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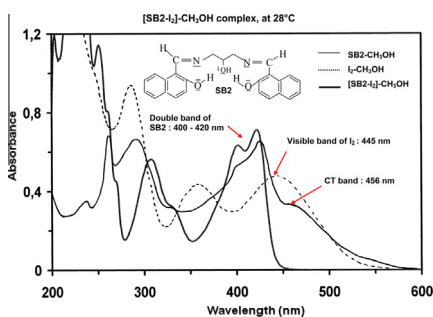
Spectrophotometric investigation of interaction between iodine and pentadentate Schiff base ligands

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HIGHLIGHTS

- Structural effect of Schiff bases on the stability constant of iodine complexes.
- Spectrophotometric evaluation of ionization potentials of selected ligands.
- Thermodynamic parameters well described by the modified Benesi–Hildebrand equation.

GRAPHICAL ABSTRACT



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This publication is dedicated to the memory of Professor Ali Hassoune Al-Taïar from USTO, who initiated the work presented here. He passed away suddenly on February 27, 2013. We will always keep him in thankful and honourable memory.

Keywords:

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ABSTRACT

The interaction between iodine as an electron acceptor (A), and three pentadentate Schiff bases, 1,3-bis(salicylideneamino)-2-propanol (SB1), 1,3-bis(2-hydroxy-1-naphthylideneamino)-2-propanol (SB2), and 1,3-bis[1-(pyridine-2-yl)methylideneamino]-2-propanol (SB3), as electron donor systems (D), was studied spectrophotometrically in methanol at 28 °C. Equilibrium constants K^{AD} and molar extinction coefficients ϵ^{AD} of the donor–acceptor complexes (AD) were determined using the modified Benesi–Hildebrand equation in conjunction with the non linear fit analysis. The method shows the formation of 1:1 type complexes as major species in solution. The free energy changes ΔG° and the energy of the charge transfer band E_{CT} were also calculated for all complexes. The iodine complex derived from SB2 seems to be more stable than those derived from SB3 and SB1. On the other hand, the ionization potential I^D of each Schiff base was estimated from the corresponding complex band energy, using an empirical equation. An inverse relationship between I^D and K^{AD} values was found. Blue and red shift observed for the 445 nm band of iodine were also discussed on the basis of theoretical considerations.

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Introduction

The interactions between electron-donors and electron-acceptors occur in different states of matter. These interactions can be strong, medium or weak, depending on the nature of the donor

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and the acceptor systems. Thus, stable inorganic complexes usually result from the interactions between strong base ligands and high acid metal ions. Interactions might also exist between organic entities, some playing the role of donors and the others the role of acceptors, forming organic–organic complexes.

The charge transfer from electron-donors (D) to electron-acceptors (A) represents an interaction leading to the formation of charge transfer complex (CTC), known for their low reaction enthalpies (in the order of a few kJ), and high rates of formation or decomposition, so that the reaction appears to be spontaneous [1]. Several authors have studied CTC, especially those derived from π -donors, such as polycyclic aromatic compounds, or n -donors such as aliphatic amines, amine oxides, ethers, picolines, pyrazolones as well as virus DNA nucleotide, with σ -acceptors such as iodine and bromine, or π -acceptors such as trinitrobenzene, benzoquinones, etc... [2–8].

It is known that the spectrophotometric study in solution, of interactions between iodine and various donor systems has attracted much attention of researchers for over half a century [9–13]. This type of interaction was revealed for the first time by Benesi and Hildebrand, when they observed a new absorption band of iodine-benzene and iodine-mesitylene mixtures in neutral solvents, like carbon tetrachloride and *n*-heptane, due to neither electron donor nor acceptor. Such phenomenon was considered as CTC formation [14].

Although extensive studies have been carried out on CTC resulting from iodine and different donor molecules [15–21], there are still some organic systems whose interactions with iodine have not been intensively studied. Among them, Schiff bases seem to be of particular interest, because of their basicity and stability, in particular those derived from salicylaldehyde and derivatives [22,23]. Indeed, interactions of Schiff bases towards various metal ions have been extensively investigated both in solution and solid state. Those derived from salicylaldehyde or derivatives are the most exploited in terms of complexation, and showed different behavior depending on the environment and the nature of the complexing agent. Such systems have been evaluated for their biological activity, their catalytic effect as well as for their liquid–liquid extraction properties [24–27].

