Charge Transfer Complexes of Aromatic Nitrocompounds with Disubstituted Naphthalenes

I. Spectroscopic Investigation of the Donor Behaviour of the 2,6- and 2,3-Dimethylnaphthalene

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The charge transfer complexes of 2,3- (I) and 2,6-Dimethylnaphthalenes (II) as electron donors with tri- and di-nitrobenzenes as electron acceptors are prepared and investigated by element analysis, IR, ^{1}H nmr and electronic absorption spectroscopy. The results showed that I yields CT complexes of 1:1 type only while II is capable of forming 1:1 and 1:2 (donor : acceptor) compounds. The spectral characteristics of the CT complexes are pointed out and discussed. The difference in the donor behaviour between I and II is explained in the light of PPP-MO calculations.

Introduction

The formation of molecular complexes of the charge transfer (CT) type between electron acceptors such as dinitro- or trinitro-benzenes and π-electron donors was the subject of a vast number of interesting investigations [1–7]. These studies were mainly concerned with the determination of the ionisation potentials of the donors or the electron affinity of the acceptors, the evaluation of their stability consonants as well as the investigation of the type of bonding between the donor and acceptor molecules, especially in the solid lattice. It has always been considered that the CT complexes formed have the stoichiometric ratio 1 : 1 (donor : acceptor), however, a few studies reported the possible formation of 1 : 2 CT complexes with anthranilic acid [6], β-naphthylamine [7], benzidine [8] or Schiff bases [9].

In the present investigation, the CT complexes formed through the interaction of 2,3-dimethylnaphthalene(I) or 2,6-dimethylnaphthalene(II) with some trinitro- and dinitro-benzenes are investigated using IR, ^{1}H nmr and electronic absorption spectroscopy aiming to throw some light on the effect of the position of the substituents on the donor behaviour of the fused ring system. The difference in the behaviour is then discussed in the light of a PPP-MO calculation.

Experimental

All compounds used in the present investigation were pure laboratory grade chemicals from B.D.H. (London) or Schuchardt (Munich).

The solid 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) in the mole ratios of 1 : 1 or 1 : 2 (donor : acceptor). The solid CT complexes separated on mixing or on cooling down the reaction mixture. The CT complexes thus obtained were filtered off, washed with small portions of ethanol and dried under vacuum. The compounds were first subjected to elemental microanalysis to check their stoichiometry; the results of analysis for their C, H and N content were in accordance with 1 : 1 complexes for the two donors with all acceptors and 1 : 2 for donor II with acceptors 1–5, i.e. those with strong acceptor character.

The IR spectra of the CT complexes were recorded with KBr discs[4] using the UNICAM SP 1000 and BEKMANN IR infrared spectrophotometers.

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The ^{1}H nmr spectra were obtained in CCl_4 as solvent using the VARIAN T 60 nmr spectrometer. The electronic absorption spectra of some complexes were recorded by the aid of the UNICAM SP 8000 spectrophotometer applying the nujol mull technique. This is because the complexes under investigation are highly dissociated in the dilute solutions suitable for recording the spectra in the uv and visible regions. The concentrations favouring the existence of the CT complexes with measurable stability are too high to be measured on the instruments available.

The PPP-MO calculations were carried out using the computer machine at the Ain Shams University applying the parameters reported in [10].

Results and Discussion

The results of element analysis of the CT complexes under investigation showed that 2,3-dimethylnaphthalene(I) yields complexes with the stoichiometric ratio 1 : 1 only. The compounds isolated from the mixtures containing twice as many acceptors than donors were actually the 1 : 1 complex with some contamination by the free acceptor which is readily eliminated by a single crystallisation. For 2,6-dimethylnaphthalene(II) 1 : 1 complexes are formed with all acceptors used but 1 : 2 complexes are only obtained with trinitrobenzenes and dinitrobenzenes having strong acceptor properties. Thus, it seems that the stoichiometry of the complex formed depends on the nature of both the donor and acceptor. The spectral characteristics of each type of the CT complexes is discussed in the following.

A) The IR Spectra (Table I):

The IR spectra of the CT complexes of the 1 : 1 type display some interesting changes as gathered from the data in Table 1. The γ_{CH} bands of the acceptors, when not masked by the intense bands of the donors, display a shift of $(4 \div 14)$ cm^{-1} to lower wavenumbers as a result of the increased π-electron density on the ring of the acceptor molecule in the CT complex [1, 4]. On the contrary, the γ_{CH} bands of the donors exhibit a shift of $8-20$ cm^{-1} to higher values. These bands are generally broadened or splitted compared to those of the free donors. The broadening or splitting of the γ_{CH} bands of the donors in this type of CT complexes can be explained on the basis of obvious changes in the energy of the donating ring from that of the non-donating one. The CT interaction leading to increased π-electron density on the acceptor ring favoures a higher polarisation of the NO_2-groups and other substituents on the ring. As a matter of fact, the asym. as well as the sym. NO_2-bands of the acceptors are mostly shifted to lower wavenumbers on CT complex formation. Also the bands of the trinitrobenzenes appear more splitted in the spectra of the CT complexes.

