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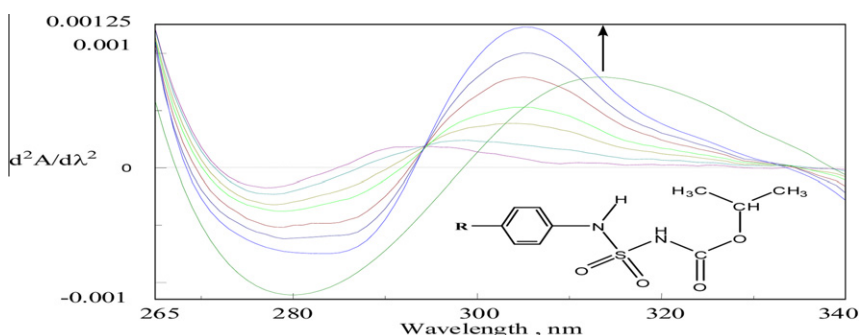
A spectrophotometric and thermodynamic study of the charge-transfer complexes of N-aryl-N'-isopropylloxycarbonylsulfamides with DDQ and TCNE

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HIGHLIGHTS

- ▶ We examine the interaction between N-aryl-N'-isopropylloxycarbonylsulfamides and DDQ or TCNE.
- ▶ Zero and second order derivative UV spectrophotometry were used.
- ▶ Spectroscopic and thermodynamic properties were determined.
- ▶ Complexes properties were influenced by acceptor–donor nature and medium polarity.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular charge-transfer complexes of three N-aryl-N'-isopropylloxycarbonylsulfamides derivatives with π -acceptors tetracyanoethylene (TCNE), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), were studied by using zero and second order derivative UV spectrophotometry in different solvents at four different temperatures within the range of 20–35 °C. The stoichiometries of the complexes were found to be 1:1 ratio between donors and acceptors using Job's method. The data were analyzed in terms of their stability constant (K), molar extinction coefficient (ϵ_{CT}), thermodynamic standard reaction quantities (ΔG° , ΔH° , ΔS°), oscillator strength (f), transition dipole moment (μ_{EN}) and ionization potential (I_D).

The results show that the stability constant (K) for the complexes was found to be dependant upon the nature of electron acceptor, electron donor, and polarity of used solvents.

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Introduction

Charge-transfer (CT) complexes that originate from a weak interaction between electron donor and acceptor molecules in biomolecular equilibrium or in model compounds intramolecular interaction have been an important topic of research in physical

chemistry and biochemistry for many decades [1–4]. Charge-transfer complexation is of great importance in chemical reactions, including addition, substitution, condensation [5], biochemical and bioelectrochemical energy transfer processes [6], biological systems, and drug–receptor binding mechanisms [7]. The important role is also played by the charge-transfer complexes in the quantitative estimations of drugs [8,9].

The properties of charge-transfer (CT) complexes formed in the reaction of electron acceptors with donors containing nitrogen,

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sulfur, oxygen atoms, have growing importance in recent years [10–22]. N-aryl-N'-isopropylcarbonylsulfamides are compounds which contain in their molecular structures a sulfamoyl moiety as pharmacophore. They have been primarily used as important synthetic intermediates in the generation of unsymmetric sulfamides [23,24] and sulfahydantoin [25]. They have been studied as acyl-CoA: cholesterol O-acyl-transferase (ACAT) inhibitors [26], and showed a broad range of inhibitory activity against several isoforms of carbonic anhydrase [27].

The objective of the present work is to carry out a spectroscopic and thermodynamic study of the complexation of N-aryl-N'-isopropylcarbonylsulfamides D1, D2 and D3 (Fig. 1) with the electron acceptors tetracyanoethylene (TCNE), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), following two procedures: in liquid phase and at the solid state.

Spectrophotometric measurements based on zero and/or second order derivative UV spectrophotometry were used to evaluate in four different solvents (chloroform, methanol, ethanol and acetone), stability constants (K), the molar extinction coefficient (ϵ_{CT}), thermodynamic standard reaction quantities (ΔG° , ΔH° , ΔS°), the oscillator strength (f), the transition dipole moment (μ_{EN}) and the ionization potential (I_D). Moreover, the solid complexes were synthesized and characterized by using FT-IR spectroscopy.

Experimental

N-aryl-N'-isopropylcarbonylsulfamides were synthesized according to literature [28]. π -acceptors tetracyanoethylene (TCNE), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from Aldrich Chemical Co. and were used without modification. The spectroscopic grade solvents (ethanol, methanol, acetone, and chloroform) were purchased from Fluka or Prolabo.

