Absorption Spectroscopic Study of the Complexation of C_{70} with Aniline and Substituted Anilines

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Complexes of fullerene C_{70} with aniline and various substituted anilines have been studied in CCl_4 medium by electronic absorption spectroscopy. An absorption band due to a charge transfer (CT) transition is observed in the visible region. The experimental CT transition energies are well correlated (through Mulliken's equation) with the ionization potentials (I_D) of the series of anilines studied. From an analysis of this correlation, the electron affinity of C_{70} has been found to be 2.28 eV. The degree of charge transfer in the ground state of the complexes has been found to be very low (0.2−0.3%). The experimentally determined formation constants of the complexes of C_{70} with N-substituted anilines exhibit a very good linear free-energy relationship (Hammett, L. P. C*hem. Rev.* **1953**, *53*, 191).

1. Introduction

The novel material [70]fullerene[1,2] is currently finding important applications in the fields of organic chemistry[3,4] and photophysics.[5,6] In agreement with theoretical prediction,[7,8] electrochemical studies[9,10] reveal that C_{70} can accept a maximum of six electrons, and reduction potentials corresponding to $[C_{70}]^{n-}$, $n = 3 - 6$, have been determined. Thus, C_{70} is expected to behave as an efficient electron acceptor in forming charge transfer (CT) complexes. Since the discovery[2], there has been a considerable amount of work done on the spectroscopic characterization of C_{60} in both ground and excited states.[11−17] However, it is only recently that the donor−acceptor complexes of C_{70} have received considerable attention. Konarev et al.[18] have determined and utilized the CT transition energies of the complexes of [60] and [70]fullerenes with a series of tetrathiafulvalenes and related donors to estimate the electron affinities of C_{60} and C_{70}. Recently, we have reported the electron donor−acceptor (EDA) interaction between C_{70} with methylbenzenes[19] and polynuclear aromatic hydrocarbons.[20] Though a number of studies have been made on the interaction of C_{60} with aromatic amines,[14,21−24] no such study has yet been carried out to quantify the interactions of C_{70} with aniline and various substituted anilines. To determine the dependence of complex stability upon the pattern of alkyl substitution of the aromatic amine donors, we have determined the formation constants by UV/vis spectroscopy in CCl_4 medium. CT bands have been located in all the cases studied. The dependence of the CT transition energies ($h\nu_{CT}$) of the C_{70} complexes on the donor ionization potentials (I_D) has been analyzed in the light of Mulliken's[25] theory, and thence the electron affinity of C_{70} has been found to be 2.28 eV. Formation constants of the complexes of C_{70} with *N*,*N*-dimethylaniline (DMA), *N*,*N*-dimethyl-*p*-toluidine (DMP), and *N*,*N*-dimethyl-*m*-toluidine (DMM) exhibit a good linear free-energy relationship.

2. Experimental Section

[70]Fullerene was obtained from SES Research Inc., Houston, Texas. Aniline, *m*-toluidine, DMA, and *N*,*N*-diethylaniline (DEA) were purified by distillation with Zn dust just before use. DMP, DMM, and *N*,*N*-diethyl-*m*-toluidine (DEM) were obtained from Sigma. The solvent CCl_4 was of HPLC grade. All spectral measurements were carried out in a Shimadzu UV-2101 PC model spectrophotometer fitted with a TB 85 thermo bath.

3. Results and Discussions

3.1. Observation of CT Bands. Figure 1 shows the electronic absorption spectra of mixtures containing C_{70} and aromatic amine in CCl_4 medium against the corresponding amine solution as reference. New absorption peaks appear in the visible range where the corresponding amines do not absorb. The absorption spectra were analyzed by fitting to the Gaussian function. The wavelengths at these new absorption maxima (λ_{max}) and the corresponding transition energies ($h\nu$) are summarized in Table 1. A survey of the literature shows that for the present series of donors experimental values of vertical ionization potentials (I_D^V) are known only for aniline, DMA, and DEA. For I_D^V of the other amines under study, the following procedure was adopted. Experimental I_D^V values of aniline, DMA, and DEA were plotted against their AM1[26] ionization potentials, and the following linear correlation was found with a correlation coefficient of 0.99.

$$\text{experimental } I_D^V = (3.03 \pm 0.42) \text{ AM1 } I_D - (18.37 \pm 3.58) \quad (1)$$

The theoretical ionization potentials of the amines *m*-toluidine, DMP, DMM, and DEM calculated by the AM1 method were used in eq 1 to get their experimental I_D^V values. Results are given in Table 1.

