

Spectroscopic studies of molecular interactions involving 2,6-diethylaniline and *N*-ethylaniline donors and iodine as an electron acceptor in different solvents

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Abstract

The charge-transfer complexes of 2,6-diethylaniline (DEA) and *N*-ethylaniline (NEA) with iodine, as a typical σ -acceptor were studied spectrophotometrically in chloroform, dichloromethane and carbontetrachloride solutions. Spectral data, formation constants and effect of solvent have been determined. Spectral characteristics and formation constants are discussed in the terms of donor molecular structure and solvent polarity. The stoichiometry of the complexes was established to be 1:1. For this purpose, optical data were subjected to the form of the Rose–Drago equation for 1:1 equilibria. The formation constant (K_{AD}) and molar absorptivities (ϵ_{λ}) of complexes were determined by least square method. Electronic absorption spectra of the anilines were measured in different solvents. Spectral data were reported and band maxima were assigned to the appropriate molecular orbital transitions. Quantum chemical calculations were performed with the aid of the Gaussian 98 set of programs. The structure were fully optimized at MP2 level using 6-31 + G** basis set. The computations show that DEA is not planar with the amino group having a somewhat sp^3 hybridization-like character.

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1. Introduction

The charge-transfer (CT) complexes are formed between electron donors, having sufficient low ionization potential, and acceptors, having sufficient high electron affinity. The transfer of an electron from a donor to an acceptor is readily possible in charge-transfer process [1]. Much of our knowledge about the behavior of CT complexes comes from the study of complexes between various donor molecules and few standard acceptor molecules, e.g. I_2 [2,3].

CT-complexes are being regarded as important materials due to their ample applications [4–7]. Such complexes have been reported as important reaction intermediates in many chemical reactions [8,9] and play a considerable role in drug interactions. These complexes have been studied in organic conductors and

photoconductors [10,11]. The question of participation of CT-complexes in organic syntheses, and in understanding reaction mechanisms has long been debated since the classical work of Benesi and Hildebrand [12].

1.1. The importance of anilines

Aniline is the precursor of a large set of molecules of biological and pharmacological interest. Biochemical studies on aniline and many of its derivatives showed that these compounds represent important biochemical active substances. They have many applications in both human and medicine [13]. The most important uses of aniline are in the manufacture of dyes and rubber chemicals. It has some importance as corrosion inhibitor. It appears to be especially suitable for protecting some metal against wet corrosion of carbontetrachloride. Some amount of aniline is used in the textile, paper and metallurgical industries, as well as catalyst, stabilizers, pesticides and insect and animal repellents. It is also used as a solvent and analytical reagent. In the pharmaceutical industry, aniline is important

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in the manufacture of sulpha drugs and synthetic sweetening agents.

Following this widespread applications of anilines in industry and medicine, we have studied spectrophotometrically and theoretically some aniline compounds such as 2,6-diethyl aniline and *N*-ethylaniline.

