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Investigation of the Intermolecular Interaction of Quinaldine-4-Phenylazomethine derivatives with dinitro and trinitrobenzenes

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Summary: The CT complexes of some Schiff bases of quinaldine-4-phenylazomethine derivatives with tri and dinitrobenzenes are prepared and investigated by elemental analysis, IR, ^{1}H-NMR and electronic absorption spectra. The results of microanalysis revealed the formation of 1:1 and 1:2 CT complexes for strong acidic acceptors, and 1:1 formation in the case of weak acidic acceptors. The formation takes place through π-π^* intermolecular charge transfer interaction while the n-π^* interaction is either of low contribution to the bonding or even absent.

Introduction

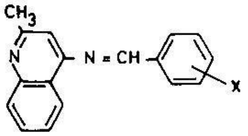
The formation of molecular complexes of the charge transfer type between electron acceptors such as di or trinitrobenzene derivatives and π-electron donors was the subject of a vast number of interesting investigations [1-5]. The interest in such studies led either to the determination of the ionization potentials, I_p, of the donors, the electron affinity of the acceptors, or the determination of their stability constants and the type of bonding between the donor and acceptor molecules, especially in the solid lattice.

In the present investigation, the CT complexes formed through the interaction of quinaldine-4-phenylazomethine derivatives with dinitro and trinitrobenzenes are studied using the IR, ^{1}H-NMR, elemental analysis and electronic absorption spectroscopy to throw some light on the donor behaviour of these molecules.

Experimental

The IR spectra of the solid complexes were recorded on a Unicam SP 1000 infrared spectrophotometer. The solid state IR spectra were obtained using the KBr disc technique. The ^{1}H-NMR spectra were obtained by the aid of the Varian EM 390-90 MHz nmr spectrometer using TMS as internal standard and Merck DMSO-d^6 as solvent. The electronic spectra were recorded on a Shimadzu UV 250 by the Nujol mull technique.

All compounds used in the present work were pure BDH laboratory grade chemicals. The donors involved in the present investigation have the general structural formula.



X=H(a), p-$N(CH_3)_2$(b), p-OCH_3(c) and p-NO_2(d).

The acceptors were picric acid (I), 3,5-dinitrosalicylic acid (II), 3,5-dinitrobenzoic acid (III), 3,4-dinitrobenzoic acid (IV), m-dinitrobenzene (V) and 2,4-dinitrophenol (VI).

The CT complexes were prepared by mixing a hot saturated solution of the donor (0.01 mole in ca. 10 ml ethanol) with a similar one of the acceptor (0.01 or 0.02 mole). The solid CT complexes separated on mixing or on cooling were filtered off, dried in vaccum and stored over $CaCl_2$. These were first subjected to elemental microanalysis to check their stoichiometry. All donors were found to give with all acceptors 1:1 complexes, which has been verified by previous workers [3,4,6,7] hence it is not necessary to give data for complexes of the 1:1 type. The Schiff base-CT complexes under investigation were also prepared in the ratio 1:2 (donor:acceptor); the results given in table 1 for some complexes are in accordance with this composition.

Results and Discussion

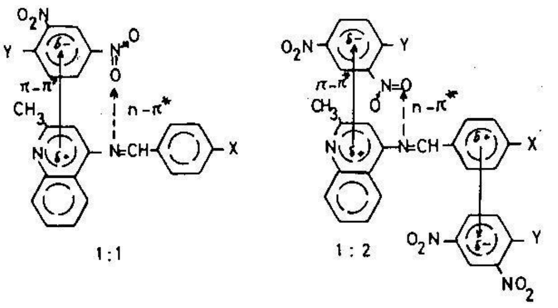
IR Spectra:

Charge transfer complexes with weak and non acidic acceptors:

The IR spectra of CT complexes shows that the γ_{CH} bands of acceptors (V,VI) shift to lower wave number while that of the quinaldine donors a-d are shifted to higher value compared to that of the free components. This indicates an increased electron density on the benzene ring of the acceptor and its decrease on that of the donor which takes place through $\pi-\pi^*$ intermolecular electron transfer from the highest occupied π-level on the donor molecule to the lowest unoccupied level of the acceptor [6,7] [D(HOMO ⟶ A (LUMO)]. The presence of the CH_3 group on the heterocyclic ring decreases its ionization potential indicating that it is the centre contributing to the intermolecular charge transfer.

