Spectral and Electrical Conductance Studies of Charge-Transfer Complexes Derived from 6-Aminoindazole Schiff Bases and Chloro-*p*-benzoquinone Derivatives

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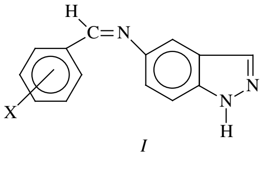
Molecular complexes of the charge-transfer (CT) type 5- or 6-aminoindazole Schiff bases with chloroanilic acid, dichlorodicyano-*p*-benzoquinone, and chloranil have been prepared and investigated by IR and electronic spectra. The type of bonding between the donors and acceptors depends on the nature of both components. The change of electrical conductance with temperature for some CT complexes was also studied aiming to clarify their semiconductor behaviour. The current—electric potential dependence was also studied and indicated an ohmic character.

The formation of molecular complexes of the charge-transfer (CT) type between donors and acceptors plays an important role in many biological processes, *e.g.* enzyme catalysis, drug action, and ion transfer through lipophilic membranes; all involve complexation between two or more distinct molecules [1, 2]. Accordingly, much interest has been paid to molecular CT complexes [3—15]. Also, it is possible that organic semiconductors of the CT type can find application as cheap sources for the construction of organic solar batteries in virtue of their semiconducting properties [16—21].

The present paper is concerned with the preparation of the solid CT complexes of Schiff bases derived from aminoindazole as donors and chloroanilic acid (1), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (2), and *p*-chloranil (3) as acceptors. The solid complexes obtained are investigated by spectral and electrical methods. These tools proved to be very helpful in investigating the type of interaction and the nature of the bonding in these compounds.

The acceptors used in the present investigation are either acidic molecule (1) or neutral molecules (2 and 3). It is expected that the molecular compounds formed with acceptor 1 would be formed through proton and electron transfer while acceptors 2 and 3 form molecular compounds through electron transfer only [22]. Accordingly, each type of CT complexes is considered separately. The donors used have the general formula



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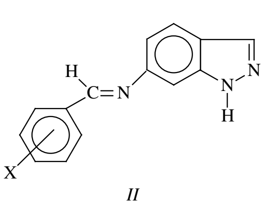


II

where X = H (*a*), *p*-$N(CH_3)_2$ (*b*), *p*-OCH_3 (*c*), *p*-OH (*d*), *o*-OH (*e*), 2-OH-naph (*f*), *p*-Cl (*g*), *p*-Br (*h*), and *p*-NO_2 (*i*).

In CT complexes of acceptor 1, an acid-base reaction involving a proton transfer from the acceptor to the donor is to be expected. This should involve, at least, one basic centre from the donor, either the azomethine nitrogen or the dimethylamino nitrogen in case of compounds *Ib* and *IIb*. A comparison between the IR spectra of the free components and those of the CT complexes reveals the presence of a broad band within the $\tilde{\nu}$ = 2400—3000 cm^{-1} range (Fig. 1).

This band can be assigned to the stretching mode of a proton attached to a quaternary positive nitrogen formed through the proton transfer from one OH group of the acceptor to the basic centre on the donor molecule. Such an interaction is supported by the shift of the C═N band of the donors to lower wavenumbers. Also, the various vibrational bands of the weaker bonded OH group at 3235 cm^{-1}, 1270 cm^{-1}, and 1212 cm^{-1} are no more observed in the spectra of the CT complexes. Also the negative charge on the oxygen of the phenolate ion would decrease the acidity of the second OH group leading to a lower probability for the transfer of the second proton from the acceptor to the donor molecule. Due to the increased electron density on the acceptor molecule, the bands due to the C═O, C═C, and C—C vibrations of acceptor 1 are shifted to lower wavenumbers, as a result of the π—π^* electron transfer.

In CT complexes of picric acid as electron acceptor with some donors, it was stated from the result of dichroic IR study of oriented crystal [23] and normal IR studies [24] that about two rings of the donor and acceptor are oriented parallel to each other with charge-transfer direction perpendicular to the planes

