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Computational studies of molecular charge transfer complexes of heterocyclic 4-methylepyridine-2-azomethine-*p*-benzene derivatives with picric acid and *m*-dinitrobenzene

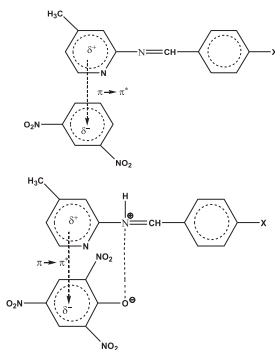
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HIGHLIGHTS

- Computational studies of molecular charge transfer complexes.
- Between aryl Schiff bases as donor and *m*-dinitrobenzene and picric acid as acceptors.
- The optimized structures for donors, acceptors and CTCs obtained from PM3 calculations.
- Vibrational modes, absorption bands and ¹H NMR spectra were calculated by HF and DFT.
- The results of HF and DFT give good agreement to the experimental results.

GRAPHICAL ABSTRACT

The structural formula of the charge transfer complexes of aryl Schiff bases with *m*-dinitrobenzene and picric acid.



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ABSTRACT

Charge transfer complexes of substituted aryl Schiff bases as donors with picric acid and *m*-dinitrobenzene as acceptors were investigated by using computational analysis calculated by Configuration Interaction Singles Hartree–Fock (CIS-HF) at standard 6-31G* basis set and Time-Dependent Density-Functional Theory (TD-DFT) levels of theory at standard 6-31G** basis set, infrared spectra, visible and nuclear magnetic resonance spectra are investigated. The optimized geometries and vibrational frequencies were evaluated. The energy and oscillator strength were calculated by Configuration Interaction Singles Hartree–Fock method (CIS-HF) and the Time-Dependent Density-Functional Theory (TD-DFT) results. Electronic properties, such as HOMO and LUMO energies and band gaps of CTCs set, were studied by the Time-Dependent density functional theory with Becke–Lee–Young–Parr (B3LYP) composite exchange correlation functional and by Configuration Interaction Singles Hartree–Fock method (CIS-HF). The ionization potential I_p and electron affinity E_A were calculated by PM3, HF and DFT methods. The columbic force was calculated theoretically by using (CIS-HF and TD-DFT) methods. This study confirms that the theoretical calculation of vibrational frequencies for (aryl Schiff bases – (*m*-dinitrobenzene and picric acid)) complexes are quite useful for the vibrational assignment and for predicting new vibrational frequencies.

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Introduction

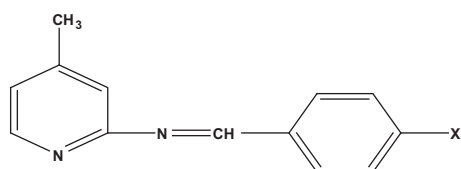
The interactions between electron donors and acceptors to form charge transfer complexes have been a great importance since these materials can be utilized as organic semiconductors [1] and photocatalysts [2]. They are also important in the study of redox processes [3]. They exist in literature as theoretical [4,5] and experimental studies [6,7]. More recently, attention has been given to the isolation and investigation of physical properties of some CT-complexes in the solid state. Some of these complexes show interesting electrical conductivity properties and have found application in many forms of electronics and solar cells [8,9]. Much of the work in this field [10,11] has been discussed in books of Briegleb, Rose, Andrews and Keefer [12], Foster [13], and Mulliken and Person [14]. Charge transfer complexes are also extensively discussed in Kosower's Physical Organic Chemistry. There are also several review articles on various aspects of charge transfer complexes [15,16].

The present investigation is concerned with the computational studies of molecular charge transfer complexes formed through the interaction of some aryl Schiff bases derived from 2-amino-4-methylpyridine which acts as a donors with *m*-dinitrobenzene and picric acid as π -acceptors. we were reported PM3 calculation results on aryl Schiff bases (a–c), *m*-dinitrobenzene, picric acid and CTCs to give the optimized structures. Vibrational modes, absorption bands and ^1H NMR spectra of picric acid, *m*-dinitrobenzene and CTCs were calculated by HF and DFT method.

Methodology

Computational

The molecular structures of aryl Schiff bases (a–c), picric acid, *m*-dinitrobenzene and charge transfer complexes in the ground state were optimized by PM3, HF method and Becke3–Lee–Yang–Parr (B3LYP) functional and supplemented with the standard 6-31G* basis set (referred to as HF calculations) and 6-31G** basis set (referred to as DFT calculations) [17,18]. Using GAUSSVIEW program [19] with symmetry considerations along with available related molecules, all structures were fully optimized. Vibrational frequency assignments were made with a high degree of accuracy. The HF and DFT theoretical calculations were made by using Gaussian 03 program package [20].