In donor b, the shift of the γ_{CH} band is more apparent with bands of the benzal ring which reveals that the existence of the strong donor $-N(CH_3)_2$ group on it lowers the ionization potential of the ring to such an extent that it will profitably be the donor centre [8].

The NO_2 bands of the acceptor display some interesting changes. The asym. NO_2 bands become broader and display some splitting and a shift to lower wavenumbers which is due to increased π-electron density on the aromatic ring of the acceptor. The sym. NO_2 band of the CT complexes also shows a shift to lower wavenumber, hence $n-\pi^*$ interaction is to be excluded [1,9,10]. For acceptor VI the shift might be due to increased strength of the intramolecular hydrogen bond, an assumption which is substantiated by the shift of the ν_{OH} bands of the acceptor to lower wavenumbers Table 2. The interaction of the quinaldine-4-phenylazomethine with dinitrobenzene derivatives in the 1:1 and 1:2 complexes can be represented as:



1:1 1:2

X=H, p-$N(CH_3)_2$, p-OCH_3, p-NO_2

Y = H(V) or OH(VI).

Table-1: Elemental analysis of some 1:2 CT complexes.

Acceptor	Formula	Carbon % Cal.	Carbon % found	Hydrogen % Cal.	Hydrogen % found	Nitrogen % Cal.	Nitrogen % found
CT complexes of quinaldine 4-phenylazomethine							
I	$C_{29}H_{20}N_8O_{14}$	49.4	49.3	2.84	2.6	19.94	20.3
II	$C_{31}H_{22}N_6O_{14}$	52.96	52.0	3.13	4.3	11.96	11.6
III	$C_{31}H_{22}N_6O_{12}$	55.49	54.4	3.28	4.3	12.53	12.4
VI	$C_{29}H_{22}N_6O_{10}$	56.64	56.2	3.58	3.9	13.67	13.8
CT complexes of quinaldine 4-p-dimethylaminophenylazomethine							
I	$C_{31}H_{25}N_9O_{14}$	49.78	49.8	3.48	3.6	11.24	11.6
II	$C_{33}H_{27}N_7O_{14}$	53.13	52.6	3.75	4.0	13.15	12.9
III	$C_{33}H_{27}N_7O_{12}$	55.51	54.4	3.92	4.0	13.74	12.8
CT complexes of quinaldine 4-p-nitrophenylazomethine							
I	$C_{30}H_{22}N_8O_{15}$	49.05	48.1	2.99	2.5	19.54	18.5
II	$C_{32}H_{24}N_6O_{15}$	52.46	51.4	3.28	3.9	11.48	12.1
III	$C_{32}H_{24}N_6O_{13}$	54.85	53.1	3.43	3.2	12.00	12.1
V	$C_{30}H_{24}N_6O_9$	54.90	53.4	3.59	4.3	13.72	13.4
VI	$C_{30}H_{24}N_6O_{11}$	52.13	51.3	3.49	6.4	13.04	13.9

Charge transfer complexes with acidic acceptors:

These complexes are formed when the donors are allowed to react with acceptors (I-IV). The IR spectra of these complexes are characterised by a group of medium intensity broad bands within the 2400-3000 cm^{-1} range which are not present in the spectra of the free donors or acceptors. These bands can be assigned to the stretching mode of the group (=$\overset{+}{N}$—H) which is formed through the transfer of a proton from the acidic centre of the acceptor to the basic C=N centre of donor. This is supported by the disappearance of the OH bands corresponding to the phenolic group of acceptors (III and IV) and the shift of the C=N bands to lower values in the spectra of the CT complexes.

The γ_{CH} bands of the donors are shifted to higher wave number while those of the acceptors are shifted to lower ones (Table 2). These bands display an identical behaviour as the CT complexes involving only the elctron transfer.

