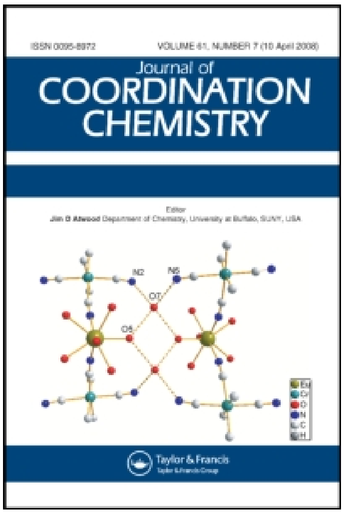

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# Proton Transfer in Crystalline Aromatic Schiff Bases and Their Electronic Properties

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# PROTON TRANSFER IN CRYSTALLINE AROMATIC SCHIFF BASES AND THEIR ELECTRONIC PROPERTIES

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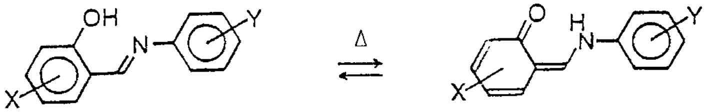
Abstract Aromatic Schiff bases having extended $\Pi$-electron systems and their charge transfer (CT) complexes have been prepared and subjected to structural, optical, and electrical conductivity studies. It is demonstrated by the X-ray crystallographic study that the hydroxyl protons form hydrogen bonds to the imino nitrogens, strength of which can be varied by chemical modification of the molecules. Intramolecular proton transfer takes place in solid state and is manifested in the thermochromic spectral changes.

**Keywords:** **Aromatic Schiff bases, proton transfer, crystalline**

## INTRODUCTION

Schiff bases which are effective as chelating ligands usually bear a functional group, -OH, near the azomethine group and the proton of the OH group should be released in the process of coordination. However, it is this proton that serves for our present purpose. As shown in Equation (1), some of salicylideneaniline derivatives are known to exhibit thermochromism in solid state arising from the proton transfer between the O and N atoms.



(1)

OH form (yellow) NH form (orange)

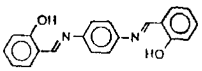
It should be noted here that the molecule in the NH form having a deeper color consists of a quinoid (electron acceptor) and an aromatic amine (electron donor) moieties and it can be regarded as an intramolecular charge transfer compound. If a sufficient amount of intermolecular charge transfer interaction is generated when these molecules are assembled in crystals, the resulting solid state electronic properties should be influenced by the proton transfer motion. In the ideal case, the proton motion could couple to the electron conduction. Our specific goal is to create novel organic conductors which utilize the proton motion as an effective "phonon". In this report is given an overview of our structural and optical studies on fundamental properties of the aromatic Schiff bases in crystalline state.

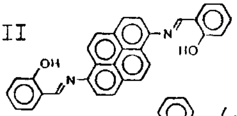
## MOLECULAR AND CRYSTAL STRUCTURES

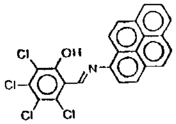
In solid state, the protons in question are involved in hydrogen bonds between the O and N atoms in both of the OH and NH forms. Table I lists selected interatomic distances involving the hydrogen bonds for some Schiff bases (I - III) and CT complexes (IV and V). While in the case of I and II, the O-H bond length is rather normal as a hydroxy group, the proton has shifted towards the N atom in III with tetrachloro-substitution on the salicylidene moiety. Further, in IV and V, the protons are located even closer to the N atoms suggesting that the electron density distribution in the

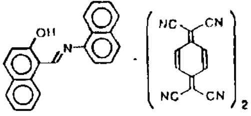
TABLE I Selected interatomic distances (Å).

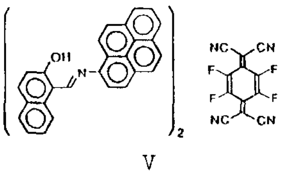
| Bond in OH form | I | II | III | IV | V |
|---|---|---|---|---|---|
| O-H | 0.97(3) | 1.01(6) | 1.17(6) | 1.70(5) | 1.38(3) |
| N--H | 1.69(3) | 1.79(6) | 1.44(7) | 1.25(7) | 1.23(3) |
| O---N | 2.607(2) | 2.614(4) | 2.534(5) | 2.540(7) | 2.496(3) |
| C-O | 1.349(2) | 1.356(5) | 1.316(6) | 1.294(7) | 1.318(4) |
| C-C(=N) | 1.448(3) | 1.442(6) | 1.434(7) | 1.423(7) | 1.418(3) |
| C=N | 1.284(2) | 1.283(5) | 1.298(6) | 1.309(8) | 1.314(4) |
| (C=)N-C | 1.421(2) | 1.413(5) | 1.413(6) | 1.421(7) | 1.403(3) |

I 

II 

III 

IV 



V

molecule changes upon CT complex formation. Other structural changes accompanied by the shift in proton location are typified by the reduction in the C-O bond length, corresponding to the increased contribution of the NH form in Equation (1). These examples demonstrate the feasibility of controlling the proton transfer equilibrium by chemical modification.

