ADDIS ABEBA UNIVERSITY

Graduate School

Department of Chemistry

M.Sc. Graduate Project

(Chem.774)

Title- *Theoretical investigation on some photophysical phenomenon expressed by isomeric equilibria*

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Content

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Henok Darsema

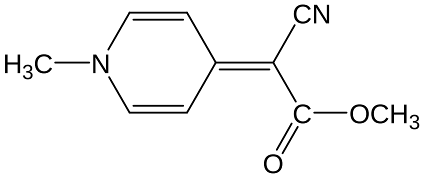
1. Introduction

The interest in the spectroscopic properties of 4-(N, N-dimethylamino) benzonitrile (DMABN) has attracted increasing attention since the first experimental observations by Lippert et.al [1]. The unusual property reported was dual fluorescence of DMABN. Dual fluorescence has successively been observed in several other electron donor-acceptor compounds. Attempts were made by different scholars to explain the unusual spectroscopic behavior of DMABN and related compounds [2,3]. Different physical models have been proposed to explain the electronic and physical structure of dual fluorescent compounds.

Grabowski and coworkers proposed a scheme involving intramolecular charge transfer with a 90^0 twisting motion of the donor group leading to the formation of an emissive transient species called intramolecular charge transfer state (TICT). Alternative models like planar intramolecular charge transfer (PICT), wagging intramolecular charge transfer (WICT) and rehybridyzation intramolecular charge transfer (RICT) have been proposed to explain the dual fluorescence phenomenon in different donor-acceptor systems. [4] Although a number of studies seem to favor the TICT model there are significant number of studies, which show that the TICT model does not hold for all dual fluorescing systems. This leaves the research in the area still wide open [3]. Beyond this an unusual dual intermolecular charge transfer is observed in solvents having charge deficient behavior. [5]

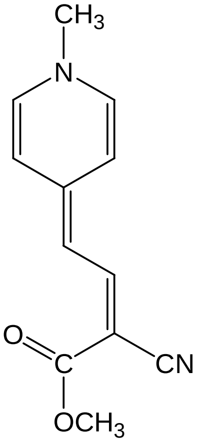
Despite the failure to reach a universal consensus on the electronic structure and physical model for such unusual spectroscopic behaviors the compounds are getting wide applications. Fluorescence markers, chemical sensors, electro optical chromophores in photo refractive dyes, and biological switches are few of the many applications [6], Thus study of these compounds is important. The chromophores investigated in this project are shown in Fig.1.1 as structures I and II.

I



methyl 2-cyano-2-(1-methyl pyridine-4(1H)-ylidene)acetate **(MCPA)**

II

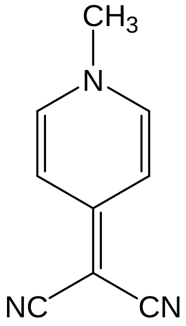


(2Z)-2-acetyl-4- (1-methylpyridin-4 (1H)-ylidene) but-2-enenitrile **(MCPN)**

Fig. 1.1- Structures MCPA and MCPN investigated.

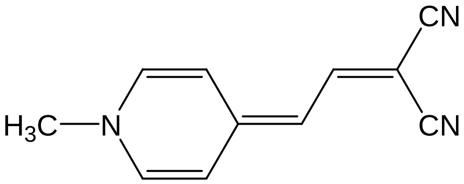
These chromophores are investigated using computational methods described in section 3. For comparison structures III and IV in Fig. 1.2 i.e. the di-cyano counter parts are also tested for dipole moments.

III



2-(1-methylpyridin-4(1*H*)-ylidene)malononitrile

IV



2-(2-(1-methylpyridin-4(1*H*)-ylidene)ethylidene)malononitrile

Fig. 1.2- Structures III and IV used for comparison purpose.

Studies for the physical models have been taking various directions. Both computational and experimental investigations have been reported [7,8,9,10]. Since the report of dual fluorescing compounds computational methods have advanced a lot. This paper reports the computational reports of two chromophores known to be dual fluorescing. In addition to the report on the investigation of the chromophores the paper goes through the theoretical back ground of computational methods. Further it highlights the physical models so far introduced. Finally a conclusion will be given based on the results obtained and on comparisons to other results.