For complexes of the 1 : 2 type formed with 2,6-dimethylnaphthalene, similar shifts are observed, though to a less extent compared to the 1 : 1 complexes. This denotes a lower magnitude of CT interaction in the 1 : 2 CT complexes compared to the 1 : 1 type. Also the γ_{CH} bands of the donor part are apparently sharper compared to the 1 : 1 complexes. Evidently the two rings of the donor interact with the two molecules of the acceptors in the 1 : 2 complex in an identical manner with the same energy, whereas in the 1 : 1 type the two rings exhibit varied π-electron densities. Also, the CT interaction in the 1 : 1 CT complex would be enhanced through a resonance interaction between the positive hole left behind the electron transfered to the acceptor ring and the second ring not participating in the CT effect.

B) The ^{1}H nmr Spectra:

The ^{1}H nmr spectra of the CT complexes compared to those of the free components reveal a shift of the signals due to the protons of the acceptors by $(0.03 \div 0.12$ ppm$)$ towards higher fields, whereas those corresponding to protons of the donor are shifted by $(0.02 \div 0.8)$ ppm down fields. These results can be interpreted on the basis of an increased shielding on the protons of the acceptors and a decreased one on those of the donors after the intermolecular CT has occurred. Also the shifts of the acceptor signals are higher for the 1 : 1 complexes than for the 1 : 2 ones, which can be due to stronger interaction in the 1 : 1 complexes since the donation power is concentrated on one acceptor molecule in the former case and distributed between two in the latter. For the donor signals, the shifts are contrary to those for the acceptors, i.e. they are higher for 1 : 2 complexes. For the 1 : 1

Table 1. Main bands in the IR Spectra of the CT complexes with acceptors forming 1 : 1 and 1 : 2 compounds.

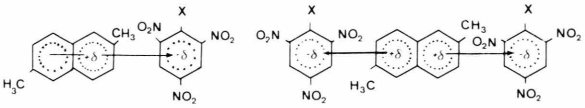
Donor	Stoichio-metry	Colour	m.p. °C	Asym. NO_2	Sym. NO_2	γ_{CH}
	Complexes with picric acid (1)					
	bands of free acceptor			1550, 1540, 1530	1350	915, 784
I	1 : 1	golden yellow	120	1550, 1535	1342	. . . , 780
II	1 : 1	canary yellow	95	1553, 1540 sh	1342, 1335	. . . , 770
II	1 : 2	golden yellow	135	1554, 1535 sh	1345	910*, 780
	Complexes with picryl chloride (2)					
	bands of free acceptor			1553, 1540	1348	918, 788
I	1 : 1	canary yellow	108	1550, 1535	1340	. . . , 783
II	1 : 1	golden yellow	138	1550, 1535	1342	913, 770 (sh)
II	1 : 2	yellow	95	1553, 1535	1345	915, 778
	Complexes of trinitrobenzene (3)					
	bands of free acceptor			1555	1345	913
I	1 : 1	canary yellow	122	1548, 1535	1340	. . .
II	1 : 1	yellow	151	1552, 1535	1342	910*
II	1 : 2	yellow	148	1550, 1535	1340	. . .
	Complexes of dinitrosalicyclic acid (4)					
	bands of free acceptor			1550, 1525	1350	925, 825
I	1 : 1	yellow	156	1525, 1505	1345	. . . , . . .
II	1 : 1	yellow	136	1540, 1530	1335, 1345	918*, . . .
II	1 : 2	brownish yellow	122	1545, 1535	1345	920*, . . .
	Complexes of dinitrobenzoic acid (5)					
	bands of free acceptor			1555, 1540	1350	823, 808, 727
I	1 : 1	pale yellow	173	1548, 1535	1341	. . . , 805*
II	1 : 1	pale yellow	163	1552	1340	. . . , 803, 718
II	1 : 2	pale yellow	173	1553, 1535	1345	. . . , 805, 722
	Complexes with 2,4-dinitrophenol (6)					
	bands of free acceptor			1540, 1520	1350	928, 825
I	1 : 1	yellow	68	1535, 1520	1345	923, 820 (sh)
II	1 : 1	canary yellow	84	1530, 1515	1340	922, 820
	Complexes with 2,4-dinitrotoluene (7)					
	bands of free acceptor			1550, 1540	1350	920, 825
II	1 : 1	pale yellow	61	1550, 1535	1345	915, 820
	Complexes with 1,3-dinitrobenzene (8)					
	bands of free acceptor			1548	1352	920, 905
I	1 : 1	pale yellow	56	1537	1343	912, 903
II	1 : 1	pale yellow	88	1537	1345	910 (broad)
	Complexes with 1-chloro-2,4-dinitrobenzene (9)					
	bands of free acceptor			1550, 1533	1353, 1335	
I	1 : 1	canary yellow	52	1545, 1530	1345, 1330 (sh)	915, 880, 845, 765
II	1 : 1	canary yellow	58	1540, 1530	1340, 1330 (sh)	912, 875, 835, 750

