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2-CHLORO-3,5-DINITROPYRIDINE AS A NEW π-ELECTRON ACCEPTOR

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SUMMARY

2- Chloro-3,5-dinitropyridine was used as efficient π-electron acceptor in the preparation of charge transfer (CT) complexes with aniline and its derivatives acting as donors. The type of interaction and structure of the formed complexes were studied using IR and electronic absorption spectral studies. The primary bonding functioning in all complexes formed is of the π-π* type. Secondary interactions such as n-π* and hydrogen bonding were also operative within the molecular complexes formed depending on the nature of the donor used.

The electron affinity (EA) of the acceptor was calculated from electronic absorption spectral studies.

INTRODUCTION

A charge transfer complex is formed between two π-electron molecules, one acting as electron donor (low ionization potential, Ip), the other as electron acceptor (high electron affinity, E_A). (1) Heteroaromatics with their capability to donate both π-and n-electrons are considered one of the best compounds acting as very efficient donors in charge transfer complex formation. Numerous works(2) were concerned with pyridine and its derivatives as electron donors in CT complex formation. This is based on the fact that the ring N-atom increases the basicity i.e. electron density; of the molecule and it is obvious that the presence of electron donating groups increases the base strength of the nitrogen atom. On the other hand, electron withdrawing groups will show a counter effect, but still the heteroaromatic ring acting as the centre of electron donation.

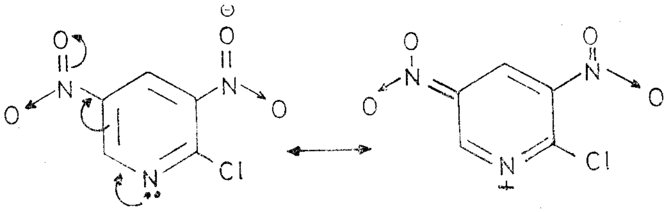
Issa et al.(3) prepared charge transfer complexes of ring substituted methylpyridine derivatives with polynitrobenzenes as acceptors and then investigated them using IR, UV and ^1H NMR.

Recently, 1–hydrazinophthalazine hydrochloride has been used as electron donor in the formation of charge transfer complexes. The acceptors are di–and tri–nitrobenzenes.(4)

Charge Transfer Complexes formed between pyrimidine, pyrazine and their 2–amino derivatives and some p–benzoquinones have been prepared and investigated using spectroscopic techniques. (5).

This investigation is a trial to prove the probable use of pyridine nucleus bearing very strong electron withdrawing groups as electron acceptor.

The presence of strong electron withdrawing groups decreases the basicity of the nitrogen ring atom with consequent decrease of the electron density on the ring causing thus a lowering of electron affinity according to the resonating structure:

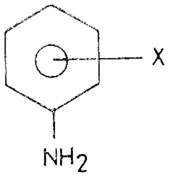


In this work, the charge transfer complexes of 2–chloro–3,5–dinitropyridine as electron acceptor with aniline and its derivatives as donors are prepared and investigated using ir and electronic absorption spectral analyses. The electron affinity of the acceptor is calculated from the electronic spectra of the molecular compounds.

EXPERIMENTAL

All chemicals used in the present investigation were pure grade **BDH** chemicals.

The working procedures for the preparation of CT complexes are the same as given before.(6) The donors used in the psesent investigation are aromatic amines having the general structural formulae:



where x is [H(a), o–Cl (b), p–Cl(c), m–Cl (d), p–Br (e), p–I (f), o–CH_3 (g), mCH_3(h), p–CH_3(i), o–OCH_3 (j), o–COOH (k), p–COOH (l), o–NO_2 (m), m–NO_2 (n) and α–naphthylamine (o)].

The acceptor used is 2–chloro–3,5–dinitropyridine. Some selected complexes were subjected to C, H, N and Cl determinations, table (1).

The vibrational spectra of the CT complexes were obtained using the KBr Wafer technique by the aid of a Perkin Elmer 140 infrared spectrometer.

The electronic absorption spectra of the various complexes in the solid state (Nujol mull technique) were recorded within the range 800–200 nm by the aid of λ 4B Perkin Elmer recording uv–visible spectrophotometer.

RESULTS AND DISCUSSION

The results of the elemental analysis of the formed complexes listed in table (1) are mostly in agreement with those required for the 1:1 (D:A) complexes.

The intermolecular interaction between the acceptor and donors used, as gathered from the results of ir and electronic absorption spectral studies, depends to a large extent on the nature of the donor. The interpretation of the results depends on the data obtained from a variety of sources, (5) that aromatic nitrogen heterocycles of the pyridine type

Table (1) Analytical data of some CT complexes.