1.1 Physical Models for Dual Fluorescence

The fundamental observations in dual fluorescence are

2- The second red shifted (bathochromic shifted) band appears only in polar solvents.
3- Parallel to the appearance of the second band the intensity of the first band becomes weaker and is not even observed in high polar solvents.

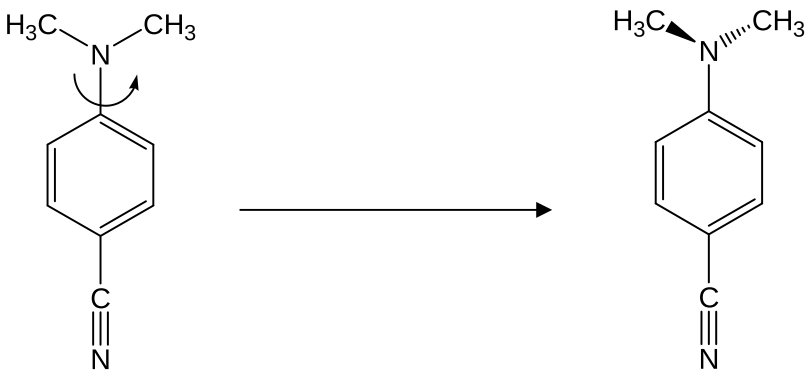
The increased quantum yield when hydrocarbons are replaced by polar solvents combined with the dependence on environment polarity is supposed by most scholars to indicate a highly dipolar excited state achievable only by a charge transfer in combination with an internal geometric relaxation out of locally excited state (L.E) and not reachable by direct excitation. This second band shows a large solvatochromic shift, which is characteristic for emission from a charge transfer state. To explain the supposed geometrical relaxation a number of monomolecular models have been proposed by different researchers. The twisted intramolecular charge transfer (TICT) model stands to be more prominent and over shadowing model for over 40 years. Generally monomolecular models interpreting the nature and structure of the intramolecular charge transfer state fall into four main classes: [3]

- TICT (twisted intramolecular charge transfer)
- PICT (planar intramolecular charge transfer)
- WICT (wagged intramolecular charge transfer)
- RICT (rehybridization intramolecular charge transfer)

The next section will go through the four models known well.

TICT (Twisted Intermolecular Charge Transfer)

A system consisting of connected donor D and acceptor A can relax towards a perpendicular conformation with full charge separation twisted intramolecular charge transfer (TICT) as shown in Figure1.3 below.

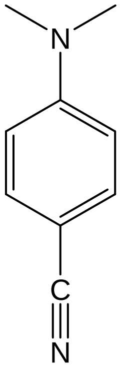


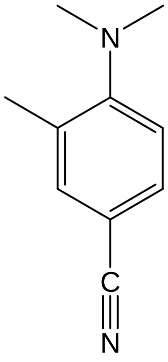
Planar (0°) **Twisted (90°)**

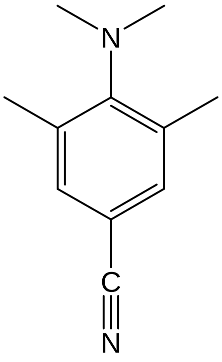
Fig. 1.3. The ground planar structure and the twisted CT state of DMABN

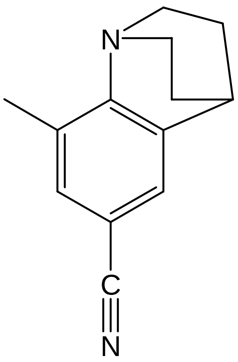
First suggested by Rotkjewicz Grellmann and Grabowski in 1973, the widely accepted TICT model predicts the intramolecular relaxation of the planar vertically excited state (locally excited) to be a highly dipolar charge transfer state with perpendicular orientation of the amino (electron donor) and benzonitrile (electron acceptor) moieties as the cause for the occurrence of the strongly red shifted fluorescence band. The twist plus the internal charge transfer together bring up the so-called TICT state. Emission from the locally excited state leads to fluorescence with normal strokes shift, where as radiative deactivation of the TICT state gives rise to the anomal largely red-shifted fluorescence.