3.2. Determination of Vertical Electron Affinity of C_{70}. The energy of a CT transition ($h\nu_{CT}$) can be expressed according

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TABLE 1: CT Absorption Maxima and Transition Energies of C_{70}–Aniline Complexes, AM1 and Experimental Ionization Potentials of the Donors, Degrees of Charge Transfer (λ), Formation Constants (K), and Molar Extinction Coefficients (ϵ')[a,b]

donor	λ_{CT}, nm	$h\nu_{CT}$, nm	experimental I_D^V, eV	AM1 I_D, eV	$10^3 \times \lambda$	formation constant (K), mol dm^{-3}	$10^4 \times$ molar extinction coefficient (ϵ'), dm^3 mol^{-1} cm^{-1}
aniline	629	1.972	7.72[b]	8.522	2.36		
DMA	542	2.288	7.12[b]	8.352	2.66	0.86	2.0
DMP	827	1.499	6.50	8.085	2.94	2.60	69.0
DMM	887	1.398	7.45	8.389	2.47	2.30	2.6
DEA	555	2.234	6.95[b]	8.264	2.70	1.15	9.3
DEM	563	2.202	7.55	8.479	2.40	0.29	30.6
m-toluidine	675	1.837	7.53	8.476	2.44		

[a] $T = 293$ K. [b] Obtained from ref 23.

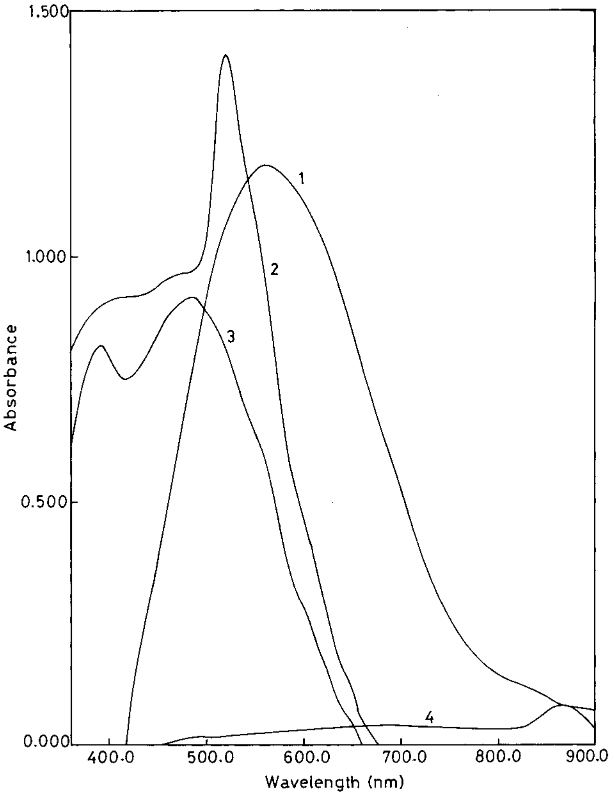

Figure 1. Absorption spectra of mixtures of (1) C_{70} (9.524×10^{-6} mol dm^{-3}) + DEM (9.607 mol dm^{-3}); (2) C_{70} (1.428×10^{-5} mol dm^{-3}) + *m*-toluidine (9.217 mol dm^{-3}), (3) C_{70} (2.285×10^{-4} mol dm^{-3}) + aniline (10.98 mol dm^{-3}); and (4) C_{70} (2.261×10^{-5} mol dm^{-3}) + DMM (6.878 mol dm^{-3}) in CCl_4 medium against the respective amines as references.

to Mulliken's theory[25] as

$$h\nu_{CT} = I_D^V - C_1 + C_2/(I_D^V - C_1) \qquad (2)$$

where C_1 is composed of the affinity of the acceptor, electrostatic interactions, and other terms.

