

π - π^* Molecular Charge Transfer Complexes of Antipyrine *Schiff* Bases with 1,4-Benzoquinone Derivatives as π -Acceptors

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Summary. Spectrophotometric studies of compounds formed by several substituted antipyrine *Schiff* bases as electron donors with 2,3-dichloro-5,6-dicyano-benzoquinone, chloranilic acid, and chloranil as electron acceptors have given results that are consistent with 1:1 charge transfer complexes. Transition energies, oscillator strengths, and dipole moments of the complexes as well as the effect of solvent upon their stability are discussed. Also their free energies and absorption cross sections have been determined.

Keywords. Antipyrines; 1,4-Benzoquinone; UV/Vis spectra; Charge transfer.

Charge-transfer-Komplexe *Schiffscher* Basen vom Antipyrintyp mit 1,4-Benzochinon-Akzeptoren

Zusammenfassung. Spektrophotometrische Untersuchungen von aus *Schiffschen* Basen des Antipyrintyps als Elektronendonatoren und 2,3-Dichlor-5,6-dicyanobenzochinon, Chloranilsäure und Chloranil als Elektronenakzeptoren gebildeten Verbindungen zeigen die Entstehung von *Charge-transfer*-Komplexen der Stöchiometrie 1:1. Neben der Berechnung von freien Energien und Absorptionsquerschnitten werden Übergangsenergien, Oszillatorstärken, Dipolmomente und der Einfluß des Lösungsmittels auf die Stabilität der Komplexe diskutiert.

Introduction

Although extensive studies have been performed on charge transfer complexes between nitrogen containing compounds and electron acceptors [1–4], there still remain many compounds whose charge transfer complexes have not yet been reported. Among them are antipyrine *Schiff* base derivatives which seem to be of particular interest with respect to complex formation with nitrogen containing heterocyclic compounds. Charge transfer complexes of some phenyl carbamates possessing local anesthetic activity as electron donors with chloranil as π -acceptor have also been investigated [5, 6].

In the present article, the charge transfer complexation of several substituted antipyrine *Schiff* bases with a number of π -acceptors studied with the aim to investigate their electron donating behaviour. Association constants (K), molar

extinction coefficients (ε), transition energies (E), free energies (ΔG^*), oscillator strengths (f), absorption cross sections (δ), and dipole moments (μ) are evaluated.

Results and Discussion

The association constants (K) and molar extinction coefficients (ε) of the CT complexes were determined by utilizing a rearranged form of the *Benesi-Hildebrand* [8, 9]:

$$[A] + [D] = \frac{\varepsilon L[A][D]}{d} - \frac{1}{K}$$

($[A]$, $[D]$: initial molar concentrations of acceptor and donor; L : path length (cm); d : optical density). The values of ε and K have been determined from the slope and the negative intercept, respectively, of the linear plot of $[A] + [D]$ against $\frac{[A][D]}{d}$ (Fig. 1). The values of the association constants together with the molar extinction coefficients for the CT complexes of **1–6** with **7–9** are shown in Table 1. The greater electron affinity of **7** compared to **8** and **9** [10] accounts for the higher stability of its complexes.

Free energy values were computed from the relation $\Delta G^* = -RT \ln K$. The complexes are found to have $-\Delta G^*$ values within the range of 0.79–4.10 $\text{kJ}\cdot\text{mol}^{-1}$, indicating a very weak nature of the complexes and spontaneous reaction between D^+ and A^- . The general trend shows that $-\Delta G^*$ increases as the electron affinity of the acceptor increases or the ionization potential of the donor decreases.

In Fig. 2, the coloured reaction product is presented on the example of the CT complex formed by compounds **1** and **8**.

The results in Table 1 reveal that the association constants do not follow the same trend as both λ_{max} and ε_1 ; they increase in the order $p\text{-OCH}_3 < p\text{-CH}_3 < \text{H} < p\text{-NO}_2 < m\text{-Cl}$. However, as reported by *Mulliken* [11], there must be a linear