In experimental studies similar compounds other than *p*-DMABN were investigated for fluorescence. These compounds showed dual fluorescence in polar solvents as expected. The following structures were studied [11]


(1)


(2)


(3)


(4)

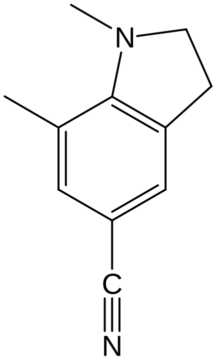

(5)

Fig. 1.4- Structures investigated for TICT model.

In Fig.1.4 above the compounds are arranged in increasing order of steric effect. Model compounds for the CT of 1, with a strong steric hindrance against co planarity of the amino and nitrile groups (2,3) or fixed 90^0 twisted configuration (4) exhibit only the CT emission; that with amino group fixed in the molecular plane (5) only the "normal" (LE) fluorescence.[8]. This phenomenon is used to prove that the amino group rotation models the CT state. Other different reports on different compounds have been presented as proofs of the TICT model. [1,7,10,12,13]

The PICT-Model

Zachariasse et al introduced the PICT model. When the two excited states are sufficiently close in energy, a change in the amino group (from pyramidal to planar) allows a vibronic coupling between them with formation of a charge transfer state. Besides this basic structural change the global process will involve also changes of the bond lengths in the molecule. In the PICT model the second singly excited state (S_2) has a substantially larger dipole moment than S_1, which preferentially decreases it's energy relative to that of S_1 upon increasing solvent polarity. When the energy gap ΔE (S_1,S_2) is sufficiently small a dynamic state reversal can occur after excitation leading to an emitting ICT state along LE and dual fluorescence appears.[2]

The WICT-Model

The WICT model (wagging intermolecular charge transfer) proposed by Gorse and Pesquer, predicts a charge transfer state, where the amino nitrogen lone pair orbital is decoupled from the benzonitrile π-orbitals by means by means of an amino wagging mode. Therefore the WICT model demands a strong deviation from planarity corresponding to large values for the wagging angle ω. This change of the pyramidalization of the amino nitrogen is considered to be the sole relaxation mode responsible for the dual fluorescence. With the wagging angle being its characterizing coordinate; a change of the amino nitrogen from planar sp^2 to pyramidal sp^3 hybridization is described as another possible hypothesis for the description of the observed dual fluorescence phenomenon. [3]

The RICT-Model

In 1996, an in plane bending of the cyano group was calculated as another possible main relaxation coordinate. With this so-called RICT hypothesis (Rehybridization by intramolecular charge transfer), an SP to SP^2 rehybridization of the carbon atom of the cyano group (acceptor), causing a relaxation by bending of the cyano angle, is presented as the main stabilizing factor the formation of the charge transfer state. [3]

2. Computational Review [14,15]

In order to describe microscopic systems, a different mechanics other than the classical mechanics was required. One promising candidate was wave mechanics, since standing waves are also a quantized phenomenon. The fundamental postulate of quantum mechanics is that a so-called wave function, ψ, exists for any system and that appropriate operators which act upon ψ return the observable properties of the system. The operator, that returns the system energy; E, as an eigenvalue is called the Hamiltonian operator; $\hat{H}$, thus we write

$$\hat{H}\psi = E\psi \qquad \textbf{(2.1)}$$

which is the Schrödinger equation, can to a good approximation be separated into one part, which describes the electronic wave function for a fixed nuclear geometry, and another part, which describes the nuclear wave function, where the energy from the electronic wave function plays the role of a potential energy. Casting the Hamiltonian into mathematical notation we have:

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_i\sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{ij}\frac{e^2}{r_{ij}} + \sum_{kl}\frac{e^2 Z_k Z_l}{r_{kl}} \qquad \textbf{(2.2)}$$

where i & j run over electrons, k and l run over nuclei, ħ is Planck's constant divided by 2π, m_e is the mass of the electron, m_k is the mass of nucleus k, ∇^2 is the Laplacian operator, e is the charge on the electron, Z is an atomic number and r is the distance between two particles.

The above Hamiltonian contains pair wise attraction and repulsion terms, implying that no particle is moving independently of all of the others. In order to simplify the problem somewhat we may invoke the so-called Born-Oppenheimer approximation. As nuclear are much heavier than electrons their velocities are much smaller. The Schrödinger equation can therefore to a good approximation be separated into one part that describes the electronic wave function for a fixed nuclear geometry and another part, which describes the nuclear wave function, where the energy from the electronic wave function plays the role of a potential energy. This separation is called the Born-Oppenheimer (BO) approximation.