Acceptor No.	X	Molecular formula	m.p. °C	Analysis % Found/(Calcd.) C	H	N	Cl
a	H	$C_{11}H_9N_4O_4Cl$	191	44.52 (44.00)	3.04 (3.00)	18.89 (18.98)	11.97 (11.86)
b	o–Cl	$C_{11}H_8N_4O_4Cl_2$	185	39.88 (39.98)	2.42 (2.40)	16.92 (15.92)	21.45 (21.48)
*f	p–I	$C_{11}H_8N_4O_4Cl$	214	31.24 (30.94)	1.89 (1.93)	13.25 (13.57)	8.40 (8.31)
h	m–CH_3	$C_{12}H_{11}N_4O_4Cl$	146	46.38 (46.53)	3.54 (3.58)	18.04 (18.00)	11.43 (11.49)
j	o–OCH_3	$C_{11}H_{11}N_4O_5Cl$	206	44.10 (44.68)	3.37 (3.16)	17.15 (17.00)	10.87 (10.58)
l	p–COOH	$C_{12}H_9N_4O_6Cl$	$>$ 280	41.92 (42.35)	3.49 (3.53)	16.30 (16.00)	10.33 (10.25)
n	m–NO_2	$C_{11}H_9N_5O_6Cl$	169	38.37 (38.36)	3.19 (3.22)	20.32 (20.33)	10.30 (10.28)

* % I_2 30.06
(29.16)

function as σ–donors by using the lone pair of electrons on the nitrogen atom and as π–acceptor by using a delocalized orbital on the ring.

The π–accepting properties of these heterocycles increase by introduction of electron withdrawing substituents into 2- and 6–positions.

The ir spectra

The ir spectra of these complexes compared to that of the free components reveal that the various vibrations of the acceptor part are shifted to lower wavenumbers while those of the donor part(3) exhibit a counter shift, table (2). This shift is characteristic to charge transfer of the π–π* type(8). It is obvious from Table (2) that the extent of the shift is largely dependent on the type of substituent on the donor molecule. A shift of the acceptor bands to much lower wavenumber values is observed if the donor molecule carries an electron donating group. This is due to the fact that the extent of charge transfer between the donor and acceptor is increased causing an increased electron density on the acceptor moiety causing a larger shift to lower wavenumber values.

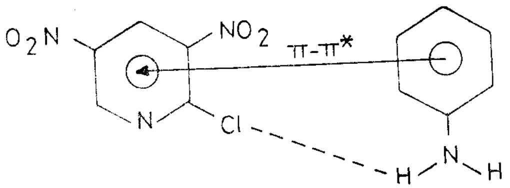
The NO_2 bands of the acceptor (1542 and 1348 cm^{-1} for asym. and sym. vibrations, respectively) display some interesting behaviours which may be of great help in elucidation of the types of bonding. The bands may shift to lower wavenumbers. This may be taken as evidence for the possible formation of the π–π* electronic transition (HOMO–LUMO) leading to increased polarization of the NO_2 group.

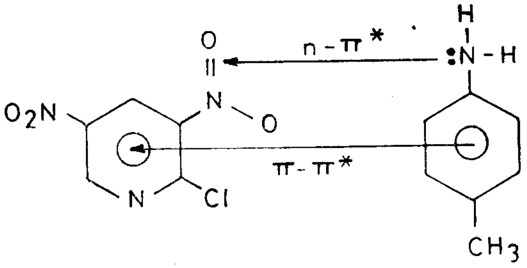
In most cases the asym. NO_2 band splits into two bands one located at higher and the other at lower wavenumber values. This indicates increased differentiation in the energy of the NO_2–groups. Such behaviour may be ascribed to the possible invoking one of the NO_2 groups in either n–π* interaction with the lone pair of electrons on the amino group of the donor molecule or hydrogen bonding with the hydrogen of the amino group. Such interaction is allowed if one figures that the acceptor may be oriented so that one of the nitro–groups is positioned in front of the amino group of the donor.

The C–Cl band of the free acceptor (651 cm^{-1}) shows a shift to high wavenumbers with but few exceptions. This may plausibly be ascribed to the presence of mutual electrostatic attraction between the hydrogen atom of the NH_2 group of the donor and the chlorine atom on the acceptor molecule if they face each other. Such conclusion is strengthened by the observed shift of the NH_2 group of the doron in most cases to lower wavenumbers. The latter assumption reveals that the shift of the nitro group to higher values is ascribed mainly to n–π* interaction.

