

Molecular Complexes of Benzylideneanilines With Some π -Electron Acceptors

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Molecular complexes of some benzylideneanilines with tetracyanoethylene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and chloranil have been studied spectrophotometrically. The formation constants (K_{CT}) and extinction coefficients (ϵ_{CT}) of 1:1 molecular complexes have been determined at different temperatures by graphical and iterative procedures. The results show that the complexes are formed by the interaction of *n*-electron of azomethine nitrogen with the antibonding π -orbital of the acceptor, where the contribution of the dative structure $D^+ \cdot A^-$ to the ground state is high. From the energies of the charge transfer transitions, attempts have been made to determine the ionisation potentials of the donors. Effect of solvent on the K_{CT} and λ_{max} of the formed CT complexes has also been investigated and discussed.

Schiff bases containing the azomethine, because of lone pair of electron on azomethine nitrogen and electron donating nature of the double bond, possess basic properties and can be classified as *n*-electron donors; this is substantiated by the formation of *n*- π electron donor-acceptor (EDA) H-bonded molecular complexes of schiff bases with hydroxylic compounds.¹ It is known that benzylideneanilines undergo photooxidative ring closure to form phenanthridines where the photocyclization is suggested to take place via a *n*, π^* excited state². It is expected that the possible electron-donor acceptor (EDA) molecular complexes formed between schiff bases and electron acceptor compounds will play an important role in such photoreactions. Moreover schiff bases deserve special mention because of their relevance to many biologically important process. In view of this it is of interest to study the EDA complexes of azomethines. However, a literature search reveals very little information on the EDA complexes of azomethines. Barboy and Feitelson³ studied the charge transfer (CT) complexes of some polyene schiff bases with some aromatic electron acceptors. Presently we have determined the formation constants of EDA complexes of some benzylideneanilines with some π -acceptors, viz. tetracyanoethylene (TCNE), 2,3 dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and chloranil (CHL). Attempts have also been made to correlate these data with the nature of *n*-electron donors and π -acceptors as well as with the nature of the solvent employed. The ionisation potentials of the donors were calculated from the energies of the CT bands.

Materials and Methods

Benzylideneanilines, viz. 4-methoxybenzylide-

neaniline(I), 4-hydroxybenzylideneaniline(II), 4-N, N-dimethylaminobenzylideneaniline(III), 2-hydroxybenzylideneaniline(IV), benzylideneaniline(V), 4-nitrobenzylideneaniline(VI) and 4-chlorobenzylideneaniline(VII) were prepared by refluxing freshly distilled aniline with the corresponding aldehyde in ethanol for 2 hr. The solids obtained upon cooling were filtered off and recrystallized several times from ethanol. The purity of these schiff bases were checked by TLC and elemental analyses. Tetracyanoethylene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and chloranil (Fluka AG purum grade) were recrystallized twice from chlorobenzene, dry methylene chloride and dry benzene respectively. Chloroform (BDH, AR) was used as such. Dichloromethane and 1,2-dichloroethane were purified according to Vogel's⁴ procedure.

Stock solutions ($1 \times 10^{-2} M$) of each of the electron donor and acceptor compounds in appropriate solvents were prepared by weight. Solutions were always prepared afresh. Absorption spectra were measured with a Shimadzu UV-2005 spectrophotometer using 1 cm matched silica cells.

Solutions of the reactants at the desired temperature (accuracy $\pm 0.05^\circ C$) were mixed in glass stoppered test tubes under the condition: $[A]_0 > [D]_0$. Except in the case of III-DDQ and III-CHL, the other EDA molecular complex solutions were left from 0.5 to 1.5 hr before recording the electronic spectra. The electronic spectra of III-DDQ and III-CHL solutions were recorded immediately after mixing since their absorbances decreased with time probably due to the decomposition of their CT complexes. The concentration of electron donors used were: $2 \times 10^{-4} M$ for I and II; and $3 \times 10^{-5} M$

Table 1— λ_{\max} , Formation Constant (K_{CT}) and Molar Extinction Coefficient (ϵ_{CT}) Values for Various 1:1 EDA Molecular Complexes in Chloroform at Different Temperatures

Electron donor	Electron acceptor	λ_{\max} (nm)	$K_{CT}(\text{dm}^3\text{mol}^{-1})$				$\epsilon_{CT}^* \times 10^{-3}$ ($\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)
			10°	15°	20°	25°	
I	TCNE	378	57.8	41.8	25.8	22.1	10.7527
II	TCNE	377	104.0	89.3	77.3	59.6	15.7313
III	TCNE	443†	523.2	428.6	370.6‡	325.2	57.9173
III	DDQ	436	7636.9	6237.4	5662.9	4657.8	198.5446
III	Chloranil	436	73.8	59.7	53.3	38.41	13.5916

*Values at 10°C.

