NOTE

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Molecular complexes of toluidines and phenetidines with tetracyanoethylene and tetracyanoquinodimethane

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Abstract : Spectra of charge-transfer molecular complexes of some substituted aromatic amines with tetracyanoethylene and tetracyanoquinodimethane have been measured. The role of molecular structure of the electron donor and electron acceptor compounds on the formation of charge-transfer complex is discussed.

Keywords : Charge transfer, formation constants, free energy change.

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Participation of aniline and substituted anilines in intermolecular charge transfer as π-donors and dependence of π-donating property on substituent groups in the ring have been studied by previous authors [1-4]. This note reports the effect of substituent methyl and ethoxy groups in toluidines and phenetidines on π-electronic density in the rings and CT complex formation with TCNE and TCNQ.

TCNE was crystallized twice from chlorobenzene and then sublimed. TCNQ, the toluidines and the phenetidines were purified by sublimation. The electronic absorption spectra were recorded using 1 cm matched quartz cells at 295°K with Shimad Zu Model 210A spectrophotometer. A typical spectrum is shown in Figure 1.

The association equilibrium constants K of the charge transfer complexes were calculated from [5]

$$(A)xl/\log (I_o/I) = 1/Kx\varepsilon_{max} \times [D] + 1/\varepsilon_{max}$$

where the terms have their usual significance. The free energy change ($-\Delta F$) and the energy of CT bond formation ($-\Delta H$) were calculated from the familiar relations,

$$\Delta F = -RT \ln K$$

$$\Delta H = -Rd \ln K/d(1/T).$$

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The stoichiometry of all complexes were determined by spectrophotometric molar ratio and continuous variation methods [6,7]. The representative results shown in Figures 2 and 3, reveal that stoichiometry of CT complex is 1 : 1. The apparent formation constants were determined from[8,9]

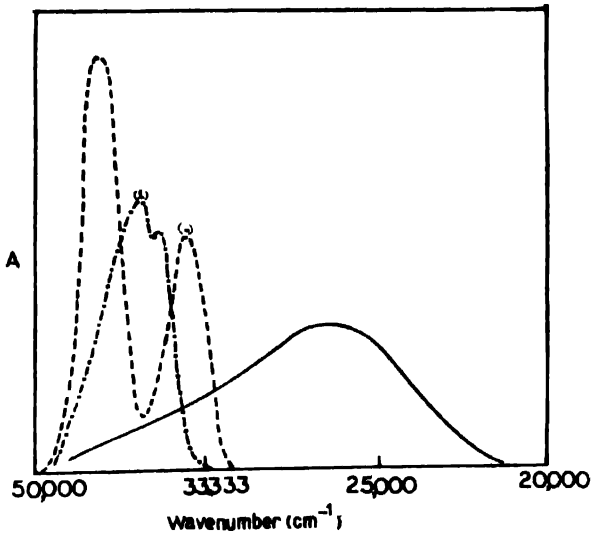

Figure 1. Electronic absorption spectra of (1) electron acceptor TCNE (10^{-4}M), (—●—) (2) electron donor, *o*-phenetidine (2×10^{-4}M), (- - - -) (3) TCNE-*o*-phenetidine CT complex (—) at 295°K

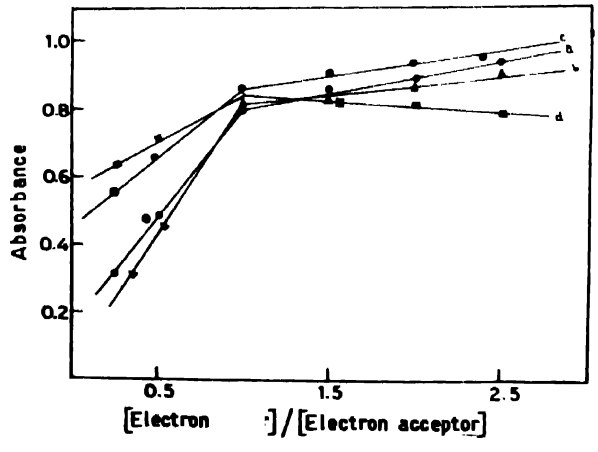

Figure 2. Molar ratio method for the CT comples (a) *o*-toluidine-TCNE, λ_{max} = 335 nm, total concentration = 0.0035M, (b) *p*-toluidine-TCNE, λ_{max} = 350 nm, total concentration =0.0031M, (c) *o*-phenetidine-TCNE, λ_{max} = 374 nm, total concentration = 0.0028M, (d) *p*-phenetidine-TCNE, λ_{max} = 360 nm, total concentration = 0.0028M.

$$K_f = (A/A_m)/(1 - A/A_m)^2 \times C$$

where A_m = limiting absorbance corresponding to maximum formation of complex, A = absorbance at electron donor concentration C.

