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Preparation and IR-Spectroscopic Study of Charge Transfer Complexes of Naphthalene Derivatives with Some Tri- and Di-Nitrobenzenes

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The charge transfer complexes of naphthalene and some of its derivatives with some trinitro- and dinitrobenzenes are prepared and investigated by ir-spectroscopy. The shifts in the bands due to functional groups as well as the γ_{CH} bands of both donor and acceptor are found to be indicative for the type of bonding in the charge transfer complex.

(Keywords: Charge transfer complexes, synthesis and IR-spectra)

Darstellung und IR-spektroskopische Untersuchungen an Charge Transfer Komplexen von Naphthalinderivaten mit Di- und Tri-nitrobenzolen

Aus den Verschiebungen der Bandenlagen bei der Komplexierung, bzw. aus der Abhängigkeit der Bandenlagen von den funktionellen Gruppen, wird der Bindungstyp der Charge-Transfer-Komplexe ermittelt.

Introduction

Charge transfer complexes (C.T.C.) of trinitrobenzene derivatives with aromatic compounds were the subject of several investigations[1–4]. The formation of molecular complexes of the C.T. type is generally favoured when the

$$D + A \rightleftharpoons D \ldots . A \rightleftharpoons D^{+} \ldots . A^{-}$$

donor molecule (D) has a low ionisation potential while the acceptor molecule (A) has a high electron affinity. The reaction is thus facilitated when (D) has electron releasing substituents and (A) has electron withdrawing ones. These conditions were found to be fullfilled with symmetrical trinitrobenzen derivatives as acceptors and many aromatic compounds as donors.

Recently[5], the formation of (C.T.C.) between a series of aromatic amines and 3,5-dinitrobenzoic acid was reported. This investigation revealed that the existence of three nitrogroups on the benzene ring is not a criterion for the formation of (C.T.C.). Thus, it seemed of interest to investigate the acceptor properties of some dinitrobenzene derivatives with various substituent groups viz 3,5-dinitrobenzoic acid (**3**), 3,5-dinitrosalicylic acid (**4**) and 2,4-dinitrophenol (**5**). As donor molecules, naphthalene and some of its derivatives with donor substituents are used in virtue of the lower π-ionisation potential of these compounds in comparison to benzene derivatives[6]. For sake of comparison, the C.T.C. of these donors with picric (**1**), and picryl chloride (**2**) are also considered.

Experimental

All materials used were pure laboratory (B.D.H.) chemicals. The C.T.C. were obtained by mixing a hot solution of the donor (0.01 mol in the least amount of hot ethanol) with an equivalent of the acceptor. The (C.T.C.) were either separated immediately or on standing; the soluble compounds were recrystallised from ethanol while the insoluble ones were just reboiled with ethanol to ensure freeing from contaminations of unreacted products. The compounds obtained displayed various colours depending on the donor and acceptor used. The products were then filtered off, dried and their melting points determined (C.f. Tab. 1 and 2).

The ir-spectra of the solid compounds were recorded on a Unicam SP 1000 infrared spectrophotometer applying the KBr wafer technique. The KBr used was finely powdered before mixing with the C.T.C. to minimise the time of grinding, thus avoiding the adsorption of the C.T.C. on the KBr surface[7,8] and preventing their decomposition to their components[9].

Results and Discussion

On considering the behaviour of the donor molecules under investigation, these compounds can be classified into two main groups. The first group comprises naphthalene (**a**), 1-methyl-naphthalene (**b**), α-naphthol (**c**) and β-naphthol (**d**), while the second one includes α-naphthylamine (**e**) and β-naphthylamine (**f**).

The behaviour of each category is considered alone. The discussion of spectral shifts due to C.T.C. formation is mainly confined to the OH, NH_2, $C=O$, NO_2 and γ_{CH} bands, since these display the most obvious shifts[2–4].

C.T.C. of Naphthalene, Methyl-naphthalene and α- or β-Naphthol

These four donor molecules are deprived of a basic centre and hence are capable of forming one type of C.T.C. involving the π-π^* bonding.