C_2 is related to the overlap of donating and accepting orbitals, and for a given acceptor, it may be assumed to be constant. Now, the quantity C_1 of eq 2 is given by

$$C_1 = E_A^V + G_o + G_1 \qquad (3)$$

where E_A^V is the vertical electron affinity of the acceptor, G_o is the sum of several energy terms (like dipole–dipole, van der Waals interaction, etc.) in the "no-bond" state, and G_1 is the sum of the energy terms in the dative state. In most cases, G_o is small and can be neglected whereas G_1 is largely the electrostatic energy of attraction between D^+ and A^-. A rearrangement of eq 2 yields

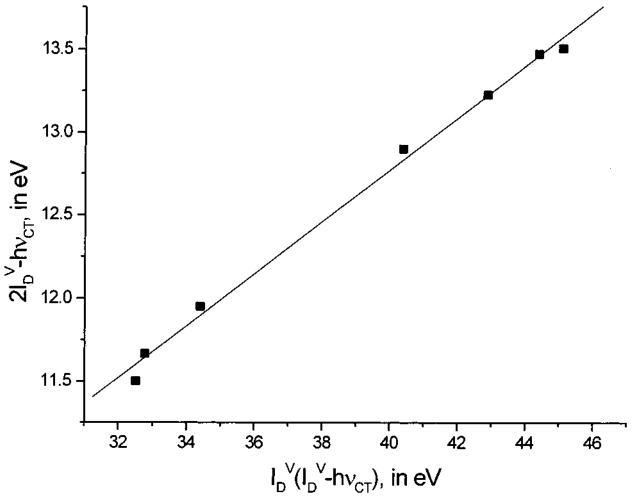

Figure 2. Plot of $2I_D^V - h\nu_{CT}$ against I_D^V ($I_D^V - h\nu_{CT}$) for C_{70}–amine complexes.

$$2I_D^V - h\nu_{CT} = (1/C_1)I_D^V(I_D^V - h\nu_{CT}) + C_1 + C_2/C_1 \qquad (4)$$

Using the observed transition energies and the experimentally determined ionization potentials (shown in Table 1), we have obtained the correlation

$$2I_D^V - h\nu_{CT} = (0.156 \pm 0.005)I_D^V(I_D^V - h\nu_{CT}) + (6.514 \pm 0.193) \qquad (5)$$

with a correlation coefficient of 0.99 (Figure 2). This confirms the CT nature of the transition that is observed, and the slope of eq 5 yields $C_1 = 6.41$ eV. Neglecting G_o and taking the typical D–A distance in π-type EDA complexes to be 3.5 Å, the major part of G_1 is estimated to be $e^2/4\pi\epsilon_o r = 4.13$ eV. Now using eq 3, E_A^V of C_{70} in solution is found to be 2.28 eV, which is in agreement with the value of 2.59 eV that we obtained in some earlier work.[20] The present E_A^V value is somewhat less than 2.73 eV obtained in the gas phase by Boltalina et al.[27] and Chen et al.[28] The difference (0.45 eV) between the electron affinity values in the gas phase and in solution is due to the solvation effect, which makes a significant contribution to G_1. Owing to the lack of suitable data, this contribution cannot be estimated correctly. A comparison with the work reported in ref 21 reveals that the CT transition energy is higher for the C_{70}·An complex than for the C_{60}·An complex (An = aniline or substituted aniline). This indicates that C_{70} is a better electron acceptor than C_{60}, as is evident from the electron affinities:[27,28] C_{60}, 2.65 eV and C_{70}, 2.73 eV (in the gas phase).