From table (2), it is obvious that a broad band with numerous peaks is located in the range 3250–2500 cm^{-1} within the complexes k and l (o–COOH and p–COOH). According to Bellamy,(9) such pattern is highly characteristic for carboxylic acid dimers, thus denoting the presence of intermolecular hydrogen bonding (C = O–OH... O = C–OH). The other discussed interactions take place within the molecular complex (π–π*, n–π* ($H_2N - NO_2$) and electrostic attraction (Cl... H_2N).

The formed complexes may be represented by the following formulae:





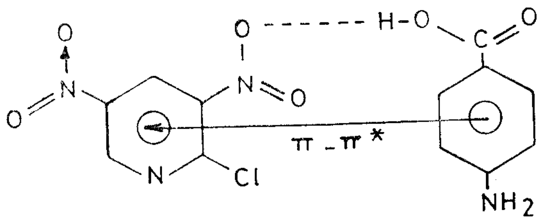


Table 2. IR bands of CT complexes of 2-chloro-3,5-dinitropyridine with aromatic amines

Donor No.	Substituent	Colour	m.p. °C	Acceptor Part						Donor Part				
				νCH		NO_2		γCH	C–Cl	νNH_2		νCH		γCH
				asym.	sym.	asym.	sym.			asym.	sym.	asym.	sym.	
a	H	orange	191	3086	—	1546	1332	777	—	3297	—	—	—	833
b	o–Cl	yellow	185	3103	2939	1513	1331	768	634	3314	—	—	—	832
c	m–Cl	yellow	163	3097	—	1583,1517	1336	784	696	3299	—	—	—	864,834
d	p–Cl	brownish orange	155	3097	—	1518	1328	761	690	3316	—	—	—	829
e	p–Br	brown	207	3086	—	1474,1545	1331	766	701	3300	3211	—	—	830
f	p–I	orange	214	3087	—	1571,1539	1329	765	699	3303	3208	—	—	827
g	o–CH_3	yellowish orange	181	3067	2943	1519	1335	762	619	3483	3301	3104	—	827
h	m–CH_3	orange	146	—	2929	1518	1336	761	696	3316	—	3102	—	869,833
i	p–CH_3	scarlet red	173	3092	—	1547,1520	1330	765	616	—	3301	—	—	827
j	o–OCH_3	majenta red	206	3028	2994	1549	1331	757	677	3293	—	3098	—	830
k*	o–COOH	orange	241	3079	—	1582	1331	757	657	—	—	—	—	827
l**	p–COOH	orange	> 280	3079	2979	1593,1507	1352	764	689	3321	—	3124	—	860,832
m	o–NO_2	orange	168	3097	2913	1591,1501	1339	781	661	—	3290	—	—	838
n	m–NO_2	yellow	169	3077	—	1527	1338	811,738	622	3312	—	3122	—	869
o	α–naphtyl	scarlet red	244	3094	—	1516	1331	778	668	3314	—	—	—	834

bands of free acceptor

νCH		νNO_2		γCH	C–Cl
asym.	sym.	asym.	sym.		
3184,3123	3076	1542	1348	823,749	651

* broad band 3250–2600 with numerous minor peaks.

** broad band 3124–2500 with numerous minor peaks.

The electronic absorption spectra

The electronic absorption spectra of the CT complexes under investigation as nujol mull Fig. (1), display a broad band within the