†445 nm in CH_2Cl_2 and 436 nm in $\text{C}_2\text{H}_4\text{Cl}_2$ at 20°C.

‡611.04 in CH_2Cl_2 and 1783.4 in $\text{C}_2\text{H}_4\text{Cl}_2$ at 20°C; corresponding ϵ_{CT} values are 34824 and 45702 ($\epsilon_{CT} = 54617$ for III-TCNE in CHCl_3 at 20°C).

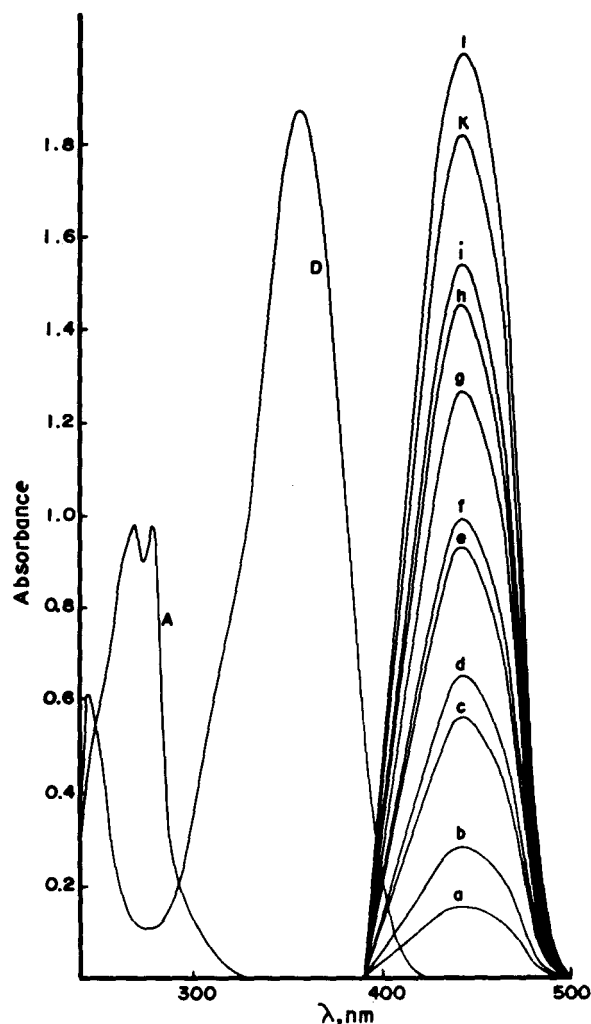


Fig. 1—Absorption spectra of $3 \times 10^{-5} M$ solution of III (D) in chloroform and of TCNE (A) and of mixtures containing fixed concentration of III ($3 \times 10^{-5} M$) and different concentrations of TCNE (same electron donor concentration used as blank) at 10°C. [TCNE conc: a, 1×10^{-4} ; b, 2×10^{-4} ; c, 4×10^{-4} ; d, 6×10^{-4} ; e, 8×10^{-4} ; f, 1×10^{-3} ; g, 1.5×10^{-3} ; h, 2×10^{-3} ; i, 2.5×10^{-3} ; K, 3×10^{-3} and l, $4 \times 10^{-3} M$]

for III. Electron acceptor concentrations used were: $0.1 - 9.0 \times 10^{-3} M$ for TCNE and CHL; and $3 - 6 \times 10^{-5} M$ for DDQ.