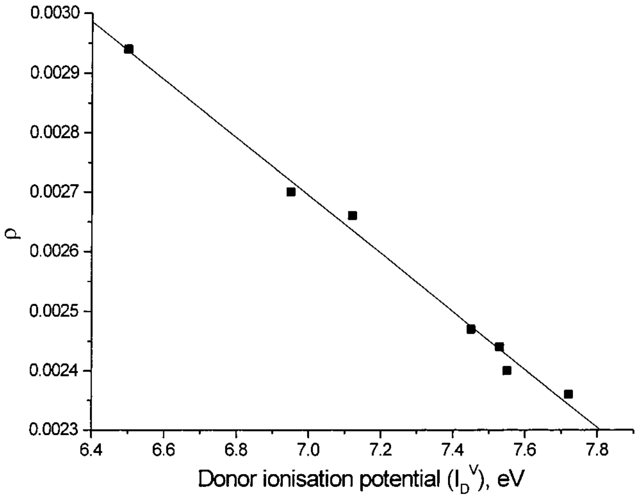

Figure 3. Degree of charge transfer (λ) of the C_{70}/amine CT complexes as a function of ionization potential.

3.3. Degree of Charge Transfer (λ). In a Mulliken two-state model,[25] the ground (ψ_g) and excited (ψ_{ex}) state wave functions of the CT complexes are described by a linear combination of dative $\psi(D°, A°)$ and ionic $\psi(D^+, A^-)$ states,

$$\psi_g = \sqrt{(1-\lambda)}\ \psi(D°, A°) + \sqrt{\lambda}\ \psi(D^+, A^-) \tag{6}$$

$$\psi_{ex} = \sqrt{(1-\lambda)}\ \psi(D^+, A^-) - \sqrt{\lambda}\ \psi(D°, A°) \tag{7}$$

where λ is the degree of charge transfer. The function $\psi(D^+, A^-)$ differs from $\psi(D°, A°)$ by the promotion of an electron from the donor to the acceptor. λ is given[23,25] by

$$\lambda = (C_2/2)/[(I_D{}^V - E_A{}^V + C_1)^2 + C_2/2] \tag{8}$$

The values of λ (calculated by using eq 8 and given in Table 1) are small and indicate that very little charge transfer occurs in the ground state. The dependence of λ on $I_D{}^V$ of the donors is shown in Figure 3. It is found that λ decreases with the increasing ionization potential of the donor, as expected.

3.4. Determination of Formation Constants (*K*). It was observed that the broad absorption band of C_{70} (measured against the solvent as reference), which is centered more or less at 472 nm, increased systematically with gradual addition of the donors, and this fact was utilized to determine K by using the Benisi–Hildebrand[29] equation with a 1-cm optical path length:

$$[A]_0[D]_0/d' = [D]_0/\epsilon' + 1/K\epsilon' \tag{9}$$

$$d' = d - d_A{}^0 - d_D{}^0 \tag{10}$$

Here, $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor, respectively, d is the absorbance of the donor–acceptor mixture measured against the solvent as reference, and $d_A{}^0$ and $d_D{}^0$ are the absorbances at 472 nm of the acceptor and donor solutions with same molar concentrations as in the mixture and at the same wavelength. The quantity ϵ' means $\epsilon_C - \epsilon_A - \epsilon_D$, where ϵ_C is the molar absorptivity of the complex and ϵ_A and ϵ_D are those of the acceptor and the donor, respectively, at the wavelength of measurement. K is the formation constant of the complex. Equation 9 is valid under the condition $[D]_0 \gg [A]_0$ for 1:1 donor–acceptor complexes. Experimental data are shown in Table 1. In all cases, very good linear plots according to eq 9 were obtained; one such plot is shown in Figure 4.