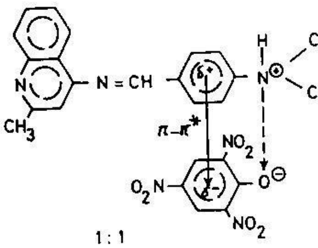
The asym. and sym. NO_2 bands exhibit a shift to lower or higher wave numbers, a behaviour which is observed with charge transfer complexes involving proton transfer [7].

In case of b, the $N(CH_3)_2$ group being more basic than the azomethine

Table-2: Important bands in the IR spectra of CT complexes with strong acidic acceptors.

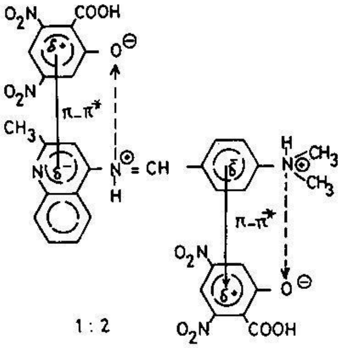
Donor	Ratio	m.p. °C	Colour	$\overset{+}{=N}$-H	ν_{OH}	asym NO_2	sym.NO_2	γ_{CH} acceptor
			Complexes with picric acid					
free acceptor					3110	1550,1540,1530	1330	784
a	1:1	162	pale yellow	2450, 2900		1590,1550	1330,1355	740,765,790
	1:2	110	pale yellow	2500, 2950	3100	1600,1560,1530	1350,1380,1385	740,770,790,800
b	1:1	80	deep yellow	2450, 2900	-	1560,1540,1510	1345,1360,1390	760,780,800
	1:2	121	pale yellow	2500, 2900	3120	1590,1550,1540	1310,1330,1360	750,760,790,795
c	1:1	147	deep yellow	2600, 2900	-	1590,1550,1540	1325,1360	750,785,795
	1:2	171	yellow	2500, 2900	3120	1580,1550,1540	1320,1360	740,750,790
d	1:2	111	pale yellow	2500, 2950	3100	1600,1560,1530	1330,1350,1380	755,770,790,800
			Complexes with 3,5-dinitrosalicylic acid					
free acceptor					3560	1540,1530	1349	915,925
a	1:1	167	pale yellow	2450, 2900	3300,3200	1590,1560	1335,1320	930,990
	1:2	166	pale yellow	2450, 2900	3500,3300	1580,1560,1520	1330,1350	930,950
b	1:1	126	pale yellow	2500, 2900	3340,3240	1545,1535	1360,1385	920,950
	1:2	136	orange	2500, 2900	3300,3200	1590,1555,1520	1340,1370	910,935
c	1:1	160	yellow	2600, 2950	3380	1580,1555,1525	1335,1360	910,940
	1:2	111	yellowish brown	2600, 2950	3520,3410	1580,1550,1520	1330,1340	910,940
d	1:2	116	pale brown	2500, 2900	3500,3200	1560,1540,1530	1350,1380	920,940
			Complexes with 3,5-dinitrobenzoic acid					
free acceptor					3090	1555,1540	1350	923,908
a	1:1	158	cream	2800, 2900	-	1590,1560,1535	1330,1355,1370	905,915,930
	1:2	105	cream	2800, 2900	3200	1570,1540	1360,1390	910,930,940
b	1:1	141	pale orange	2500, 2950	-	15601540,1530	1330,1390	910,920,950
	1:2	116	orange	2500, 2950	3090	1565,1535,1525	1330,1350	910,935
c	1:1	167	green	2600, 2900	-	1590,1565,1525	1365,1330	905,945
	1:2	161	cream	2600, 2900	3090	1590,1560,1530	1330,1355,1370	905,920,930
d	1:2	79	pale brown	2500, 2900	3100	1570,1550	1360,1390	910,940
			Complexes with 3,4-dinitrobenzoic acid					
free acceptor					3100	1550	1350,1325	930,945
a	1:1	171	cream	2500, 2900	-	1580,1560,1520	1330,1350,1370	920,960,990
	1:2	165	white	2500, 2900	3180,3080	1555,1490	1330,1370	880,920
c	1:2	104	pale yellow	2700, 2900	3090,3180	1530,1540,1585	1350,1570	910,980