Once the electronic Schrödinger equation has been solved for a large number of nuclear geometries and possibly also for several electronic states the potential energy surface (PES) is known. (PES is a hyper surface defined by the potential energy collection of atoms overall possible atomic arrangement). This can be used for solving the nuclear part of the Schrödinger equation.

When the only terms in the Hamiltonian are the one electron Kinetic energy and nuclear attraction terms, the operator is separable & may be expressed as

$$\hat{H} = \sum_{i}^{N} h_i \tag{2.3}$$

where N is the total number of electrons and h_i is the one electron Hamiltonian defined by

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} \tag{2.4}$$

where M is the total of nuclei, Z is an atomic number, and r is the distance between two particles, ∇^2 is the Laplacian operator. Eigen functions of the one electron Hamiltonian defined above must satisfy the corresponding one electron Schrödinger equation.

$$h_i \psi_i = \varepsilon_i \psi_i \tag{2.5}$$

Because the Hamiltonian operator defined by equation (2.1) is separable, it's many electrons eigen functions can be constructed as products of one electron eigen function.

That is

$$\psi_{HP} = \varphi_1 * \varphi_2 * \varphi_3 * \dots\dots\dots\dots * \varphi_N \tag{2.6}$$

where φ's are single electron wave functions and ψ_{HP} is the total electron wave function. A wave function of the above form is called Hatree product wave function. One point to not is that the above Hamiltonians in equation 2.3 depend not on one electron, but instead on all possible pair wise interactions.

To solve this, Hatree in 1928 proposed an iterative 'self-consistent field' SCF method. In the first step of the SCF process, one guesses the wave function ψ for all of the occupied molecular orbital and uses these to construct the necessary one-electron operators h_i. Solution of each differential (equation 2.5) provides a new of φ_i, presumably different from the initial guess. So, the one electron Hamiltonians are formed using these presumably more accurate ψ to determine each necessary charge density (ρ_j) associated with electron j, which in turn gives an interaction potential with all of the other electrons occupying orbitals according to the following equations.

$$V_i(j) = \sum_{i=j} \int \frac{\rho_j}{r_{ij}} dr \qquad \textbf{(2.7)}$$

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + V_i\{j\} \qquad \textbf{(2.8)}$$

This process is repeated to obtain a still better set of φ_i's. At some point, the difference between a newly determined set and the immediately preceding set falls below some threshold criterion and we refer to the final set of φ_i's as the 'converged' SCF Orbitals.

Since electrons are fermions having a spin of ½ the total electronic wave function must be antisymetric with respect to the interchange of any two-electron coordinates. The antisymmetry of the wave function can be achieved by building it from Slater determinants (SDS). For the general case of N electrons and N spin orbitals a Slater determinant is given as:

$$\phi_{SD} = \frac{1}{\sqrt{N!}} \begin{pmatrix} \varphi_{11} & \cdots & \cdots\cdots & \varphi_{N1} \\ \cdots\cdots & \cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \varphi_{1N} & \cdots\cdots & \cdots\cdots & \varphi_{NN} \end{pmatrix} \quad \textbf{(2.9)}$$

where ϕ_{SD} is the Slater type orbital wave function, $\varphi_{N(N)}$ s' are single electron wave functions, and $\frac{1}{\sqrt{N!}}$ is a normalization factor.

Fock first proposed the extension of Hatree's SCF procedure to Slater determinantal wave functions in order to meet the anti-symmetric nature of electrons. Just as with Hatree product orbitals the H-F molecular orbitals can be individually determined as eigen functions of a set of one-electron operators but now the interaction of each electron with the static field of all of the other electrons includes exchange effects on the coulomb repulsion. Fock introduced an operator including the coulomb self-interaction ***J*** and exchange element ***K***.

$$\hat{F}_i = h_i + \sum_j^N \left(\hat{J}_i - \hat{K}_j\right) \quad \textbf{(2.10)}$$

where F_i is an effective one-electron energy operator, which is called the Fock operator describing the kinetic energy of an electron, the attraction to all the nuclei and the repulsion to all the other electrons via the $\hat{J}$ and $\hat{K}$ operators. Some years later, Roothan described matrix algebraic equations that permitted HF calculations to be carried out using a basis set representation for the molecular orbitals.

