



Spectral investigation of the intramolecular charge-transfer in some aminotriazole Schiff bases

Y.M. Issa*, H.B. Hassib, H.E. Abdelaal, I.M. Kenawi

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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ABSTRACT

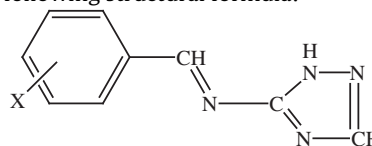
3-Amino-1,2,4-triazole Schiff bases were reported to contain intramolecular charge-transfer. The enhancing and depressing effects were remarkable as the substituent was changed from electron-donating to electron-withdrawing groups. The path of the resonating delocalization was reversed in the case of the p -NO₂ group. To validate these results we effectively used Weinhold et al's natural bond orbital analysis to assess the UV and FT-IR spectrophotometric monitoring of the change reflected in this phenomenon when the substituent in the benzene ring is altered. The NBO analysis was simulated by *ab initio* computations at the HF/6-31G(d) level of theory, in order to properly detect any possible presence of a hydrogen bond association. The changes occurring in electron occupancies of double-centered bonds, antibonding orbitals and in lone-pair orbitals appraised the results, as did the s and p character listings of the two-centered bonds and the simultaneous changes occurring in the geometric parameters of the molecules in question. Contrary to its normal preference, in these molecules the nitrogen used sp^2 hybrid orbitals for its interaction, housing its electron lone-pair in the third p hybrid orbital. Furthermore, NBO analysis reflected the presence of a very soft intramolecular hydrogen association (C–H... π), labelled by UV and FT-IR assignments, between the benzene and triazole rings in all Schiff bases but p -N(Me)₂. The n - π^* stabilization energy decreased in the order: p -OH > p -OCH₃ > p -Cl > p -CH₃ > H > p -NO₂ > o -OH. The relation between the band position and Hammett substitution constant is interpreted in relation to the molecular structure.

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1. Introduction

Charge-transfer is a natural phenomenon that would prevail within molecules when the constituting atoms possess differing electronegativities. This defining feature, along with the natural van der Waals radii, will stabilize the molecule by influencing its geometric orientation. It consequently dictates, to a large extent, the chemical interactions of the compound, having either a positive or negative effect on the potential of the molecule to be available for technological utility in many material aspects including medicinal bioactivity. For example, in their work [1], Emregul et al. pointed out the importance of Schiff bases as corrosion inhibitors, whereas, these compounds were also found to be strong catalyst carriers [2,3], thermo-stable materials [4–6], as well as, powerful ligands in metal ion complex formation [7]. They were also found to possess high potential for useful applications in biological systems [8,9].

The syntheses of new Schiff-based model compounds containing different central groups, together with a variety of side group substitutions, was a recent attribution [10] to the chemistry of these bases. It is a well established fact that the coupling of the 3-amino-1,2,4-triazole molecule along with the biologically active azomethine linkage ($-\text{CH}=\text{N}$), results in a moiety of remarkable pharmacological potential [11]. In previous work, some of us [12] prepared heterocyclic Schiff bases derived from 3-amino-1,2,4-triazole and differently substituted aromatic aldehydes. These bases had the following structural formula:



where X = H (a), p -CH₃ (b), p -OCH₃ (c), o -OH (d), p -OH (e), p -NMe₂ (f), p -NO₂ (g) and p -Cl (h).

Using ¹H NMR, ¹³C NMR and mass spectral techniques, they reported that the rate of exchange, relaxation time, concentration of solution and also the types of solvents used clearly affected the shape, position and integration value of the signal of the aromatic (CH) proton within the triazole ring. They further concluded that

* Corresponding author. Tel.: +20 2 35868094; fax: +20 2 35728843.
E-mail address: yousrymi@yahoo.com (Y.M. Issa).