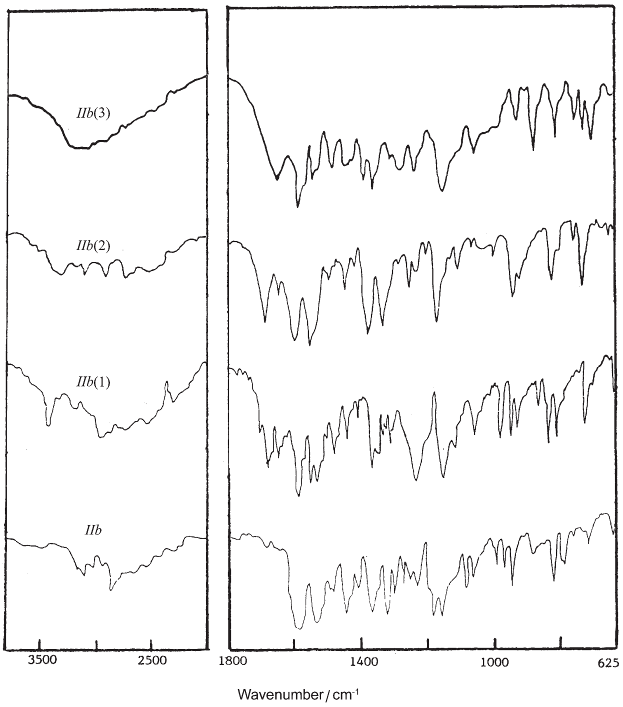
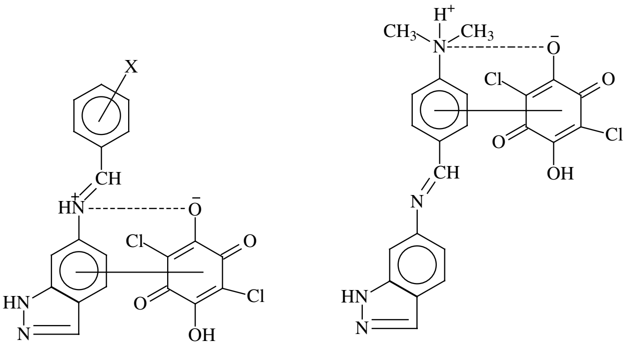


Fig. 1. IR spectra of *IIb* and its CT complexes with the acceptors 1, 2, and 3.

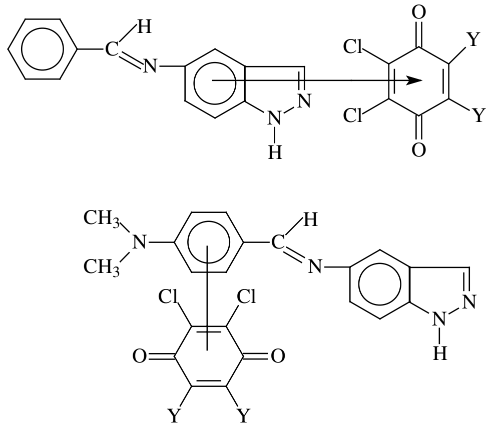
of the two rings. Also the X-ray investigation of single crystal of the complexes indicated that the distance between the two molecules forming the CT complexes was found to be 2.7—3.4 Å [25, 26].

Thus, the CT interaction with acceptor 1 can be formulated as follows



The complexes formed with acceptors 2 and 3 involve only a charge interaction. Accordingly, the spectral shifts would be ascribed to the increased electron density on the acceptor and its decrease on the donor molecule. Thus, the bands of the donor parts are mostly shifted to higher wavenumbers whereas those of the acceptor molecules display a counter shift. The shifts of the γ_CH bands of the indazole ring are more pronounced than those of the γ_CH bands of the benzal ring except for donor *b*; for this donor the shift of the γ_CH of the benzal ring is higher than that for the indazole ring. Thus the indazole ring is the origin of the CT donation for all donors except donor *b* where the benzal ring is the donor centre.

For the acceptors molecules the ν(C=O) and ν(C≡N) are shifted to lower wavenumbers as a result of the increased electron density on the acceptor compared to its free state. Accordingly, the bonding between the donor and the acceptor molecules may be formulated as



where Y = CN for acceptor 2 and Cl for 3.

The electronic absorption spectra of the solid CT compounds as Nujol mull compared to those of the free donors and acceptors reveal the existence of new bands within the λ = 470—540 nm range which are not observed in the spectra of the free components. The appearance of one band denotes that no n—π^* interaction is liable to occur besides the π—π^* interaction.

The energy of the CT band corresponding to the π—π^* interaction is used in determining the π-ionization potential (P_I) of the donors using the Briegleb equation [27]. The P_I values thus obtained are comparable with those determined from the electronic absorption spectra of the free donors applying the relation

$$P_\mathrm{I} = a + b\nu_\mathrm{o}$$

in which ν_o is the energy of the HOMO → LUMO (π—π^* transition). $\{a\}$ and $\{b\}$ are constants amounting to 4.39 and 0.857, 5.156 and 0.778 or 5.11 and 0.701 [28, 29].

The electrical conductivities for the CT complexes of donor *IIb* with the three acceptors were measured. Fig. 2 illustrates the plot of $\log\{\sigma\}$ as a function of the reciprocal of temperature (1000 K/T) in accordance with the following equation

$$\sigma = \sigma_\mathrm{o}\mathrm{e}^{-\Delta E/kT}$$

where σ is the electrical conductivity at a given temperature T, σ_o is the initial conductivity (the pre-exponential factor), ΔE is the activation energy of conduction, and k is the Boltzmann constant.