Absorption spectra of mixture of the donors toluidines and phenetidines with the acceptors, TCNE and TCNQ show new maxima on the long wave length side of the characteristic absorption bands of the constituents in methylene chloride solution. Formation of CT complex is confirmed from the broadness of the new absorption bands and colour of the solution.

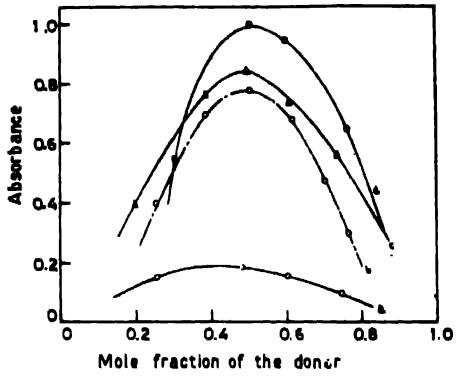

Figure 3. Continuous variation method for the CT complex (a) *o*-toluidine-TCNE, λ_{max} = 335 nm, total concentration = 0.0035M, (b) *p*-toluidine-TCNE, λ_{max} = 350 nm, total concentration = 0.0031M, (c) *o*-phenetidine-TCNE, λ_{max} = 374 nm, total concentration = 0.0028M, (d) *p*-phenetidine-TCNE, λ_{max} = 360 nm, total concentration = 0.0028M

Table 1. Absorption wavelength λ_{max}, molar extinction coefficient ε_{max} and transition energies E_T for the absorption bands of CT complexes formed between the amines and TCNE, TCNQ in methylene chloride at 295°K, and the formation constant K_f.

Electron donor	Electron acceptor	λ_{max} (nm)	ε_{max} (lit.mol^{-1} cm^{-1})	Transition energy energy E_T (Kcal mol^{-1})	K_f (lit. mol^{-1})
o–toluidine	TCNE	335	1685	84.63	1.3×10^3
m–toluidine	TCNE	348	2425	82.61	1.5×10^3
p–toluidine	TCNE	352	2875	80.65	2.8×10^3
o–phenetidine	TCNE	374	2312	75.82	3.3×10^3
m–phenetidine	TCNE	340	3289	84.55	1.9×10^3
p–phenetidine	TCNE	360	2591	78.66	3.1×10^3
o–phenetidine	TCNQ	428	920	66.17	5.0×10^3
p–phenetidine	TCNQ	480	1330	59.07	8.0×10^3

Table 1 includes the absorption maxima (λ_{max}), molar extinction coefficient (ε_{max}), transition energy (E_T) and apparent formation constant (K_f) of intermolecular CT complex. The observed tendency of electron donor amines to form CT complex is $o < m < p$ in the case of toluidines and $m < p < o$ in the case of phenetidines. The intermolecular CT bonding energies ($-\Delta H$) and hence the stability of the complexes are in the order $p > m > o$, in the case of toluidines and $o > p > m$ in the case of phenetidines (Table 2).

Table 2. Thermodynamic parameters of TCNE complexes with aromatic amines in methylene chloride at different temperatures.

Temperature (°K)	K (lit. mol^{-1})	ε_{max} (nm) (lit. mol^{-1}cm^{-1})	$-\Delta F$ (Kcal/mol)	$-\Delta H$ (Kcal/mol)
		o-toluidine		
290.5	2.56	1470	0.542	
297.5	2.30	1562	0.491	1.818
305.5	2.17	1724	0.491	
		m-toluidine		
290.5	3.58	2083	0.742	
297.5	3.31	2272	0.706	2.117
305.5	3.04	2500	0.671	
		p-toluidine		
290.5	4.00	2500	0.797	
297.5	3.80	2631	0.786	3.111
305.5	3.41	3030	0.739	
		o-phenetidine		
290.5	6.60	1818	1.085	
297.5	5.37	2083	0.991	3.529
305.5	4.64	2439	0.929	
		m-phenetidine		
290.5	4.42	2941	0.851	
297.5	4.10	3030	0.831	1.886
305.5	3.77	3448	0.798	
		m-phenetidine		
290.5	4.91	2325	0.916	
297.5	4.57	2500	0.895	2.825
305.5	4.31	2631	0.887	

Table 3. Charge-transfer absorption maxima λ_{max}, for complexes of electron donor amines with TCNE in methylene chloride at room temperature (295°K) and the ionisation potential I^D of donors.