Table 1. Characteristic IR-bands of C.T.C. of naphthalene, methylnaphthalene [illegible]

Acceptor	Colour	M. p. °C	ν_{OH}	C=O	NO_2 Asym.	NO_2 Sym.	γ_{CH} Acceptor	γ_{CH} Donor
C.T.C. of naphthalene (for naphthalene $\gamma_{CH} = 785\ cm^{-1}$)								
1	Yellow	142	3100		1560, 1552, 1540	1347	780	800
2	Lemon yellow	82			1553, 1540	1350	750	791
3	Pale yellow	186	3400	1703	1550, 1543	1360	920, 805, 718	792
4	Lemon yellow	145	3450, 3200	1690	1540	1346	915, 810	790
5	Lemon yellow	96	3270		1540	1348	915, 820	790
C.T.C. of methyl naphthalene ($\gamma_{CH} = 795, 785\ cm^{-1}$)								
1	Golden yellow	138	3100		1560, 1555, 1540	1345	778	804, 780
2	Pale yellow	86	—	–	1553	1347	775	798, 775
3	Yellow	195	—	1700	1552	1350	920, 805, 720	798, 776
4	Yellow	139	3440, 3200	1690	1560, 1545	1348	915	803, 788
5	Yellowish green	95	3270	—	1548, 1540	1350 1335	918, 820	820
C.T.C. of α-naphthol ($\nu_{CH} = 3300\ cm^{-1}$, $\gamma_{CH} = 790, 765\ cm^{-1}$)								
1	Brick-red	193	3095	-	1560, 1550, 1540	1348	776	803, 778
2	Orange-brown	112	3440	—	1550, 1540	1345	760	793, 770
3	Yellowish green	192	3470	1710	1550, 1540	1348	918, 803, 715	798, 775
4	Pale-brown	166	3440, 3300	1700	1548	1348	910	802, 778
5	Pale-brown	99	3450, 3270	—	1548	1348 1335	915, 815	795, 775
C.T.C. of β-naphthol ($\nu_{CH} = 3280\ cm^{-1}$, $\gamma_{CH} = 845, 815, 743\ cm^{-1}$)								
1	Orange	155	3100	—	1560, 1550, 1540	1348	778	872, 823, 760
2	Golden yellow	103	3490	—	1553, 1540	1348	770 (sh)	853, 821, 753
3	Orange yellow	198	3480	1712	1546	1348	920, 805, 718	855, 825, 755
4	Yellow	124	3480, 3300	1698	1540 (b)	1345	918, 820	855, 820, 743
5	Golden yellow	93	3430, 3280	—	1540 (b)	1350 1335	918, 812	850, 818, 742

Table 2. *Characteristic IR-bands of C.T.C. of naphthylamines*

Acceptor No.	Colour	M.p. °C	ν_{NH_2} or $\nu_{NH_3^+}$	ν_{OH}	C=O	NO_2 Asym.	NO_2 Sym.	γ_{CH} (Acceptor-part)	γ_{CH} (Donor-part)
C.T.C. of α-naphthylamine ($\nu_{NH_2} = 3420, 3350, 3240\ cm^{-1}$, $\gamma_{CH} = 792, 770\ cm^{-1}$)									
1	Yellowish green (s)	184	2800, 2600	—	—	1540	1340	773	790, 775
2	Scarlet red (M.C.)	198	3270	—	—	1550, 1540	1350	770	800, 785
3	Brick red (M.C.)	199	3400	3480	1710	1551	1348	915, 805, 715	792, 774
4	Olive green (s)	198	2880, 2600	3230	1695	1538	1352	892, 810	810, 792
5	Reddish brown	108	2940, 2800	—	—	1549	1348 1330	908, 815	792, 775
C.T.C. of β-naphthylamine ($\nu_{NH_2} = 3400, 3315, 3220\ cm^{-1}$, $\gamma_{CH} = 815, 755, 743\ cm^{-1}$)									
1	Yellowish (brown)	200	2850, 2700	—	—	1550	1347	777	800, 780
2	Orange (brown)	117	3280	—	—	1550, 1540	1348	775	800, 775
3	Yellow	201	—	—	—	1550	1350	920, —, 718	798, 775
4	Yellow	219	2850, 2600	3250	1698	1540	1350	923, 810	810, 790, 768
5	Pale (brown)	100	2940, 2800	—	—	1550	1350 1335	918, 820	840, 742
Characteristic bands in the IR-spectra of the acceptors									
1	Picric acid			3110	—	1555, 1540, 1530	1350	784	
2	Picryl chloride			—	—	1553, 1540	1548	788	
3	3,5-dinitrobenzoic acid			3190	1707	1555, 1540	1350	923, 808, 727	
4	3,5-dinitrosalicylic acid			3570 3460 3100	1700 1675	1540, 1530	1349	925, 825	
5	2,4-dinitrophenol			3270	—	1540, 1520	1350	928, 825	

Such an interaction takes place through the transfer of an electron from the highest filled π-level on the donor molecule to the lowest vacant π^*-level on the acceptor one. Also, the possibility of intermolecular hydrogen bonding and n-π^* transfer in C.T.C. of naphthols should be considered.