Historically, two philosophies began to emerge at this stage with respect to how best to make further progress. The first is that considers the Hatree-Fock equations as powerful and can be improved by some sort of parameterization to reproduce key experimental quantities. This led to the so-called semi-empirical molecular orbital theories.

The second, views Hatree Fock theory as a stepping-stone on the way to exact solution of the Schrödinger equation. It was anticipated that developing the technology to achieve the Hatree Fock limit with no further approximations would not only permit the evaluation of the chemical utility of the Hatree Fock limit, but also facilitate moving on from the base camp to the Schrödinger equation summit.

2.1 Semi-empirical methods

The cost of performing an HF calculation scales, formally as the fourth power of the number of basis functions. This arises from the number of two electron integrals necessary for constructing the Fock matrix. Semi-empirical methods reduce the computation by reducing the number of these integrals. The first step in reducing the computational problems is to consider only the valence electrons explicitly; the core electrons are accounted for by reducing the nuclear charge or introducing function to model the combined repulsion due to the nuclei and core electrons. Further only a minimum basis set is used for the valence electrons.

The large majority of semi empirical methods today use only s-and p-function and the basis function are taken to be Slater type orbitals (STO's) i.e. exponential functions

$$S_{nlm}(r,\theta,\phi) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\phi) \qquad \textbf{(2.11)}$$

where ζ is an exponent that can be chosen according to a simple set of rules developed by Slater that depend on the atomic number, n the principal quantum number for the valence orbital, and the spherical harmonic functions $Y_l^m(\theta,\phi)$ that depends on the angular momentum and quantum number *l* and *m*. STO's have a number of features that make them attractive. The orbitals have the correct exponential decay with increasing r, the angular component is hydrogenic, and more importantly, from a practical point of view, overlap integrals between two STO's as functions of inter atomic distance are readily computed.

The central assumption of semi-empirical methods is the Zero Differential Overlap (ZDO) approximation, which neglects all products of basis functions depending on the same electron coordinates when located on different atoms. Denoting an atomic orbital on center A as μ and another on center B as υ the ZDO approximation corresponds to μ.υ = 0. Note that it is the product of functions on different atoms that is set equal to zero not the integral over such a product. This has the following consequences

1. The overlap matrix is reduced to a unit matrix,
2. One –electron integrals involving three centers, two from the basis functions and one from the operator, are set to Zero.
3. All three and four center two electron integrals, which are by far the most numerous of the two electron integrals, are neglected.

To compensate for these approximations, the remaining integrals are made into parameter and their values are assigned on the basis of calculations or experimental data. Exactly how many integrals are neglected, and how the parameterization is done, defines the various semi-empirical methods.

1. Neglect of Diatomic Differential Overlap (NDDO) hosts nothing further than the ZDO approximation. Thus, all integral (μν / λσ) are retained provided μ and ν are on the same atomic center A and λ and σ are on the same atomic center B, but not necessarily the center hosting μ & ν.
2. Intermediate neglect of Differential Overlap approximation (INDOs) in addition to the NDDO approximations INDO approximation neglects all two-center two-electron integrals, which are not of the Coulomb type. Furthermore, in order to preserve rotational invariance, i.e. the total energy should be independent of a rotation of the coordinate system, some of the integrals must be made independent of the orbital type (i.e. an integral involving a *p*-orbital must be the same as with an *s*-orbital) This has a

consequence that one –electron integrals involving two different functions on the same atom and a potential operator from another atom disappear.

3. Complete Neglect of Differential Overlap approximation (CNDO) approximation only the coulomb one-center and two-center two-electron integrals remain. The approximations for the one – electron integrals in CNDO are the same as for INDO.

The main difference between CNDO, INDO and NDDO is the treatment of the two electron integrals. While CNDO and INDO reduce these to just two parameters, all the one and two-center integrals are kept in the NDDO approximation. There are three methods that can be used for transforming the NDDO /INDO/CNDO approximations into working computational models.

1. The remaining integral can be calculated from the functional form of the atomic orbital.
2. The remaining integrals can be made into parameters, which are assigned values based on a few experimental data.
3. The remaining integral can be made into parameters, which are assigned values based on fitting to many (usually molecular) experimental data.