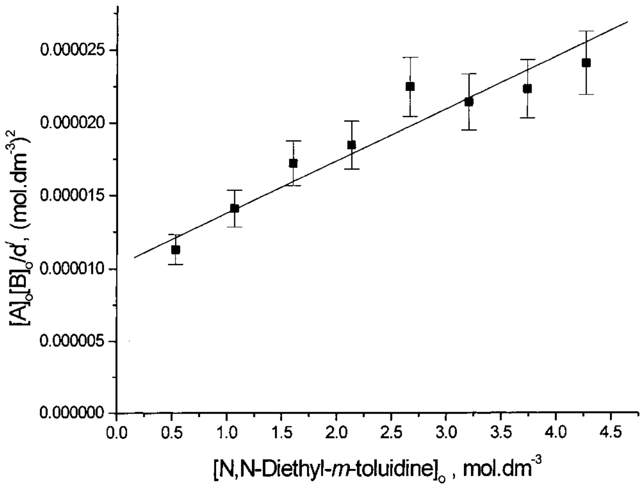

Figure 4. Benesi–Hildebrand plot for the C_{70}–DEM system at 293 K.

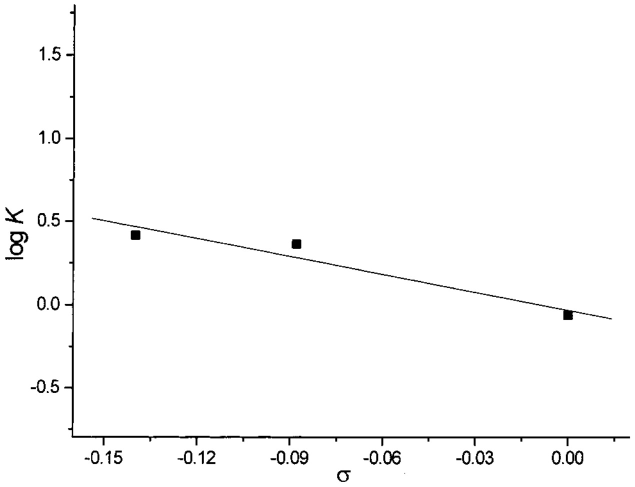

Figure 5. Hammett plot for the complexes of C_{70} with DMA, DMM, and DMP at 293 K.

Values of K of the complexes obtained from such plots are given in Table 1. With the same donor in a given solvent, the formation constant of a C_{70} complex is usually higher than that of a C_{60} complex. This was observed in some earlier works.[20,30] For example, in CCl_4 medium, $K = 0.67$, 1.67, 10.24, and 6.8 dm^3 mol^{-1} for complexes of C_{60} with naphthalene, phenanthrene, anthracene, and pyrene, respectively, whereas for the corresponding C_{70} complexes, $K = 10.6$, 59.2, 489.7, and 64.6 dm^3 mol^{-1}, respectively. The value of $K = 1.15$ dm^3 mol^{-1} for the C_{70}/DEA complex determined in the present work is also higher than that (0.18 dm^3 mol^{-1}) for the C_{60}/DEA complex obtained earlier.[22] The values of K (Table 1) for C_{70}–DMA, C_{70}–DMP, and C_{70}–DMM exhibit (Figure 5) a good linear free-energy relationship (Hammett).[31,32]

$$\log K = (-3.56 \pm 0.99)\sigma + (-0.03 \pm 0.09) \tag{11}$$

The negative slope (Hammett ρ parameter) indicates that the interaction between C_{70} and the anilines is of an associative nature and that the attachment of the methyl group to the meta and para positions of DMA increases the donor ability of the aromatic amine.

4. Conclusions

Ground-state complex formation between C_{70} and various anilines has been established. The $h\nu_{CT} - I_D{}^V$ dependences in

C_{70} complexes with anilines have been obtained. Degrees of charge transfer have been estimated for each of the C_{70}−aniline systems. The very low values of ρ indicate that the CT complexes studied here have neutral character in their ground state. The vertical electron affinity ($E_A{}^V$) of C_{70} in CCl_4 solution has been estimated. The complexes have been shown to exhibit a Hammett-type linear free-energy relationship. Finally, it has been observed that C_{70} acts as a better acceptor than does C_{60} in forming CT complexes.

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