Where X=*p*-N(CH₃)₂ (a), H (b) and *p*-NO₂ (c)

The structural formula of aryl Schiff bases

Results and discussion

Molecular structure of donor and acceptor molecules

The results of the optimized molecules were combined together (donor–acceptor) to produced CTCs then optimized it by PM3 method (Fig. 1). The calculated geometric parameters for the aryl Schiff bases (a–c), picric acid and *m*-dinitrobenzene which obtained by HF/6-31G* method are shown in Tables 1 and 2.

As shown in Table 1, the title compounds contains a clear “aryl Schiff bases” double bond C(1)=N(1) in 1.260 Å which is comparable with those observed in other Schiff bases [21,22]; whilst, the distances of C(8)–N(1) and C(7)–N(3) are 1.406 Å and 1.442 Å,

respectively. As they are obviously longer than C(1)–N(1), they should be single bonds. All bond lengths and bond angles are within normal ranges and comparable to those corresponding in other similar compounds [22]. The bond lengths N(2)–C(8) (1.319 (2) Å) and N(2)–C(11) (1.322 Å) fall between C–N and C=N bonds because of the conjugation effects in the molecule [22]. The compound “picric acid” double bond C(1)=C(2) is 1.378 Å which is comparable with those observed in other picric acid [23]; whilst, the distances of C(1)–N(1) and C(6)–O(7) are 1.456 Å and 1.333 Å, respectively. As they are obviously the distances of C(1)–N(1) were longer than C(1)–C(1), they should be single bonds. All bond lengths and bond angles are within normal ranges and comparable to those corresponding in other similar compounds [23]. The double bond C(1)=C(2) in *m*-dinitrobenzene is 1.384 Å which is comparable with those observed in other *m*-dinitrobenzene [24]. All bond lengths and bond angles are within normal ranges and comparable to those corresponding in other similar compounds [24].

Assignments of vibrational frequencies

Interaction involving electron transfer

Vibrational spectroscopy is used extensively in organic chemistry for the identification of functional groups of organic compounds as well as the studies on molecular conformation, reaction kinetics, etc. Assignment for complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamentals [25]. The type of CT interaction is observed when the donors react with non-acidic acceptors such as *m*-nitrobenzene, Table 3. The IR spectra of CT complexes compared to the simple component reveal an apparent shift of the γ_{CH} bands of the acceptor to lower wavenumbers, while those of donor are shifted to higher values Fig. 2, a behavior which is characteristic of the π – π^* CT interaction (π HOMO_D– π^* LUMO_A). This leads to increased π -electron density on the acceptor molecule and its decreases on the donor one. The shifts of the γ_{CH} bands of the donor molecule in case of 1:1 complexes are higher for the bands of the pyridine ring for donor (b) and (c) indicating that this ring would be the origin of CT interaction. For donor (a) the shift of the γ_{CH} bands is more apparent with bands of benzyl ring. It seem accordingly that the existence of the strong donor N(CH₃)₂ group on the benzyl ring would lower its ionization potential [26] to such an extent that it will be profitably the donor center [27].

The NO₂-bands of the acceptor display some interesting changes the asymmetric NO₂-bands become boarder and show some splitting in the spectra of the charge transfer complexes with non-acidic acceptor. This behavior reflects an increased differentiation of the energy states of the NO₂-group in the charge transfer complex than in the free acceptor. The asymmetric NO₂-bands appear in the spectra of the free acceptors as two adjacent peaks. The lower energy bands display a shift to lower wavenumber indicating a stronger polarization if the NO₂-groups corresponding to these bands which originates from the increased electron density on the ring of acceptor. The asymmetric NO₂-band of the CT complexes with the acceptor (such as *m*-nitrobenzene) shows a shift to lower wavenumber, hence n – π^* interaction is to be excluded [28,29].

Interaction involving proton and electron transfer

This type of interaction occurs when the donors used are allowed to react with acceptors having strong acidic properties such as picric acid. The IR spectra of these complexes display drastic changes compared to those of their components Fig. 2. The γ_{CH} bands of donors shift to higher wavenumbers while those of the acceptors are shifted to lower ones, a behavior which is characteristic of the π – π^* CT interaction as in the first type. Also, the IR

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