N would preferably be the proton acceptor for the 1:1 complexes. Thus, the bonding with picric acid can be formulated as:


1:1

The spectra with acceptor II display for 1:1 complex a $\nu_{C=O}$ at 1770 cm^{-1} and ν_{OH} at 3190 cm^{-1} while for III the $\nu_{C=O}$ appears at 1707 cm^{-1} and bands due to the carboxylate ion at 1600-1490 cm^{-1}. The presence of $\nu_{C=O}$ band in such complexes with II reveal that COOH group of salicylic acid do not contribute to the proton transfer in complex formation. The presence of the ν_{OH} and $\nu_{C=O}$ bands as single peaks explain the absence of the rotational isomerism that is existing in the noncomplexed acceptor [7] II (Table 2).

For 1:2 CT complexes, the OH band of the second acceptor is observed with donor b where it is expected that the C=N basic centre is capable of accepting the proton from the acidic acceptor (II,III). However, with weak acidic acceptors, the OH bands of the second acceptor molecule are still observed in the IR-spectra of complex with b because the $-HN(CH_3)_2$ centre formed in 1:1 type lowers the basicity of the C=N nitrogen so that it will accept the proton from the strong acidic acceptors only. The 1:2 complexes can be represented as:


1:2

^{1}H-NMR Spectra:

To support the results of the ir-spectra concerning the type of interaction between the donors and acceptors under investigation the ^{1}H-NMR spectra of the complexes compared to starting materials were studied. The signal due to the two protons of the two OH groups of II appearing at 8.7 ppm is shifted to higher field by a small magnitude and its area decreases to one proton. This reveals that one OH group has been involved in the CT complexes. The signals of the donor rings display a small shift down field as a result of the decreased shielding effect on the protons of the donor ring in the CT complexes.

Compounds formed through electron transfer:

The ^{1}H-NMR of CT complexes with V and VI compared to the reactants reveal a shift of the signals of the protons of the acceptor to higher field, while those of the donor shift to lower field. The downfield shift of the methyl signal is more obvious when this group is attached to the aniline ring. This provides further support to the assumption mode on the basis of IR-spectra that the heterocyclic ring is the donating system in the CT interaction.

Table-3: Important bands in the IR spectra of CT complexes with non or weak acidic acceptor.

Donor	Ratio	m.p. °C	Colour	$=\overset{+}{N}-H$	OH	asym.NO_2	sym.NO_2	γ_{CH} acceptor
			Complexes with m-dinitrobenzene					
free acceptor						1545	1352	905,920
a	1:1	77	cream	--	--	1550,1570	1335,1360	905,910,945
	1:2	71	cream	--	--	1560,1555,1590	1350,1380	910,930,990
b	1:1	71	brick red	--	--	1530,1555	1350,1390	925,955,980
	1:2	69	brown	--	--	1540,1550,1590	1330,1360	900,940
c	1:1	70	cream	--	--	1530,1555,1580	1335,1360	905,910,950
	1:2	92	cream	--	--	1520,1550,1580	1335,1360	905,910
d	1:2	121	deep cream	--	--	1530,1545,1555	1330,1350,1380	910,930,990
			Complexes with 2,4-dinitrophenol					
free acceptor					3270	1540,1520	1350	825,928
a	1:1	189	yellow	--	--	1510,1540,1555	1325,1360	830,850,870,910
	1:2	197	pale yellow	--	3280,3400	1520,1540,1560	1350,1385	820,840,880
b	1:2	104	limone	--	3220,3390	1540,1550,1610	1310,1350,1375	825,880,920
c	1:2	102	pale yellow	--	3220	1420,1550,1580	1320,1340	840,850,915

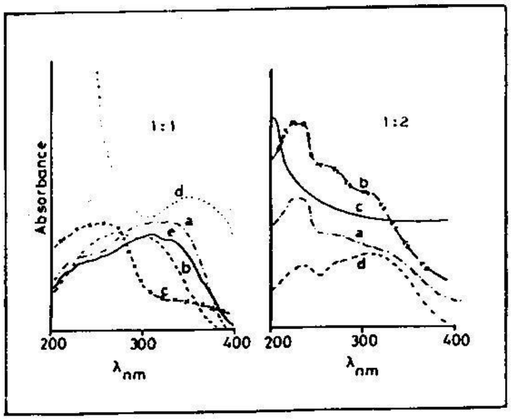


Fig.1: The electronic absorption spectra of some CT complexes of donor a with some acceptors
a- I, b- II, c-V, d-VI (1:1)
a- I, b- II, c-III, d-IV, e-VI (1:2).