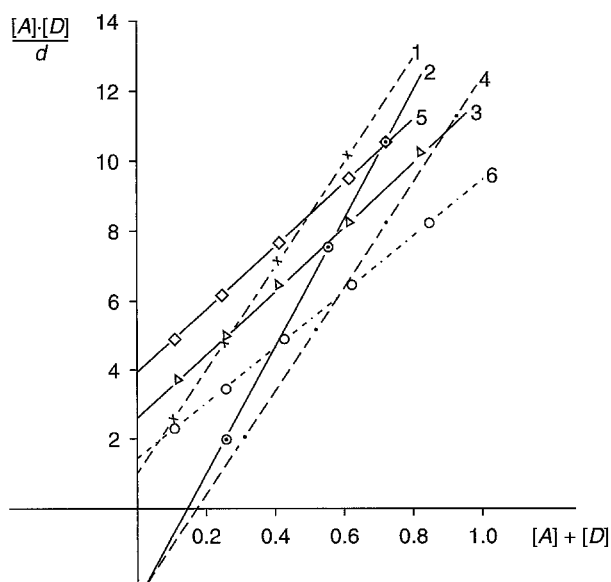


Fig. 1. Spectroscopic determination of equilibrium constants and molar extinction coefficients for charge transfer complexes of *Schiff* bases **1–6** with **7** at 25°C

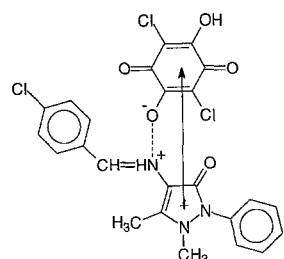


Fig. 2. Structural representation of charge transfer complex formed by compounds **1** and **8**

Table 1. Charge transfer spectroscopic data for CT complexes of antipyrine Schiff bases with 1,4-benzoquinones as π -acceptors (CH_2Cl_2 , 25°C)

	λ_{max} (nm)	K_{CT} (mol^{-1})	ϵ_{max} ($\text{mol}^{-1}\cdot\text{cm}^{-1}\cdot 10^4$)	E (eV)	f	μ	δ ($\times 10^8$)	ΔG^* ($\text{kJ}\cdot\text{mol}^{-1}$)	I_p (eV)
Donor: 1									6.4
7	330	1.43	2.58	3.77	0.13	7.92	3.7	0.80	
9	332	0.91	3.39	3.75	0.21	7.52	8.9	3.85	
8	330	0.625	6.24	3.77	0.13	9.27	2.6	2.89	
Donor: 5									7.6
7	330	0.22	2.20	3.77	0.15	9.42	4.05	1.13	
9	330	0.45	4.07	3.77	0.15	7.32	4.85	2.26	
8	325	1.3	1.55	3.83	0.14	6.33	5.5	0.96	
Donor: 2									7.8
7	415	0.21	3.68	3.0	0.45	6.83	2.85	1.00	
9	390	1.25	2.41	3.19	0.12	10.94	9.2	3.47	
8	327	0.22	2.55	3.80	0.53	5.92	2.55	1.51	
Donor: 6									6.8
7	395	0.21	5.22	3.15	0.14	2.91	1.33	3.93	
9	385	0.35	3.66	3.23	0.35	3.55	0.5	3.56	
8	425	0.23	5.94	2.93	0.12	3.26	5.96	3.06	
Donor: 3									7.4
7	330	0.25	2.81	3.77	0.13	4.97	5.5	4.10	
9	325	0.33	2.35	3.83	0.14	5.82	6.1	3.60	
8	325	0.38	2.82	3.83	0.14	6.84	4.1	2.68	
Donor: 4									7.7
7	370	0.41	1.71	3.89	0.15	5.81	6.5	3.98	
9	324	0.58	3.65	3.84	0.14	5.44	6.1	3.43	
8	425	0.23	5.94	2.93	0.12	3.26	5.96	3.06	

* The values have measured in CH_2Cl_2 at 25°C

coefficient for the CT complexes. This abnormal correlation between K and ϵ values in the present study may be caused by steric factors in the donor system. Consequently, the K values of the CT complexes of a series of donors with different acceptors can be used as an indicator of the electron affinities rather than the values of the wavelengths at maximum absorption.

The values of ionization potentials (I_p) are determined from electron absorption spectra of the free donor applying the relation $I_p = a + bv^\circ$; where v° is the energy of the HOMO-LUMO $\pi-\pi^*$ transition of the free donor in the gas phase which is taken approximately for that in solution (the solvation energy is low compared to electronic excitation energy), whereas a and b are constants amounting to 4.39 and 0.85 [12], 5.156 and 0.778 [13], or 5.11 and 0.701 [14].