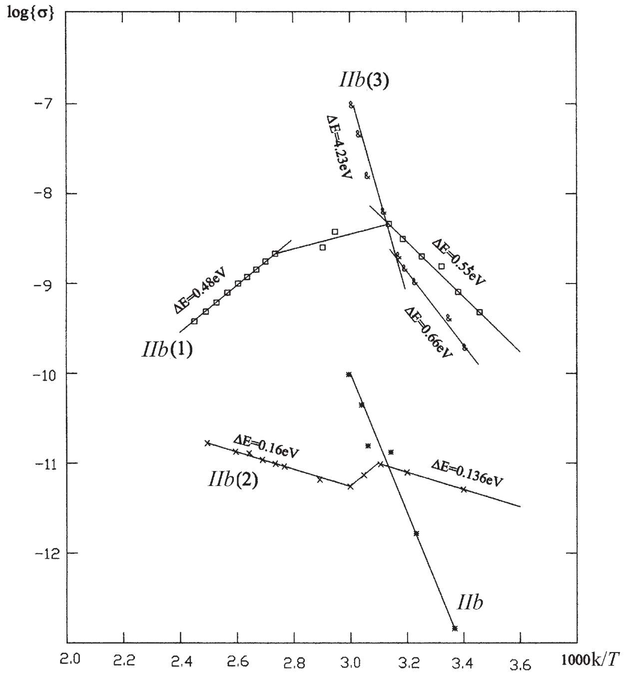


Fig. 2. Relation between log $\{\sigma\}$ and 1000 K/T. Temperature dependence of the electrical conductivity of CT complexes of donor *IIb* with acceptors 1, 2, and 3.

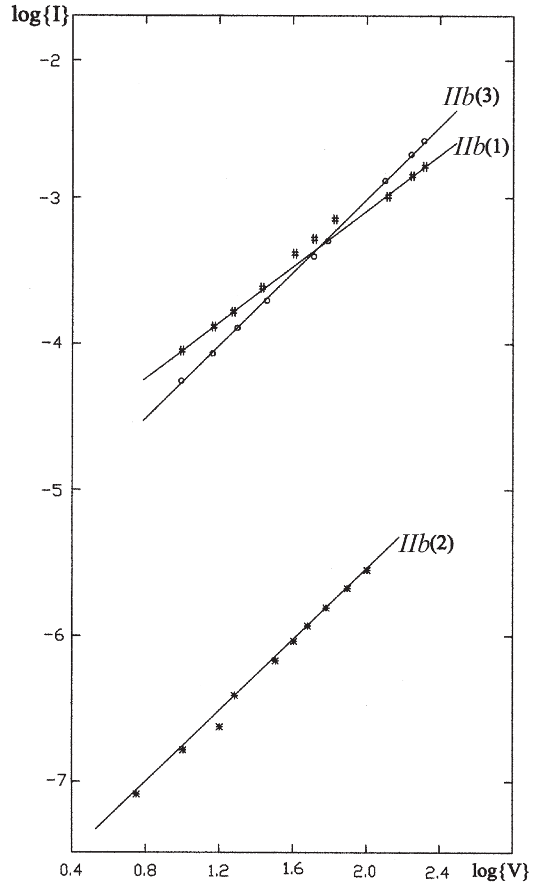


Fig. 3. Log $\{I\}$—log $\{V\}$ characteristic of CT complexes of donor *IIb* with acceptors 1, 2, and 3.

The CT complexes under investigation are considered to be among those organic compounds that are semiconducting. In addition, the CT complexes of acceptor 1 show a metallic behaviour at higher temperature.

The temperature dependence of the electrical conductivity is characterized by two activation energies indicating that the mode of conduction changed during the conductivity measurement [16] with the change of temperature.

The conductivity of organic molecular complexes is known to increase with the electron affinity (E_A) of the acceptor [30—32]. Accordingly, the activation energy decreases as the conductivity of the compounds increases.

For the CT complexes of acceptors 2 and 3 the activation energies were found to decrease from acceptor 2 to 3. The irregular behaviour of chloroanilic acid complex is in accordance with the fact that the molecular complexes of acceptor 1 are different from those of acceptors 2 and 3, since it takes place through electron and proton transfer.

The *I vs. V* plots on a log-log scale for the CT complexes of donor *IIb* with acceptors 1—3 show straight line relation, which indicates that the CT complexes have an ohmic character (Fig. 3).

EXPERIMENTAL

The chemicals used in the present investigation were pure laboratory grade chemicals available from BDH.

The IR spectra were recorded on the Perkin—Elmer double-beam spectrophotometer using the KBr-disc technique [24]. The electronic spectra (Nujol mull) were obtained by the aid of the Shimadzu 240 UV/VIS recording spectrophotometer. The electrical conductivity and the electric potential (I—V) measurements were made on a Super Megohmmeter (Model RM 170) electrometer. The samples were pressed into discs of 13 mm diameter and 1.3 mm thickness under a pressure of about 29.4×10^6 Pa. The surfaces of the discs were painted carefully with a silver paste. The temperature was measured in air using a Cu/CuNi Comark thermometer placed close to the sample.

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