Figure 1 shows crystal packing for I as an example. The molecules are nearly perfectly planar and form one-dimensional columns of parallel stacking. Segregated stacking of donors and acceptors is one of the features desirable for conductive organic CT complexes and such parallel stacking of Schiff base molecules as in I should be more favorable in terms of electrical conductivity. This stacking mode is achieved also in II but the crystal packing is loose since the molecules are not planar. Compound III contains "mixed" stacked molecules with donor and acceptor portions stacked alternately. At any rate, these single-component solids are insulators and substantial decrease in resistivity is observed when the Schiff bases are combined with acceptors such as TCNQ, $F_4$TCNQ, and iodine. In semiconducting complexes IV and V, however, the molecular stacking is of "mixed" fashion. It is necessary to control the crystal packing mode for further enhancement in conductivity.

## OPTICAL PROPERTIES

Figure 2a illustrates thermochromism of I showing single-crystal electronic absorption spectral changes with temperature. The absorption spectra J recorded at 4.2K represent $\Pi \rightarrow \Pi^*$ transition in the OH form. As temperature rises, a new absorption band at 2.4 eV grows in. Assigning this band to the NH form, the activation energy for the proton transfer in Equation (1) is evaluated to be 0.1 eV. The large Stokes shift of the emission spectra at low temperatures (Figure 2b) is characteristic of the internal proton transfer process and confirms the origin of the thermochromism.

Figure 3 gives an example of single-crystal IR spectra, in which the broad absorption band peaked at 2580 cm$^{-1}$ is assigned to the OH stretching mode in I. Its breadth and low-frequency shift are characteristic of fairly strong hydrogen bonds. IR spectra are now being collected for other derivatives as well and analyzed for correlation to certain structural parameters.

The present study demonstrates that the internal proton transfer in Schiff bases is quite feasible and controllable in crystalline state and more advances are anticipated with more elaborate molecular assembly designs.

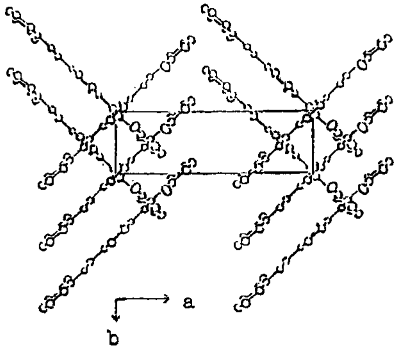


FIGURE 1 Crystal packing of I.

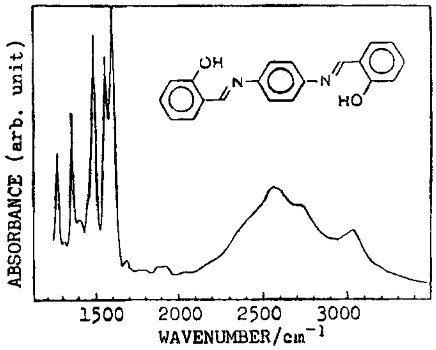


FIGURE 3 IR specra of I.

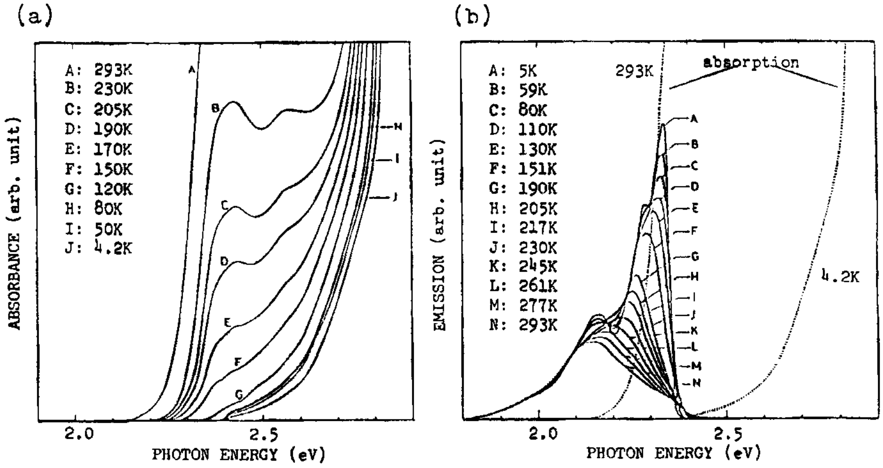


FIGURE 2 Absorption (a) and emission (b) spectra of I.