The present investigation was undertaken to describe the spectrophotometric behaviour of some selected pentadentate Schiff bases as n - or π -donors, towards molecular iodine as σ -acceptor. These Schiff bases, presented in Fig. 1, have the same alkyl chain and differ from their aromatic nucleus, influencing thus their electronic effect. The presence of different coordination sites of these systems, such as imine and alkoxo groups, phenolic and naphthyl hydroxides, leads to a large variety of interactions towards acceptor systems.

To the best of our knowledge, there are only a few reports of this type of Schiff bases in the literature [28–31].

Experimental part

Materials and techniques

The bi-sublimated iodine (>99%) was purchased from Merck, stored in dessiccator and used without further treatment. Methanol was from Merck and was used as received. The pentadentate Schiff bases SB1, SB2 and SB3 (Fig. 1), were prepared and purified according to the general procedure described in the literature [32–34]. The purity of the ligands was checked by using Fourier transform infrared spectroscopy, nuclear magnetic resonance, elemental analysis and UV–visible spectroscopy.

Fourier transform infrared spectroscopy

Fourier transform infrared FTIR were recorded in the transmission mode using a Perkin Elmer 2000 model. The number of accumulated scans was 16 with a spectral resolution of 4 cm^{-1} .

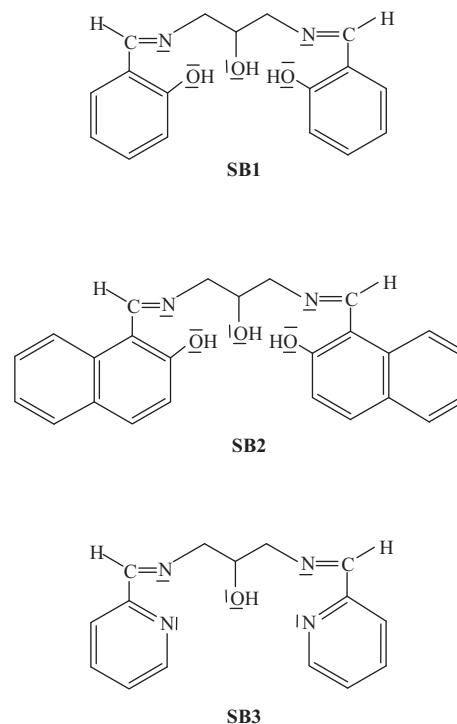


Fig. 1. Chemical structures of the pentadentate Schiff bases.

Nuclear magnetic resonance

The ^1H NMR and ^{13}C NMR spectra were taken on an FT-NMR (300 MHz) Bruker instrument. Deuterated chloroform (with 0.03% tetramethylsilane) and deuterated dimethylsulfoxide (with 0.06% tetramethylsilane) were used as NMR solvents. They were obtained in high quality (>99%), from Eurisotop (Gif sur Yvette, France), and used as received.

Elemental analysis

The elemental analysis was realized by the central service of analysis of the CNRS. The following elements were analysed: C, H, N, O.

Ultraviolet/visible spectroscopy

The UV–visible measurements were taken on a double beam Perkin Elmer spectrophotometer Lambda 20, using Hellma quartz cells of 1.0 cm path length.

Sample preparation

The initial methanolic solutions of iodine and Schiff bases were freshly prepared, in 50 ml volumetric flasks, using the following concentrations:

$[\text{I}_2]_0 = 10^{-3}\text{ M}$, for $[\text{SB1-I}_2]$ and $[\text{SB3-I}_2]$ complexes, $[\text{I}_2]_0 = 5 \times 10^{-4}\text{ M}$, for the $[\text{SB2-I}_2]$ complex.

$[\text{SB1}]_0 = [\text{SB3}]_0 = 2 \times 10^{-3}\text{ M}$, and $[\text{SB2}]_0 = 5 \times 10^{-4}\text{ M}$.

Then, a series of nine samples was prepared for each complex, in 10 ml volumetric flasks, maintaining a fixed volume of iodine (1 ml), and varying quantity of Schiff bases (from 1 to 9 ml). The volume of all solutions was adjusted to 10 ml by methanol. Then, the spectra of all complexes were recorded at room temperature (28°C) between 200 and 600 nm.

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