Molecular complexes of TCNE with acetonilides: Part 1
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Molecular complexes of TCNE with some acetonilides have been studied using electronic spectroscopy. Each complex exhibits two charge transfer bands which are attributed to the formation of two isomeric complexes $R_1$ and $R_2$, differing in the orientation of the donor and acceptor molecules. The ionization potentials of highest occupied and penultimate molecular orbitals of the donors have been calculated from the positions of the CT bands. The stabilities of the complexes with $R_1$ configuration are found to be greater than those with $R_2$ configuration. The stabilities of both the complexes increase with increase in electron releasing ability of the substituents. In general, the stabilities of the acetonilide-TCNE complexes are found to be greater than those of the TCNE complexes with correspondingly substituted benzenes. This is attributed to the stronger dipole-dipole interactions in acetonilide-TCNE complexes than the dipole-induced dipole interactions in the benzene-TCNE complexes.

Extensive studies have been made on the molecular complexes of TCNE with a variety of aromatic compounds and substituted benzenes as donors. The $\pi$-complexes (I) of TCNE with aniline and N-alkylanilines were found to be very much unstable and decomposed soon into stable $\sigma$-complexes (II).

The greater stability of the $\sigma$-complex than that of the $\pi$-complex was attributed to the zwitterionic structure of the former, due to the interaction of the non-bonded electrons of the N atom with benzene ring.

If this is the case, the suppression of the formation of zwitter ion is expected to stabilise the $\pi$-complex. For this purpose, acetylated anilines were chosen in the present study because the amide resonance (III) retards the zwitter ion formation.

Materials and Methods
The acetonilides were prepared by acetylation of substituted anilines. The solids obtained were recrystallised twice from methanol and were TLC-pure. Spectrograde chloroform was used as solvent. A sample of TCNE (Fluka A G) was twice recrystallised from chlorobenzene and was vacuum-sublimed.

The electronic spectra were recorded at 25°C on a Specord UV-VIS double beam spectrophotometer using a matched pair of quartz cells of 1 cm path length. Freshly prepared solutions of TCNE (4.33 x 10$^{-4}$ M) and acetonilides (0.01 to 0.30 M) were mixed just before recording the spectra. Colour changes observed on mixing the donor and acceptor indicated complex formation. The complexes were stable for several hours unlike those of N-alkylanilines.

The formation constants of the complexes were determined by Benesi-Hildebrand method. The linearity of the Benesi-Hildebrand plots indicated the formation of 1:1 complexes which was also verified by Job’s continuous variation method.

Results and Discussion
The complex of acetonilide and TCNE was pale yellow in colour and exhibited two CT bands at 390 nm and 420 nm. Complexes with substi-
tuted acetanilides also exhibited two bands (except that of p-bromoacetanilide). The position of the first band (390 nm) was almost the same in all the complexes. The position of the second band (420 nm), however, varied with the substituent (Table 1). The ratio of the intensities of the two bands remained constant on dilution indicating the presence of complexes of only one composition.

The two CT bands of acetanilide may be due to the excitation of electrons of the donor from two different orbitals (of small energy difference) to a single lowest unoccupied molecular orbital (LUMO) of the acceptor or excitation of electrons from the same energy level of the donor to two different energy levels of the acceptor. In the former type of charge transfer, for a common acceptor and different donors, it was shown that the difference between the $\lambda_{max}$ of two CT bands is dependent on the nature of donor used. In the latter type of charge transfer, the difference remains constant for any donor. As the difference in $\lambda_{max}$ of the two bands of the acetanilides-TCNE complexes varied from donor to donor, the complexes were inferred to be of the former type (Table 1). The bands are, therefore, due to the excitation of the two electrons from the highest filled orbitals, $\psi_s$ and $\psi_{as}$ of the acetanilides, to the lowest empty orbital of the TCNE.

This type of complexes differ in the relative orientation of the donor and acceptor molecules. The $\psi_s$ and $\psi_{as}$ orbitals of the donor differ in their nodal planes. The symmetrical orbital $\psi_s$ has a transverse nodal plane (IV) whereas the anti-symmetrical orbital $\psi_{as}$ has a longitudinal plane (V).