The main changes in the spectra of the donor and acceptor molecules in the C.T.C. in comparison to the free components can be summarized as follows:

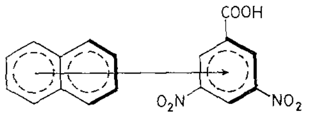
(1) The ν_{OH} bands of the phenolic group still retain their existence though being slightly shifted to lower wave numbers on C.T.C. formation. The increased electron density on the ring of the acceptor molecule in the C.T.C. favours the charge migration from this ring to the NO_2-groups hence leading to a stronger intramolecular hydrogen bonding with the phenolic OH-groups. A similar behaviour is observed for the carboxylic OH-group of 3,5-dinitrosalicylic acid **4**. On the contrary, for 3,5-dinitrobenzoic acid **3**, the ν_{OH} band is shifted to higher wave numbers, which originates from the destruction of the intermolecular hydrogen bonding, existing in the solid lattice of **3** alone, through C.T.C. formation. The band of naphthols is largely shifted to higher wave numbers but are 160–150 cm^{-1} less than those of the nonbonded OH-group. The shift of the ν_{OH} band to higher wave numbers is explained by the transformation of the dimers into monomeric structures on C.T.C. formation.

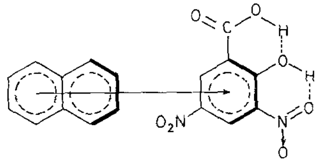
However, the lower value in comparison to free OH-groups would originate from the increased charge migration from the OH-groups to the naphthalene ring as a result of C.T. from it to the acceptor molecule. Also the possibility of intermolecular hydrogen bonding between the OH- and NO_2- or C=O-groups facing it on the acceptor molecule as well as n-π^* interaction might be the origin of the lower value for the ν_{OH} band in the spectrum of the C.T.C.

As a matter of fact, C.T.C. of naphthols have mostly intense reddish to brownish colours contrary to naphthalene and methyl naphthalene which yield yellow compounds. The difference in colour is due to the existence of the OH-group, which favours the interaction of the n-π^* type. This latter involves the transfer of an n-electron from the OH-group to a vacant π^*-level on NO_2- or C=O-group facing it on the acceptor molecule[1–3].

(2) The C=O-band of **3** displays a shift to lower wave numbers in case of **a** and **b** which is in accordance with increased charge density on the acceptor ring; this increases the mesomeric interaction between the ring and the C=O-group. On the contrary the C=O-band in the spectra of naphthol C.T.C. are shifted to higher values which is characteristic of C.T.C. involving n-π^* interaction[2,5].

The two C = O-bands in the spectrum of **4**, which was ascribed to the existence of two rotational isomers, are turned to a single one in those of the C.T.C. If **4** would behave in an identical manner as **3**, then the isomer characterized by the band at 1,695 cm^{-1} would be only dominating in the C.T.C. while the other isomer is no more existing. Accordingly, the naphthalene—3,5-dinitrobenzoic acid and naphthalene—3,5-dinitrosalicylic acid C.T.C. can be formulated as follows:





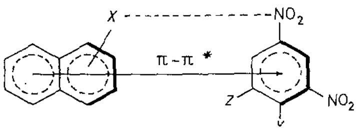
(3) The NO_2-bands of all acceptors in the C.T.C. of this group of donors still retain their appearance in the simple compounds but are slightly shifted to higher wave numbers. The splitting of the asymmetric NO_2-bands in case of some C.T.C. with **1**, **2** and **3** becomes more obvious denoting a higher differentiation of the energy states of the NO_2-groups. This behaviour was observed previously with C.T.C. of aniline derivatives with some trinitrobenzenes[3,4].

(4) The γ_{CH} bands of the acceptor molecules are shifted to lower wave numbers whereas those of the donor molecules are displaced in the opposite direction. This shifts are indicative for π-π^* interaction[2,4,5] leading to a decrease of the electron density on the naphthalene ring and its increase on that of the nitro compound. Although the magnitude of the shift is not very regular, yet the following order may be given:

(i) For one and the same acceptor, the shift in the γ_{CH} band of the donor molecule increases in the direction: naphthalene < methyl naphthalene < α-naphthol < β-naphthol.