The electronic absorption spectra were recorded in the range 400–220 nm using a Jasco UV-530 spectrophotometer equipped with a Jasco EHC-477S thermostat ($\pm 0.1^\circ\text{C}$) using 1.0 cm matched quartz cells. FT-IR spectra of the reactants and the formed complexes were recorded as KBr pellets using Spectrum one Perkin Elmer FT-IR.

The solid charge-transfer complexes were isolated by taking equimolar amounts of the donor and the acceptor and dissolved separately at room temperature in the minimum volume of a mixture methanol/dichloromethane (1:1, v/v). The two solutions were mixed and the resulting mixture was stirred overnight at room temperature. The resulting solid compound precipitated was first filtered off, washed several times with methanol/dichloromethane mixture to remove any unreacted materials, and finally dried.

Results and discussion

Electronic spectra

In solution, the complexation of N-aryl-N'-isopropylcarbonylsulfamides by acceptors (TCNE or DDQ) was demonstrated by spectrophotometry at UV–vis at 20°C .

The UV–vis spectrum of each of N-aryl-N'-isopropylcarbonylsulfamides studied was altered in the presence of the acceptor (TCNE or DDQ). Following the progressive addition of acceptor on donor solutions, characteristic phenomena of the charge-transfer complexes formation were noticed: batho or hypsochromic shifts, increase in the intensity of the absorption band or appearance of new absorption bands in a region where neither free donors nor acceptors have any measurable absorption.

As shown in Figs. 2 and 3, the absorbance spectra of D1 in solutions containing various amounts of DDQ or TCNE in chloroform,

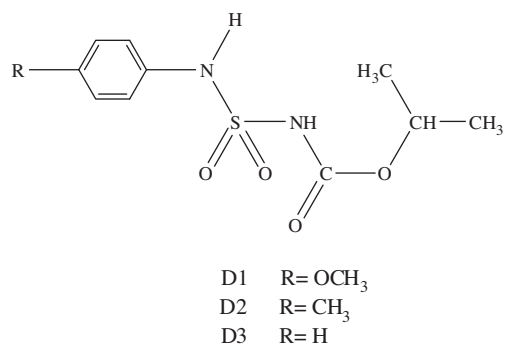


Fig. 1. N-aryl-N'-isopropylcarbonylsulfamides used in this study.

was examined. It was intended to serve as a model of the three N-aryl-N'-isopropylcarbonylsulfamides derivatives studied.

Fig. 2 shows electronic absorption spectra of D1 in chloroform containing various concentrations of DDQ. The donor D1 ($4 \times 10^{-4}\text{M}$) displays a broad absorption band which spreads out from 259 nm to 276 nm. Upon the addition of the DDQ, this band shifts left, increases in intensity and culminates at 268 nm. Moreover, the absorption band at 354 nm increases in intensity. These findings indicate the formation of a charge-transfer complex of D1 with DDQ.

Fig. 3 displays absorption spectra of D1 in chloroform with progressive concentrations of TCNE. As the TCNE concentration increases, the absorbance at 267 nm enhances and a new absorption band at 287 nm appears which is clearly due to the charge-transfer complex.

Second order derivative spectra

Second order derivative UV spectrophotometry was used to eliminate the overlap noticed in the spectra of complexes resulting from the contributions of the absorbance of the acceptor and/or of the donor. In addition, this method emphasizes subtle spectral features of the data by presenting them in a new and visually more accessible way.

As an example, the second derivative spectra of the charge-transfer complex formation of the same compound already measured by direct spectrophotometry are respectively presented in Fig. 4.

The main instrumental parameters that affect the shape of derivative spectra are the wavelength speed, the wavelength increment ($\Delta\lambda$) over which the derivative is obtained, and the smoothing. These parameters need to be optimized to give well-resolved

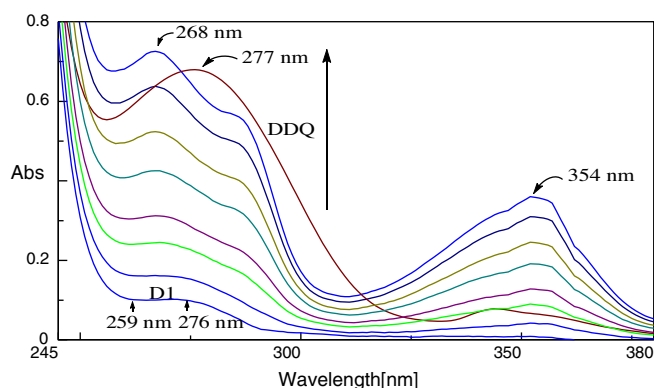


Fig. 2. Absorption spectra of D1 ($4 \times 10^{-4}\text{M}$) in chloroform containing various concentration of DDQ.

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