If Mulliken's maximum overlap principle is applied, two isomeric complexes with the following orientations are expected (VI, VII). For mono- and di-substituted benzenes having electron releasing groups, theory predicts that the longer wavelength (lower energy) band arises from the $R_s$ configuration (VI) and the shorter wavelength (higher energy) band from $R_a$ configuration (VII), of the complex.

**Effect of substituents on CT bands**

The shorter wavelength CT band (390 nm) of acetanilide-TCNE complex is little affected by the change in substituents (Table 1). This is because it arises due to donation of electron from the $\psi_{as}$ orbital which does not encompass the substituent.

Significant changes, however, were noticed in the long wavelength CT band (420 nm). It was shifted to longer wavelengths by the electron donating groups, viz., N(CH$_3$)$_2$, OCH$_3$ and CH$_3$, and the shifts were in the order: N(CH$_3$)$_2$ > OCH$_3$ > CH$_3$ > H.

The shifts of the bands can be explained in terms of mesomeric and inductive interactions of the substituents. The $+M$ effect of N(CH$_3$)$_2$ and OCH$_3$ and the $+I$ interaction of CH$_3$ boost up the energy of the $\psi_s$ orbital and bring it closer to the LUMO of the TCNE and, therefore, shift the CT band to longer wavelengths.

The 400 nm band of the p-bromoacetanilide complex is broad. It may be due to the overlap of
two CT bands with a small difference in the $\lambda_{\text{max}}$. The 420 nm band of acetanilide complex must have suffered a hypsochromic shift due to the bromo substituent which, by its inductive influence, stabilises (lowers the energy) the donor level. This results in merging of the two bands and appearance of a broad band.

The $h\nu_{\text{CT}}$ was found to bear a linear relationship with Hammett $\sigma_p^+$ constants (Fig. 1).

**Ionization potentials**

The ionization potentials of the substituted acetanilides were calculated using Briegleb's equation$^{16}$ and are shown in Table 1.

$$h\nu_{\text{CT}} = 0.83 I^0 - 4.42 \text{ eV}$$

The ionization potentials of acetanilides obtained from the shorter wavelength CT bands were found to be nearly constant and ranged between 9.12 and 9.15 eV. These are very close to the ionization potential of benzene (9.24 eV). The ionization potentials obtained from the longer wavelength bands differed widely. Acetanilides with electron releasing groups have lower ionization potentials (7.62 eV to 8.80 eV). The IP of $p$-bromoacetanilide (9.08) is a little higher than that of acetanilide.

**Formation constants of the complexes**

As the two CT bands observed for complexes of each of the acetanilides were considered to be due to two isomeric configurational complexes, the formation constants were determined for both the complexes individually and are presented in Table 1.

The formation constants of the complexes with $R_\alpha$ configuration are greater than those of $R_\gamma$ configuration. This may be due to the steric hindrance offered by NHCOCH$_3$ and the $p$-substituent to the approach of TCNE onto the benzene ring in $R_\gamma$ configuration. The approach of the acceptor is, however, unhindered in the $R_\alpha$ configuration and, hence, this complex is more stable.

The association constants of the complexes increase with electron releasing ability of the substi-
tuents in the benzene ring and are in the order: \(N(CH_3)_2 > OCH_3 > CH_3 > H > Br\).

The logarithmic functions of the formation constants of both the isomeric complexes were found to bear linear relationship with the \(-\)Hammett \(\sigma^*_p\) constants (Fig. 2).

It is interesting to note that the stabilities of the complexes of substituted acetanilides with TCNE are greater than those of the correspondingly substituted benzenes-TCNE complexes.

The stability of the complex, besides the ionization potentials of the donor, depends on the polarisability\(^1\), dipole moment of the donor\(^2\) and the polarising power of the acceptor\(^3\). In a series of complexes with the same acceptor, stability depends upon the polarisability and dipole moment of the donor. The attractive forces in benzene-TCNE complex are the dipole-induced dipole. In acetanilide they are dipole-dipole interaction. The non-bonded electrons of the N-atom interact with benzene ring and enable acetanilide to acquire greater polarity (zwitter ion structure) and form a strong complex with TCNE. Hence, the stabilities of these complexes are higher than those of benzene-TCNE complexes.

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References