The values of transition energy reported in Table 1 have been calculated from λ_{\max} of the electronic spectra applying the following equation:

$$E_{CT} = \frac{1243.667}{\lambda_{\max}}$$

Further information about the relative basicities of the donors under investigation can be inferred from the E values. A comparison of the transition energies of the charge transfer complexes with the ionization potential values of the electron donors forming these complexes reveals a regular relationship which is in accordance with the results obtained by *McConnel* [15]. The energy of charge transfer transitions is influenced by the hetero atom of the electron donor in such a way that the E value is proportional to the tendency of the hetero atom to donate its lone-pair in the electron delocalization.

The integrated intensity of the absorption bands was computed from the oscillator strength (f) and the transition dipole moment (μ) following approximative equations [10, 11]:

$$f = 4.32 \times 10^{-9} \varepsilon_{\max} \cdot v_{1/2}$$

$$\mu = 0.0958 [\varepsilon_{\max} \cdot v_{1/2} / v_{\max} \cdot v_{1/2}]^{1/2}$$

ε_{\max} is the molar absorbance at CT maximum, v_{\max} is the frequency of the CT maximum in cm^{-1} , and $v_{1/2}$ is the half width in cm^{-1} . It has been reported that, as the resonance interaction increases, f and μ should increase too. Consequently, the values of f and μ should decrease in the order of decreasing basicity of the donors. However, the results of Table 1 do not fit this trend. This irregularity of f and μ values perhaps stems from substituent effects of the electron donors 1–4.

Correlating oscillator strengths and absorption cross sections (δ), it was found that the values of f depend on the maximum values of δ and the band width according to equation

$$f = 1.13 \times 10^{12} \cdot \int_{v_1}^{v_2} \delta \, dv.$$

The stoichiometry of the CT complexes of the electron donors 1–4 with acceptors 7–9 was determined by application of *Job's* method of continuous variation [16] which provides symmetrical curves with maxima at a mole fraction of 0.5, confirming a 1:1 stoichiometric ratio. The linearity of the plots of the *Benesi-Hildebrand* equation further support this result.

The maximum absorption wavelength of the complex between 3 and 7 was measured in a number of solvents. Table 2 lists the results obtained, demonstrating that the position of the maximum absorption wavelength varies as much as 50 nm. The behaviour of the molecular complex in different solvents is similar to that of

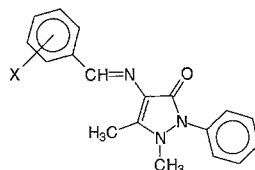
Table 2. Effect of solvents on the position of the maximum wavelength band of the complex [3/7] in different organic solvents at 25°C

	λ_{\max} (nm)	ξ_{\max} (mol ⁻¹ ·cm ²)	E (kJ·mol ⁻¹)	Dielectric constant
Methylene chloride	540	62	9.63	9.1
Benzene	532	87	9.75	2.3
Cyclohexane	523	18	9.92	2.5
Diethylether	520	100	10.00	4.3
Acetone	495	26	10.51	20.7
Chloroform	480	68	10.84	4.8
Carbon tetrachloride	460	60	11.30	2.2

aryl nitrones. In the case of the oxygen containing solvents, no correlation appears between the polarity of the solvents and the transition energy. This is attributed to the complexation between the solvent itself and **7**. In solvents without oxygen, the transition energy of the molecular complex decreases as the polarity of the solvent increases. Accordingly, the transition energy of the molecular complex is inversely proportional to the polarity of the nonoxygenated solvent.

Experimental

Antipyrine Schiff bases **1–6** were prepared as previously reported [3]. Their general formula is given below.



1: X = *p*-Cl; 2: X = *p*-OCH₃; 3: X = *m*-Cl; 4: X = *p*-OH; 5: X = *m*-NO₂; 6: X = H

2,3-Dichloro-5,6-dicyanobenzoquinone (**7**), chloranilic acid (**8**), and chloranil (**9**) were commercial samples. The purity of all samples was shown to be better than 99.8% by VPC. The solvents used (methylene chloride, benzene, cyclohexane, diethyl ether, acetone, chloroform, and carbon tetrachloride) were purified according to Ref. [7]. $3 \times 10^{-2}M$ stock solutions were prepared by dissolving accurately weighed amount of compound in the organic solvent. Five different concentrations were used to calculate K values at 30°C. The spectroscopic measurements were carried out within few minutes after mixing donor and acceptor solutions. Perken-Elmer λ -3B spectrophotometer.

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