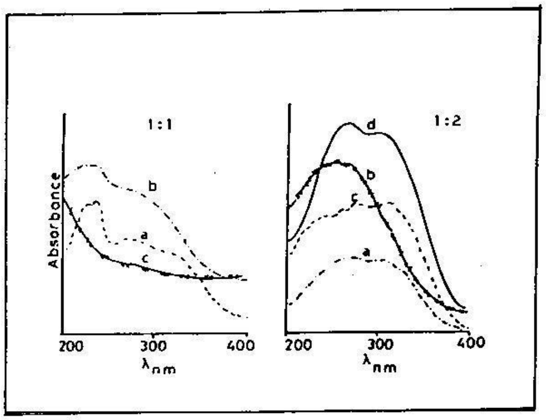


Fig.2: The electronic absorption spectra of some CT complexes of donor c with some acceptors
a- I, b- II, c-V, d- VI for (1:1) and (1:2).

Compounds formed through $\pi-\pi^*$ *and proton transfer:*

In the spectra of the CT complexes of III with different donors, the broad signal due to the OH group is no more observed, a new signal with an integration equivalent to one proton is observed at 7.8-8.6 ppm for quinaldine derivatives. This signal can be assigned to the new centre $=\overset{+}{N}-H$ which is absent in the spectra of the free donors and acceptors. Thus, the bonding of donors a,c with strong acidic acceptors in the 1:1 complexes takes place through both electron and proton transfer; Table 3.

The CT complexes of acceptors I, III with b exhibit a sharp signals denoting that no proton is bonded to the azomethine nitrogen. However, the complexes display a splitting of $-N(CH_3)_2$ signals in 3.1-3.2 ppm range as a result of the presence of the proton on the dimethylamino nitrogen.

Table-4: ^{1}H-NMR signals for CT complexes of quinaldine phenylazomethine derivatives with some di and trinitrobenzenes.

ratio and	signal of acceptor						signal of donor									
position	H^2	H^3	H^4	H^5	H^6	OH	H^2	H^3	H^5,H^8	H^6,H^7	$H^{4'}$	$H^{4''}$ *	$H^{3'},H^{6'}$	$H^{2'},H^{5'}$	$\overset{+}{=N-H}$	=CH
Complexes of quinaldine 4-p-dimethylaminophenylazomethine																
Complexes with picric acid																
free A or D	--	8.46	--	8.46	--	6.16	3.60	9.80	8.20	7.80	3.20	3.10	6.20	6.90		6.80
1:1	--	8.4	--	8.40	--	--	3.95	9.85	8.50	7.85	3.20	3.20	6.75	7.00	8.65	6.85
1:2	--	8.30	--	8.30	--	--	3.10	9.75	8.50	7.85	3.20	3.20	6.70	6.90	8.70	6.80
Complexes with 3,5-dinitrosalicylic acid																
free A	--	--	8.70	--	5.60	8.70										
1:1	--	--	8.45	--	--	7.0	4.00	9.85	8.55	7.90	3.20	3.20	6.75	6.90	8.80	6.80
1:2	--	--	8.5	--	--	6.7	4.20	9.85	8.35	7.80	3.15	3.20	6.80	6.90	8.80	6.70
Complexes with 3,5-dinitrobenzoic acid																
free A	8.8	--	--	--	8.8	7.67										
1:1	8.4	--	--	--	8.4	--	3.50	9.75	8.40	8.00	3.20	3.20	6.20	6.90	9.00	6.80
1:2	8.4	--	--	--	8.4	--	3.70	9.75	7.90	7.70	3.20	3.20	6.70	6.85	9.00	6.80
Complexes with m-dinitrobenzene																
free A	9.0	--	8.43	7.7	8.43	--										
1:1	8.8	--	8.1	7.7	8.1	--	3.50	9.70	8.70	8.70	3.10	3.10	6.50	6.90	7.90	6.80
1:2	8.9	--	8.1	7.8	8.1	--	3.50	9.75	8.65	8.65	3.20	3.10	6.50	6.90	8.00	6.70
Complexes of quinaldine 4-phenylazomethine																
Complexes with picric acid																
free A or D	--	8.46	--	8.46	--	6.16	3.50	6.50	7.45	7.70	8.20	--	8.20	6.70	--	7.65
1:1	--	8.35	--	8.35	--	--	4.10	6.50	7.60	7.85	8.50	--	8.50	6.70	8.65	7.80
1:2	--	8.15	--	8.15	--	9.1	4.50	6.50	7.60	7.85	8.25	--	8.25	6.60	8.60	7.80
Complexes of quinaldine 4-p-methoxyphenylazomethine																
Complexes with picric acid, free D							2.40	6.50	8.20	7.65	3.70	--	6.80	7.50	--	7.70
1:1	--	8.30	--	8.30	--	--	2.50	6.55	8.20	7.80	3.70	--	7.00	7.50	8.55	8.10
1:2	--	8.45	--	8.45	--	6.50	2.55	6.55	8.30	7.25	3.50	--	6.90	7.70	8.55	8.60