* Shoulder

complexes of (I), the signals due to the protons in positions 1 and 4 display the highest shifts whereas the signals of the protons in positions 6 and 7 exhibit the lowest changes. The signals of the CH_3 groups show apparently high shifts down fields. The ^1H nmr change in this case reflects high deshielding for the protons of the disubstituted ring; hence it would be the site contributing more to the CT interaction; most probably this ring would act as the donor site [11]. This is in accordance with previous conclusions based on MO calculations that for condensed ring systems, the ring carrying the electron donating substituent would be the origin of the CT interaction [12].

For the 1 : 1 complexes of (II) the signals of the aromatic protons tend to be less sharp and some of them even appear splitted. This results from the symmetry of the molecule in the free state which is not maintained for the 1 : 1 complex. The signal of the CH_3 group is most affected being almost doubled in the spectrum of the complex compared to that of the free donor. This behaviour can be explained by the assumption that the protons of the ring donating the charge to the acceptor are more deshielded in the complex and hence its signals would appear more shifted down field than those of the other ring. For the 1 : 2 complexes of (II), both rings are contributing equally to the charge migration and accordingly the charge distribution in both rings would be the same and the signals are sharper than for the 1 : 1 compounds.

The results obtained for the ^{1}H nmr spectra and the conclusions drawn therefrom are quite concordant with those gained from the IR spectra. Based on these results, the charge migration interaction for (I) and (II) can be formulated as follows:



C) The Electronic Absorption Spectra:

The electronic absorption spectra of the CT complexes under investigation as nujol mull display only one CT band within the (415 ÷ 475) nm region corresponding to the $\pi - \pi^*$ intermolecular CT interaction. This point of view is supported by the calculation of the energy of the CT band for the complexes and comparing it with the experimental results. The E_{CT} for the CT complexes with trinitrobenzene are calculated using the relation

$$E_{\mathrm{CT}} = I_{\mathrm{P}} + (E_{\mathrm{A}} - 4.7) .$$

The ionisation potentials of the donors were determined using the relation given by Briegleb [13]

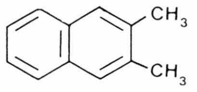
$$I_{\mathrm{P}} = 5.11 + 0.701\, \nu_0 ,$$

in which ν_0 is the frequency corresponding to the lowest $\pi - \pi^*$ transition in the electronic absorption spectrum of the free donor.

The values obtained for I and II were found to amount to 8.19 and 8.09 eV, respectively. From these values, the E_{CT} for the complexes with trinitrobenzene amounts to 2.79 and 2.66 eV for the two donors which is not much different from the experimental values 2.89 and 2.86 eV.

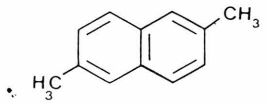
The interesting observation with the electronic absorption spectra is the blue shift of the CT band in the spectra of the 1 : 2 complexes (10 ÷ 15) nm relative to the CT bands in the spectra of the 1 : 1 complexes. This shift denotes a higher CT energy for the 1 : 2 complexes relative to the 1 : 1 type. This would result from the blocking of the resonance between the two rings in the 1 : 2 complexes.

The results of the present investigation show that 2,3-dimethylnaphthalene can form only 1 : 1 complexes where the ring carrying the two methyl groups acts as the donor center. On the other hand, the 2,6-dimethylnaphthalene is capable of forming 1 : 1 and 1 : 2 CT complexes. This behaviour can be explained by calculating the bonding coefficient for the two rings of both donors applying PPP-MO calculations which are found to be as follows:



$\sum_{1}^{4} c_i^2$ (HOMO) = 0.5004

$\sum_{5}^{8} c_i^2$ (HOMO) = 0.4804



$\sum_{1}^{4} c_i^2$ (HOMO) = 0.4832

$\sum_{5}^{8} c_i^2$ (HOMO) = 0.4832

These values indicate that in case of I donation would largely occur from the substituted ring carrying a higher electron density in the frontier orbital. The lower bonding coefficient of the nonsubstituted ring makes it difficult to donate an electron to an acceptor molecule, especially after the electron transfer from the substituted ring. Thus donor I can form only 1 : 1 complexes. On the contrary, for II the two rings have similar bonding coefficients and accordingly they exhibit equal probabilities to act as electron donors; and hence the formation of 1 : 1 and 1 : 2 complexes with II is quite probable.

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