Electron acceptor	Electron donor	λ_{max} (nm)	$h\upsilon_{CT}$ (ev)	I^D(ev)
TCNE	*o*-toluidine	335	3.58	7.75*
	m-toluidine	348	3.44	7.75*
	p-itoluidine	352	3.40	7.65*
	o-phenetidine	374	3.20	7.45
	m-phenetidine	340	3.52	7.74
	p-phenetidine	360	3.33	7.57

* Reference [11]

The trend of CT complexation ability and formation constant may be related with the electron density at *o*-, *m*-, *p*-sites, due to methyl and ethoxy substitution in the phenyl ring. In toluidines, the inductive effect of methyl group tends to increase the electron density and

shows a greater effect in the para (σ = –0.17) than in the meta (σ = –0.069) or ortho position. Moreover in ortho-toluidine steric effect of the CH_3 group in the ortho position relative to $-NH_2$ group may hinder reaction and make it a weaker donor than the meta isomer. But with ethoxy group, the opposing inductive and tautomeric effects lead to σ values +0.15, –0.25, –0.35 in meta, para and ortho position respectively. The tautomeric effect specially increases electron density in para and ortho positions. The substantially large electron density in ortho position seems to play a large role in determining π-donor property of *o*-phenetidine in complex formation and more than compensates any ortho effect, which, however, may be smaller than in *o*-toluidine because the ethoxy group is linked with the ring through the sp^2–hybridized oxygen atom and the C_2H_5 group is rather away from the ring. Since high resonance interaction in the π-base leads to large delocalization of charge, the π-electron donor phenetidines having higher basicity are found to possess higher formation constant than the toluidines.

Examination of the spectra of complexes of *o*- and *p*-phenetidine with TCNE and TCNQ in methylene chloride medium shows that the absorption maxima of *o*-phenetidine-TCNQ and *p*-phenetidine-TCNQ complexes lie at longer wavelengths with respect to the maxima due to the corresponding complexes of the two phenetidines with TCNE. Since both TCNE and TCNQ contain four strong electron withdrawing cyano groups, the larger electron affinity of TCNQ should be ascribed to the planarity and symmetry of TCNQ structure. If the relative π-complexing ability of TCNE and TCNQ with *o*-phenetidine and *p*-phenetidine be examined with reference to the formation constants K_f (Table 2), it is noted that with respect to TCNE, π-base strengths of *o*- and *p*-phenetidine are nearly of the same order of magnitude but with respect to TCNQ, *p*-phenetidine is more basic than *o*-phenetidine. Intermolecular CT depends on the π-orbital overlap of the electron donor and electron acceptor molecules and it is necessary to take into account the molecular size, geometry, symmetry and steric factors which contribute to the overlap. Consideration of π-donor strength of the donor system only is not sufficient. Apparently planarity of rings and high symmetry of the interacting *p*–phenetidine and TCNQ molecules both having π–ring systems ensure large overlap. This cannot be said in connection with overlap between *p*–phenetidine and the π–acid TCNE which does not have π–ring structure.

Relation between charge transfer energy ($h\upsilon_{CT}$) of the lowest intermolecular CT bands and the ionisation potentials of the donors with a certain acceptor is of the form [10]

$$h\upsilon_{CT} = a \times I^D + b \qquad (1)$$

where *a* and *b* are constants for a given acceptor. Values of $h\upsilon_{CT}$ for the TCNE charge transfer complexes of the aromatic donors used to calculate *a* and *b* in eq. (1) are given in Table 2 together with reported values of ionisation potentials (I^D) of *o*–, *m*–, *p*– toluidines [11]. Analysis of the data by a least square method assuming the error to be in the measurement of $h\upsilon_{CT}$ gives *a* and *b* the values shown in eq. (2),

$$h\upsilon_c = 1.09 \times I^D - 5.00 \qquad (2)$$

Values of I^D of the toluidines in Table 3 recalculated from eq. (2) show that average difference between experimental and calculated values is 0.05 ev. From this eq. (2) we have calculated the I^D values of the donor phenetidines. There is a regularity in the relative values of transition energy and ionization potential (I^D) of the π-donors.

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