1.2. Literature survey

Anilines and its derivatives have considerable donor strength but as donor molecules, they can't be classified into either n -donors or π -donors because the lone pair orbital electrons on the nitrogen atom of the amine group involved in conjugation with the π -orbitals of the benzene ring. The donor properties of the anilines increase when an ethyl group is introduced either on the nitrogen atom or in the benzene ring, due to the positive inductive and hyperconjugative effects of ethyl groups. For that anilines have been widely used as donors with different acceptors in many charge-transfer complexation studies. Budni and Magadam [14] have investigated spectrophotometrically molecular complexes of 2,3,5,6-tetrachloro-7-nitro-1,4-naphthoquinone with aromatic anilines in carbontetrachloride solvent. Kumar et al. [15] have studied molecular complexes of DDQ with aniline, spectrophotometrically, by stabilizing the complexes in a low polar solvent (CCl_4), at low temperatures and under low donor concentrations. Complexation between *o*-chloranil and a series of anilines have been studied spectrophotometrically at room temperature [16]. Bugeanu and Sahini [17] calculated the stability constants and dipole moments of aniline complexes with iodine acceptor by different methods. The visible spectra of some molecular complexes of aromatic primary amines with iodine have been recorded in chlorine-containing aliphatic solvents [18]. The formation of charge-transfer complexes between iodine and aniline, *N,N*-dimethylaniline, 2,6-dimethylaniline and 2,4,6-trimethylaniline in CHCl_3 , CH_2Cl_2 , $\text{CH}_2\text{Cl}_2\text{-CHCl}_3$ (1:1) and CH_2Cl_2 have been studied by Kwon et al. [19]. The ultra-violet and visible absorption spectra of the complexes of iodine and aniline have been reported by Kusakawa and Nishizaki [20]. Andrabi [21] has determined the formation of yellow colored charge-transfer complexes of aniline, *N*-methylaniline, *N,N*-dimethylaniline and *N,N*-diethylaniline with nitromethane in carbontetrachloride by UV-vis spectrophotometry. The equilibrium constant for complexation of C60 and aniline in toluene measured by Sibley et al. [22] and the absorption spectra of the complexation of fullerene C70 with aniline were obtained [23]. The UV spectrum of *p*-nitroaniline [24], meta-nitroaniline [25], acetoacetanilide, benzoylacetanilide [26] and various *para*-substituted benzyldene aniline molecules at room temperature [27] have been studied. Aly et al. [28] have studied the spectroscopic and thermodynamic behavior of the charge-transfer complexes between 4-([2,2] paracyclophanoyl) amines and π -acceptors. Ying et al. [29] have studied the spectral and thermodynamic behavior of the charge-transfer complexes formed by vitamin K_1 , K_3 and *N*-substituted anilines. Pal et al. have investigated charge-transfer complex of menadione (vitamin K_3) with a series of anilines [30].

Ballesteros and Santos, have reinvestigated the molecular structures, vibrations and rotation of methyl group in *o*-methylaniline in S_0 and S_1 states by laser induced fluorescence spectroscopy and ab initio calculations [31].

In the present study, the charge-transfer complexes of 2,6-diethylaniline (DEA) and *N*-ethylaniline (NEA) with iodine, as a typical σ -acceptor were studied spectrophotometrically in chloroform, dichloromethane and carbontetrachloride solutions. Electronic absorption spectra of the studied anilines were measured in different solvents. Quantum chemical calculations were performed with the aid of the Gaussian 98 set of programs for DEA and aniline.

2. Experimental

The solvents used throughout this work are carbontetrachloride, dichloromethane, absolute ethanol, methanol, acetonitrile and dimethylformamide. These solvents were supplied by Fluka and purified by the conventional methods reported in literature [32].

Liquid samples of 2,6-diethyle aniline (purity: 99.5%, bp = 114°, and density: 0.906 g/cm³) and *N*-ethyle aniline (purity: 98%, bp = 205°, and density: 0.963 g/cm³) were obtained from Sigma-Aldrich Chemical Company. Crystalline Iodine was obtained as Analar Grade from MERK Chemical Company. It was further purified by sublimation.

Stock solutions of iodine were prepared freshly before use. The exact concentrations of iodine solutions in different solvents were prepared by weight and checked by measuring its UV-vis absorbance (520 nm, and 960 M⁻¹ cm⁻¹ at room temperature).

Stock solutions of the aniline compounds were prepared by weight just before measurement to avoid slow air oxidation.

The UV-vis absorption spectra of solutions were generally measured according to the methods reported in literature [33,34] using PERKIN ELMER Lambda-2 UV-vis spectrophotometer. Quartz cell, 1.0 cm path length, was used. The spectra in all cases were reproduced. All UV-vis spectroscopic measurements were obtained in different organic solvents diluted with appropriate concentration (see Table 1). The charge-transfer complex solutions were generally prepared by mixing the donor- and the acceptor- solutions by accurate dilution from stock solutions. Mixtures were left for about 15 min to reach equilibrium and then recorded against the solvent as reference. The results were found to be highly reproducible. Stock solutions of donors and acceptors were prepared. Separate combinations of the stock solutions were made, each containing a fixed concentration of acceptor solution and different donor concentrations. Spectra of these mixtures and the pure individual components were recorded.

2.1. DEA-I₂/CCl₄

Stock solution of DEA (0.1359 g, 3.64 × 10⁻² M) in carbontetrachloride (25 ml) and I₂ (0.1983 g, 7.81 × 10⁻³ M) in carbontetrachloride (100 ml) were used. The following DEA + I₂ mixtures (in ml) were prepared: 1 + 1, 2 + 1, 3 + 1, 4 + 1, 5 + 1 and 6 + 1.

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