(ii) For one and the same donor, the shift in the γ_{CH} band of the acceptor follows the order: Picryl chloride > picric acid > 3,5-dinitrobenzoic acid > 3,5-dinitrosalicylic acid > 2,4-dinitrophenol.

Accordingly, the magnitude of the shift in the position of the γ_{CH} band depends on the donor and acceptor character of the reacting components. The shift tends to be higher as the donor character of the naphthalene derivative increases and as well with increased acceptor character of the nitro compounds. The compounds formed can be generally represented as follows:



	1	**2**	**3**	**4**	**5**
Z	NO_2	NO_2	COOH	COOH	H
Y	Cl	OH	H	OH	OH

(for X = OH, n-π^* and intermolecular hydrogen bonding can take place).

C.T.C. of Naphthylamines

The C.T.C. obtained with naphthylamines have either reddish or yellowish colour depending on the acceptor and position of the NH_2-group in the amine (Tab. 1). The spectra of the reddish compounds can be considered as superposition of those of the free components and display the band shifts characteristic of the π-π^*, the n-π^* transitions and intermolecular hydrogen bonding. The spectral shifts are more or less identical to those of amines with low basicity with picric acid[3, 4] or 3,5-dinitrobenzoic acid[5], which reveals the formation of (C.T.C.) of the molecular complex type. This type of interaction would also be analogous to that in case of naphthols.

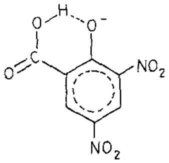
The spectra of the yellow compounds on the other hand, display drastic changes in comparison to the simple constituents which can be summerized as follows:

(1) The ν_{NH_2} bands within the (3,400-3,200 cm^{-1}) and the δ_{NH_2} band near 1,635 cm^{-1} as well as the ν_{OH} bands of the phenolic group in acceptors **1**, **4** and **5** or of the COOH-group of acceptor **3**, are no more observed in the spectra of the C.T.C. being replaced by those due to the NH_3^+-ion within the 3,000-2,500 cm^{-1} ($\nu_{NH_3^+}$) and 1,500-1,450 cm^{-1} ($\delta_{NH_3^+}$)[10]. This behaviour indicates that the yellow compounds belong to C.T.C. of the salt type.

(2) The asymmetric NO_2-bands display a less asymmetric appearance being mostly shifted to higher wave numbers. The more symmetrical envelope denotes that the NO_2-groups became more or less the same energy after proton transfer and the destruction of intermolecular hydrogen bonding between the NO_2- and OH-groups. The symmetric NO_2-bands are shifted slightly to lower wave numbers.

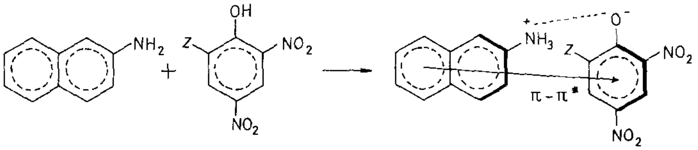
(3) For acceptor **4**, the C=O-band at 1,695 cm^{-1} are shifted to higher wave numbers in comparison to the free component. This shift denotes that the COOH-group retains its identity in the C.T.C. and that the phenolic group is the acidic centre participating in the proton transfer and salt formation. The shift of the C=O-band to higher values indicates that the interaction between the C=O- and OH-centers of the COOH-group is lowered probably through the formation of an intramolecular hydrogen bond between the carboxylic OH-group and the

phenolate ion. Thus the structure of the 3,5-dinitrosalicylic acid in the C.T.C. of the salt type would be as follows:



The C=O-band of acceptor **3** displays varied behaviour depending on the amine used. For α-naphthylamine C.T.C., the band shifts to higher wave numbers indicate that the COOH-group retains its identity in the C.T.C., which thus involves π-π* and n-π* interaction. The C.T.C. of β-naphthylamine with **3** is of proton transfer type and the C=O-band is largely shifted to lower wave numbers.

(4) The γ_{CH} bands of the naphthylamine component are shifted to higher wave numbers, while those of the acceptors are shifted to lower values. This behaviour is characteristic of the π-π* interaction which is expected in addition to the electrostatic forces between the phenolate and NH_3^+-ions. Thus the formation of the C.T.C. of the salt type may be formulated as follows:



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