Results and Discussion

Formation constants

The electronic spectra of presently studied EDA molecular complexes are reported in Table 1. In the region 377-443 nm a new band appears, not displayed by either component alone, which can be attributed to a single intermolecular CT transition. Typical spectral results at 10°C are shown in Fig. 1 for III and/or TCNE chloroform solutions. Similar absorption spectra were observed in solutions of III with DDQ or CHL. Generally in the case of molecular complexes with TCNE or CHL, the electronic spectra were scanned against the same electron donor or CHL concentration as in the test solution, respectively. This is done to eliminate the possible overlap that may arise between the EDA molecular complex band and that of the electron donor or CHL. The appearance of a well-defined isobestic point in the spectra recorded for III-DDQ chloroform solutions (Fig. 1) confirms the fact that the studied EDA molecular complexes are of 1:1 type. The formation constants (K_{CT}) and molar extinction coefficients (ϵ_{CT}) of the different 1:1 EDA molecular complexes studied in the temperature range 10-25°C were determined using Scott equation⁵ (Eq. 1) under the condition: $[A]_0 > [D]_0$,

$$\frac{[D]_0[A]_0}{A} = \frac{1}{K_{CT}\epsilon_{CT}} + \frac{[D]_0 + [A]_0}{\epsilon_{CT}} - \frac{C}{\epsilon_{CT}} \quad \dots (1)$$

In Eq. (1) C is the concentration of 1:1 EDA complex. Iterative procedures along with the least-squares criterion were used to obtain the best values of K_{CT} and ϵ_{CT} at 10°, 15°, 20° and 25°C (Table 1).

Examination of the data given in Table 1 clearly indicates that the stabilities of the EDA complexes of the same donor follow the order of the electron

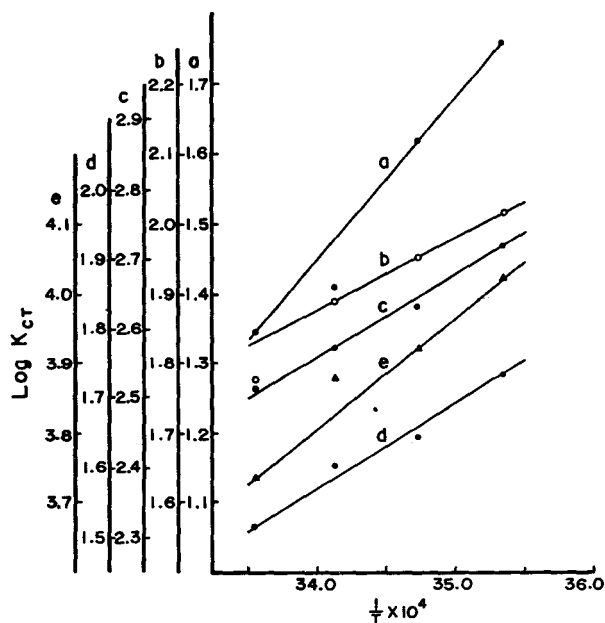


Fig. 2—Plots of $\log K_{CT}$ versus $1/T$ in $CHCl_3$ for the EDA molecular complexes [a, I-TCNE; b, II-TCNE; c, III-TCNE; d, III-DDQ; and e, III-CHL]

affinities of π -acceptors: DDQ > TCNE > CHL. On the other hand, stabilities of EDA complexes of various electron donors with the same π -electron acceptor (TCNE) increase with increase in strength of the basic character of the nitrogen of azomethine moiety, i.e. $4-OCH_3 < 4-OH < 4-N(CH_3)_2$. This behaviour strongly suggests that the formation of EDA complexes of benzylideneanilines (I-VII) with π -electron acceptors is mainly due to the transfer of a non-bonding electron π from the azomethine nitrogen to the antibonding π -orbital of the acceptor. Therefore, these EDA complexes can be considered as strong $n-\pi$ complexes as judged by the relatively high values of K_{CT} (cf Table 1). This is in accordance with the behaviour that, only loose molecular complexes are formed by π -donors, as the electron comes from a delocalized molecular orbital, while n -donors give rise to much stronger and more stable complexes as the interaction is more or less localized. It is worthwhile to note that no new bands are observed for the EDA complexes of electron donors IV-VII-DDQ/TCNE/CHL in chloroform solutions even on using high concentrations of the reactants or if the mixture solutions are left for a few days. This can be attributed to the expected low basicity of the azomethine nitrogen due to the presence of electron-withdrawing group 4-Cl or 4-NO₂ attached to the benzylidene moiety (compounds VI, VII) or due to the blocking of the nitrogen n -electrons through intramolecular H-bonding (compound IV).

