinitrosalicylic acid⁸. For acceptor **5**, the $\text{C}=\text{O}$ band still exists in the spectra of CT complexes comprising the $\pi-\pi^*$ interaction only. The band is slightly shifted to lower wavenumbers. This shift would be the resultant of the shift to higher values on destruction of the intermolecular hydrogen bonding, occurring in the free acceptor, and the shift to lower wavenumbers due to increased polarisation of the $\text{C}=\text{O}$ bond in the D...A complex.

(iv) The νNH bands of *d*, *e* and *f* are generally shifted to higher wavenumbers as a result of the decreased charge density on the donor molecules.

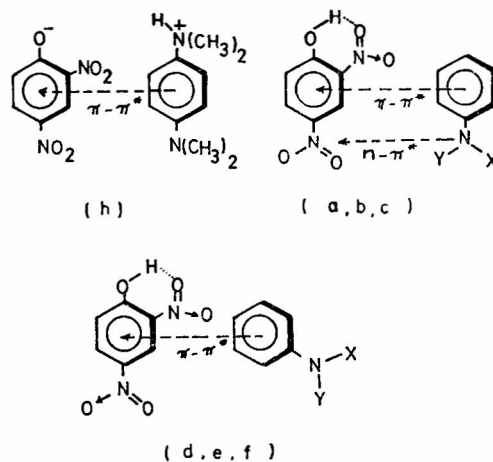
(v) The νOH band of **5** appears at 3400 cm^{-1} in the spectra of the D...A complexes of the $\pi-\pi^*$ type, thereby supporting the explanation given above for the destruction of the intermolecular hydrogen bonding. The low value of this band compared to that of free OH groups⁹, can be explained (i) by the increased charge density on the acceptor molecule which favours a shift of νOH to lower value and (ii) the possible existence of intermolecular hydrogen bonding between the carboxylic OH group and the basic centre.

As in the case of D...A complexes of picryl chloride (**1**) and trinitrotoluene (**2**), complexes formed with donors *d*, *e* and *f* are not capable of participating in the $n-\pi^*$ transition due to the reasons already outlined.

Donor-acceptor complexes of acceptor (6) — The IR spectra of the CT complexes of **6** with various donors (Table 1) indicate that this acceptor can form the

D...A complexes involving proton transfer with donor *h* only. This is due to the higher basic character of this compound as compared to other donors. The νOH band of **6** at 3280 cm^{-1} is no more observed in CT complex of *h* and the $=\text{N}^+-\text{H}$ bands in the region $3000-2400\text{ cm}^{-1}$ appear in the spectrum of the CT complex. The ν_{as} and $\nu_{\text{s}}\text{NO}_2$ appear as single bands indicating that the energy states of the two NO_2 groups become more or less equal after the elimination of the intramolecular hydrogen bonding in the acceptor molecule on CT complex formation. The δCH bands display the shifts characteristic of the $\pi-\pi^*$ CT interaction.

The CT complexes of donors *a-g* display the shift of νOH to lower wavenumbers. This is also the case with $\nu_{\text{as}}\text{NO}_2$ corresponding to the H-bonded NO_2 group. This reveals the strengthening of the intramolecular hydrogen bonding in the D...A complexes. The $\nu_{\text{as}}\text{NO}_2$ of the free NO_2 group is shifted to lower values in the case of CT complexes with *d*, *e*, *f* and *g*. This behaviour is similar to that of complexes involving only the $\pi-\pi^*$ CT interaction. For donors *a*, *b* and *c* the $\nu_{\text{as}}\text{NO}_2$ is shifted to higher wavenumbers compared to the free acceptor. This shift can be explained by the occurrence of the $n-\pi^*$ interaction between the NO_2 -group as acceptor and the N-atom of the donor molecule¹⁰. Thus D...A complexes with 2,4-dinitrophenol can be represented by structures (II-IV).



It may be concluded from the results presented that the type of D...A complex formed between N-substituted anilines and acceptors having an acidic centre depends on both the basicity of the donor molecule and the acidic character of the acceptor acting as a proton donor. With the weak acidic acceptor **6** (2,4-dinitrophenol) only the strong basic tetramethyl-*p*-phenylenediamine forms a complex involving proton transfer. With the medium acidic **5** (3,5-dinitrobenzoic acid) *a*, *b*, *c* and *h* form the proton transfer CT complexes. The donor *g*, with the strong acceptor CHO-group in *p*-position to the basic centre, would have lower basic properties compared to donors *c* or *h*; hence cannot form complex of the proton transfer type with **5**. Donors *d*, *e* and *f*

also display weaker basic properties hence form D...A complexes of the π - π^* interaction type. With the more acidic acceptors 3 and 4, donor *g* forms the proton transfer complexes. The other donors of apparently weak basicity can not form complexes involving proton transfer.

References

1. DALE, B., FOSTER, R. & HAMMICK, D. L. *J. chem. Soc.*, (1954), 3986; FOSTER, R. & THOMSON, T. J., *Trans. Faraday Soc.*, **59** (1963), 2287.
2. ROSS, S. D. & LABES, M. M., *J. Am. chem. Soc.*, **79** (1957), 76.
3. IWATA, S., TSUMBURA, H. & NAGAKURA, S., *Bull. chem. Soc. Japan.*, **37** (1964), 1506.
4. KROSS, R. D. & FASSEL, V. A., *J. Am. chem. Soc.*, **79** (1957), 38.
5. BRIEGLEB, G. & DELLE, H., *Z. Elektrochem.*, **64** (1960), 347.
6. ISSA, R. M. & EL-ESSAWAY, M. M., *Z. physik. Chem.*, (Leipzig) **253** (1973), 96.
7. BELLANATO, J., *Spectrochim. Acta*, **16** (1960), 1344.
8. ISSA, Y. M., HINDAWEY, A. M., NASSAR, A. M. G. & ISSA, R. M., (Under publication).
9. BELLAMY, J. L., *The infrared spectra of complex molecules* (Methuen, London), 1958.
10. HINDAWEY, A. M., ISSA, Y. M., MARGHALANI, Y. A. & ISSA, R. M., *Mh. Chem.*, (in press).