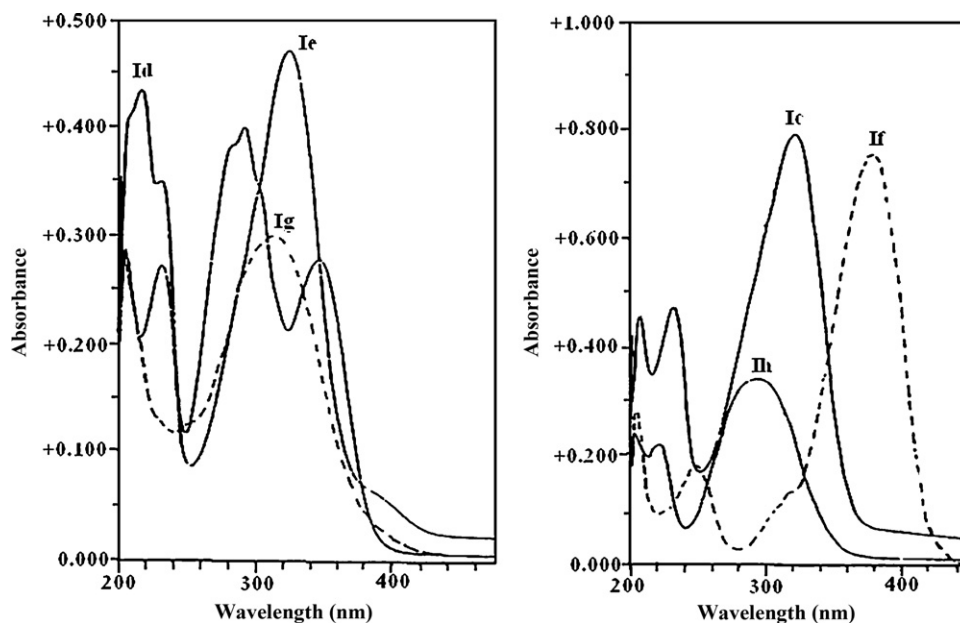


Fig. 1. Electronic absorption spectra of (c [3×10^{-5}], d–h [2×10^{-5}] mol dm $^{-3}$) Schiff bases solutions in ethanol at room temperature.

the electronegativity of the different substituents that are attached to the phenyl ring, had a marked effect on the intramolecular charge-transfer (CT) within the molecules in question. They confirmed their results by the different schemes of fragmentation in the mass spectral analysis [12].

In this work, we use UV and FT-IR spectrophotometric techniques to describe the change occurring in the transfer of charge down the conjugated bonds of the same heterocyclic Schiff bases. The electronic absorption spectra were studied in different polar solvents and the absorption bands assigned to their corresponding electronic transitions. The relation between these band positions and the Hammett substitution constant [13,14] is interpreted to molecular structure. The energy (E_{CT}) and ionization potential (calculated using the Briegleb equation) [15] of the intramolecular CT transition bands were compared to the experimental values obtained from λ_{max} of the electronic absorption spectra. FT-IR spectrometry was utilized to assign the wavenumbers relating to the different substituents, in order to further evaluate the substituent effect on the enhancement and depression of the CT along the molecular skeleton.

To assess the results obtained from the spectrophotometric identification of such intramolecular CT, *ab initio* computational algorithms, including the natural bond orbital analysis (NBO) [16], were executed utilizing the *Gaussian W03 package of program* [17]. The energies, ionization potentials, dipole moments and geometric parameters were computed by applying the restricted Hartree–Fock level of theory with a medium basis set 6-31G(d). Since the effect of electron correlation on charge density is insubstantial enough to be unable to disrupt the consistency of the work [18], we chose the above level of theory in order to avoid being misled by any effects that would underestimate the H-bond interaction and misread the association distance.

The change in the natural hybrid orbital (NHO), leading to the NBO character of the two-centered bond, was inspected stringently to identify the effect of the resonating delocalized π -electrons existing in various sites within the molecule. Such delocalization could be responsible for π - π^* transition along the molecular skeleton. Consequently, the withdrawing (donating) effects caused by the substituents in the benzene ring were simultaneously studied. This was further followed up by inspecting the changes occurring in electron occupancies of double-

centered bonds, antibonding orbitals, as well as, in lone-pair orbitals.

2. Experimental

All the chemicals used were analytical grade from either Fluka (Germany) or Aldrich (USA), whereas, the heterocyclic Schiff bases were prepared according to a previously reported method [12].

The UV electronic absorption spectra were recorded using a Hewlett-Packard 8452A Diode Array Spectrophotometer. Stock solutions of the studied materials (mostly 10^{-3} M) were freshly prepared by accurately weighing the required amount of solid and dissolving it in the appropriate volume of the solvent in question (methanol, ethanol or DMSO). Solutions required for spectral measurements were prepared by appropriate dilutions from stock solutions. All measurements were performed at room temperature using quartz cuvettes with a path length of 10 mm.

The infrared spectra were recorded on a Mattson 4020 Galaxy series spectrophotometers as KBr pellets pressed between two polished steel plates in a cylindrical dye with a hydraulic press.

2.1. Theoretical methodology

Ab initio computational algorithms, including the natural bond orbital analysis (NBO) [16], were executed by the *Gaussian W03 package of programs* [17]. The energies, ionization potentials, dipole moments and geometric parameters were computed by applying the Hartree–Fock method with a medium basis set. All structures were optimized at the restricted HF/6-31G(d) level of theory with the natural population analysis. The change in the natural hybrid orbital (leading to the NBO) character of the two-centered bond was inspected stringently to identify the effect of the resonating delocalized π -electrons existing in several sites within the molecule.

3. Results and discussion

3.1. Electronic absorption spectral studies and NBO analysis

The electronic absorption spectra of the investigated heterocyclic Schiff bases (c–h) are shown in Fig. 1, whereas, their molar absorptivities (ϵ mol $^{-1}$ dm 3 cm $^{-1}$) and maximum wavelengths

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