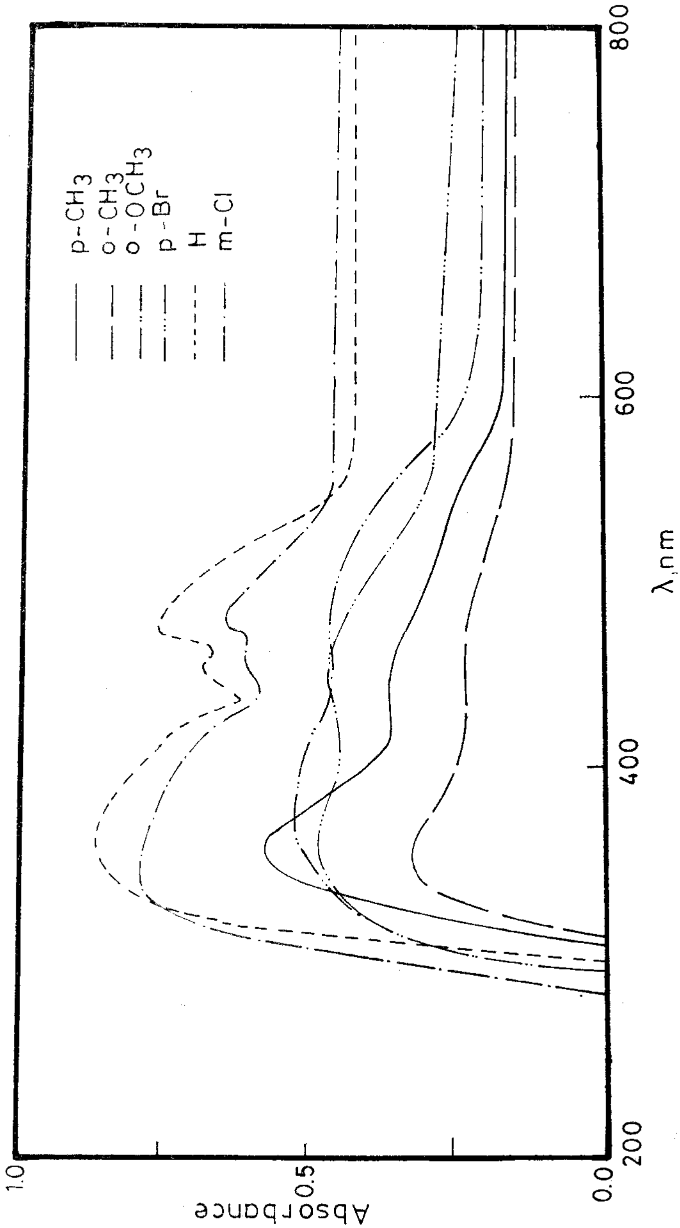


Fig. 1. The electronic absorption spectra of the CT complexes under investigation as nujol mull

wavelength range 419–483 nm. This band is ascribed to charge transfer interaction of the $\pi-\pi^*$ type. The energy of charge transfer interaction was obtained from the absorption spectra using the relation:(10)

$$E_{CT} = \frac{1239.9}{\lambda_{CT}\mathrm{nm}}$$

The results are given in table (3).

Table (3). Electronic absorption spectra of CT complexes of 2–Cl–3,5–dinitropyridine

Compound No.	X	CT band ($\pi-\pi^*$)		$n-\pi^*$ (NO_2)
		λmax, nm	E_{CT} eV	λmax, nm
a	H	479.1	2.588	359.1
c	m–Cl	478.2	2.593	347.4
d	p–Cl	480.9	2.578	357.9
e	p–Br	476.0	2.605	365.0
f	p–I	483.0	2.567	363.5
g	o–CH_3	480.0	2.583	357.9
h	m–CH_3	463.0	2.678	354.0
i	p–CH_3	466.6	2.657	354.0
j	o–OCH_3	436.5	2.841	366.6
k	o–COOH	420.3	2.950	368.1
l	p–COOH	461.0	2.690	396.9
n	m–NO_2	484.5	2.559	360.0
L	α–naphthyl	419.0	2.959	389.0

Most complexes display a second more intense broad band within the wavelength range 347–396 nm. This band is ascribed to $n-\pi^*$ transition within the nitro group in free acceptor (270 nm) and it involves the excitation of an oxygen lone pair electron into an unoccupied π–orbital. Such transition is sensitive to substitution and association. In almost all cases the transition is red shifted on complex formation denoting the invoking of the NO_2 group of the acceptor into hydrogen bond formation and / or $n-\pi^*$ interaction with the donor.

Calculation of the electron affinity (E_A) of the acceptor:

The electron affinity of 2-chloro–3,5–dinitropyridine is calculated from electronic absorption spectral data using Briegleb equation(11)

$$E_{CT} = Ip - E_A - C$$

where E_{CT} = energy of the charge transfer of complex
Ip = ionization potential of the donors.
E_A = electron affinity of the acceptor.
C = coulombic forces between the electron transfered and the positive hole left behind taken as 4.7 eV(10).

The results are given in table (4). The electron affinity of the acceptor ranges from 1.792 to 0.122 eV.

Table (4). Electron affinity of the acceptor.

Compound No.	X	E_{CT} eV	I*p eV	E_A eV
a	H	2.588	7.7	0.412
d	p–Cl	2.578	9.07	1.792
e	p–Br	2.605	8.98	1.675
f	p–I	2.567	8.73	1.463
h	m–CH_3	2.678	7.50	0.122
n	m–NO_2	2.559	8.70	0.841

* Ip values as taken from (12).

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