Table 2—Transition Energy (E_{CT}), Enthalpy Change (ΔH) and b^2/a^2 Values of Intermolecular CT Band of EDA Complexes

Electron donor	Electron acceptor	E_{CT} (kJ mol ⁻¹)	$-\Delta H$ (kJ mol ⁻¹)	b^2/a^2	IP (eV)
I	TCNE	316.69	44.18 ± 1.20	0.139	9.58
II	TCNE	317.53	19.75 ± 2.10	0.062	9.59
III	TCNE	270.22	22.72 ± 0.63	0.084	8.93
III	DDQ	274.56	23.39 ± 0.96	0.085	9.20
III	Chloranil	274.56	30.17 ± 1.63	0.110	8.51

The ϵ_{CT} values for different CT molecular complexes studied are inconsistent with the K_{CT} values, since it is theoretically expected that the higher the K_{CT} of CT complex, the larger the intensity of CT band. However, unexpectedly very high ϵ_{CT} can be attributed to the CT transition borrowing intensity from that of the donor transition ($D-D^*$). This is due to the possible interaction between the CT state ($D^+ - A^-$) and the donor excited state D^* .

The enthalpy changes (ΔH) connected with the complex formation for the different EDA complexes studied have been determined from the formation constant values at a series of temperatures (Table 1) making use of Van't Hoff plots (Fig. 2). The data obtained are given in Table 2.

According to Mulliken^{6,7} the wavefunctions of the ground (ψ_N) and excited states (ψ_E) of 1:1 intermolecular CT complex can be expressed by Eqs. (2) and (3)

$$\psi_N = a\psi_0 + b\psi_1 \quad \dots (2)$$

$$\psi_E = a^*\psi_1 + b^*\psi_0 \quad \dots (3)$$

where ψ_0 and ψ_1 are the wavefunctions of the non-bonding structure (D,A) and CT dative structure $D^+ - A^-$ respectively. The ratio between the coefficient of the dative bond and the non-bond wavefunctions is given by the relation (4)^{6,7}.

$$\frac{\Delta H}{h\nu} = \left(\frac{b}{a}\right)^2 \quad \dots (4)$$

The calculated values of this ratio (Table 2) indicate that the contribution of the dative structure to the ground state is relatively high. This is inconsistent with the strong nature of the studied EDA complexes.

Ionisation potentials of the electron donors

Attempts have been made to determine the ionisation potentials (IP) of benzylideneanilines (I-III) using the empirical equations derived by Aloisi and Pignataro⁸ (see Eqs. 5-7).

$$IP(eV) = 5.00 + 1.53 \times 10^{-4} \nu_{\text{CHL}} \text{ cm}^{-1} \quad \dots (5)$$

$$IP(eV) = 5.21 + 1.65 \times 10^{-4} \nu_{\text{TCNE}} \text{ cm}^{-1} \quad \dots (6)$$

$$IP(eV) = 5.76 + 1.5 \times 10^{-4} \nu_{\text{DDQ}} \text{ cm}^{-1} \quad \dots (7)$$

Although these empirical equations were obtained for complexes of aromatic π -donors, good results were obtained on applying these equations to π -aromatic electron donors^{9,10} also. The values obtained are recorded in Table 2. However, IP values for benzylideneanilines are not available in literature. Generally the IP values for I-III are inconsistent with the corresponding K_{CT} values of their EDA complexes with TCNE. Furthermore, the IP values of electron donor III in the three π -electron acceptor complexes do not differ significantly suggesting that the donor orbital involved in the CT transition is the same for all these electron acceptors used.

Effect of solvent

The K_{CT} values have been calculated for the III-TCNE molecular complexes at 20°C in CHCl_3 , CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$ (Table 1). It is evident that K_{CT} increases as the dielectric constant of the solvent increases ($D = 4.806$, 9.08 and 10.65 , respectively for CHCl_3 , CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$). This behaviour can be explained on the principle that the dative structure ($\text{D}^+ - \text{A}^-$) would be more stabilized in solvents of high dielectric constant, owing to increasing dipole-dipole or dipole-induced dipole interactions. Accordingly the contribution of the dative structure

($\text{D}^+ - \text{A}^-$) to the ground state increases as the dielectric constant of the solvent increases.

The little red shift observed in the λ_{max} of CT complex band on changing the solvent from CHCl_3 to dichloromethane, can be explained on the principle that for strong CT complexes, the difference in dipole moment between the ground and excited state is expected to be small. Accordingly one might expect that increase in the dielectric constant of the solvent results in a small stabilization energy difference in ground and excited states, i.e. little red shift in λ_{max} . However, the observed blue shift in λ_{max} in the case of dichloroethane relative to that in CHCl_3 can be presumably attributed to specific electron donor- $\text{C}_2\text{H}_4\text{Cl}_2$ interactions.

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