* H^4 is the splitted signal gained from CH of $-NH(CH_3)_2$.

Table-5: The electronic absorption data and the CT energy of some CT complexes.

D	I_p donor	ratio (D:A)	Acceptor (A)									
			I		II		III		V		VI	
			λ_{CT}	E_{CT}	λ_{CT}	E_{CT}	λ_{CT}	E_{CT}	λ_{CT}	E_{CT}	λ_{CT}	E_{CT}
a	7.99027	1:1	370	3.36	390	3.19	--	--	--	--	--	--
		1:2	420	2.96	360	3.45	--	--	410	3.03	405	3.07
b	7.8042	1:1	360	3.45	440	2.80	460	2.70	550	2.26	--	--
		1:2	370	3.36	--	--	400	3.11	470	2.64	400	3.11
c	7.9419	1:1	420	2.96	355	3.50	--	--	--	--	--	--
		1:2	360	3.45	--	--	--	--	340	3.66	--	--

λ (nm) , E_{CT} (ev).

In case of 1:2 complex of all donors except b, the OH signal of the second acceptor is observed. For complexes with b the C=N group is capable of accepting the proton of the second molecule of strong acidic acceptor I, III, IV but not from the weak acids in which the signal due to the OH of the second acceptor is observed. This indicates that the $-NH(CH_3)_2$ group diminishes the basicity of C=N group. In case of 1:1 complexes the protonation of C=N e.g. complexes with a and c, lowers the basicity of the quinaldine nitrogen to such an extent that it hinders the proton transfer to the nitrogen of the heterocyclic ring. The shifts of the acceptor signals to higher field are of higher magnitude in the 1:1 complexes while for the donors the shifts are higher in case of the 1:2 complexes.

The electronic absorption spectra:

The electronic absorption spectra of the CT complexes formed with acceptors I-VI display single CT band at 340-550 nm corresponding to $\pi-\pi^*$ intermolecular charge transfer interaction with E_{CT} equal to 3.66 - 2.26 eV Figs. 1,2. The nature of the band is substantiated by calculating the energy of the CT interaction E_{CT} using the relation given by Briegleb [11]. The values calculated from the equation are 3.66 - 3.03 eV with m-dinitrobenzene. The absorbance of the $n-\pi^*$ bands reveals that $n-\pi^*$ interaction would be hindered in these CT complexes.

The CT complexes formed with strong acidic acceptors exhibit one CT band within 340-500 nm which lies at short wavelength compared to that of the complexes not involving proton transfer due to high I_p of the protonated azomethine donors. The CT bands of the 1:2 complexes are observed at shorter wavelength compared to those of 1:1 type as a result of the blocking of the resonance between the two rings in the former type of compounds.

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