Three versions of modified Intermediate neglect of Differential Overlap (MINDO) models exist. MINDO/1, MINDO/2, MINDO/3. The first two thought gave poor results the MINDO/3 produced the first general-purpose quantum chemical method which could successfully predict molecular properties at a relatively low computational cost. MINDO/3 is rarely used in modern computational chemistry, having been succeeded in accuracy by the NDDO methods below.

Modified NDDO models

The MNDO, AM1, and PM$_3$ methods are parameterizations of the NDDO model, where the parameterization is in terms of atomic variables, i.e. referring only to the nature of a single atom. MNDO, AMI and PM$_3$ are derived from the same basic approximations (NDDO), and differ only in the way the core-core repulsion is treated and how the parameters are assigned. Each method considers only the valence *s*-and *p*-functions, which are taken as Slater type orbitals with corresponding exponents ζ_s and ζ_p.

The core- core repulsion is the repulsion between nuclear charges, properly reduced by the number of core electrons. The "exact" expression for this term is simply the product of the charges divided by the distance. Due to the inherent approximations in the NDDO method, however, this term is not cancelled by electron terms at long distances, resulting in a net repulsion between uncharged molecules or atoms even when their wave functions do not overlap. Consequently the core-core term must be modified to generate the proper limiting behavior, which means that two-electron integrals must be involved. The specific functional form depends on the exact method. Each of the MNDO, AM1 and PM3 methods involve at least 12 parameters per atom, orbital exponents, one electron terms, parameters per atom, orbital exponents, one electron terms, two electron terms, parameters used in the core- core repulsion, and for the AM 1 and PM3 methods use additional constants.

Modified Neglect of Diatomic overlap (MNDO)

The core-core repulsion of the MNDO model has the form:

$$V_{nn}^{MNDO}(A,B) = z_A z_B \left\langle s_A s_B / s_A s_B \right\rangle \left(1 + e^{-\alpha_A R_{AB}}\right) \tag{2.12}$$

where the α exponents are taken as fitting parameters, V_{nn}^{MNDO} is the nuclear repulsion energy Z_A and Z_B are nuclear charges r is the interatomic distance, and $\left\langle s_A s_B / s_A s_B \right\rangle$ is the overlap integral. Electron correlation in MNDO is only included implicitly via the parameters from fitting to experimental results. Although MNDO has been succeeded by the AM1 & PM3 methods it is still used for some types of calculations where MNDO is known to give better results.

After some experience with MNDO, it became clear that there were certain systematic errors. For example in some cases activation energies are too large. The source was traced to too repulsive an interaction in the core-core potential. To remedy this, the core-core function was modified by adding Gaussian functions and the whole model was re-parameterized, which gave rise to the so called Austin model 1 (AM1). The core-core repulsion of AM1 has the form.

$$V_{nn}(A,B) = V_{nn}^{MNIDO}(A,B) + \frac{Z_A Z_B}{R_{AB}} \left(\sum_k a_{kB} e^{-b_{ka}(R_{AB}-C_{kA})^2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB}-C_{kB})^2} \right) \qquad \textbf{(2.13)}$$

V_{nn} is the nuclear repulsion between two atoms A and B, V^{MINDO} is the MINDO potential Z_A and Z_B are nuclear charges of atoms A and B. a, b, and c are parameters describing Gaussian functions centered at various distances.

The parameterization of MNDO and AM1 had been done essentially by hand, taking the orbital parameters from atomic data and varying the rest until a satisfactory fit had been obtained. Since the optimization was done by hand, only relatively few reference compounds could be included. The optimization process was made automatically by deriving and implementing formula fro the derivative of a suitable error function with respect to the parameters.

All parameters could then be optimized simultaneously, including the two electron terms and a significantly larger training set with several hundred data could be employed. In this re-parameterization, the AM1 expression for the core-core repulsion was kept except that only two Gaussians were assigned to each atom. These Gaussian parameters were included as an integral part of the model, and allowed to vary freely. This gave rise to the Modified Neglect of Diatomic Overlap-parametric method 3 (MNDO-PM_3 or PM_3 in short), which is essentially AM1 with all the parameters fully optimized.

Since AM1 contains more adjustable parameters than MNDO and since PM_3 can be considered as a version of AM1 with all the parameters fully optimized, it is expected that the error decrease in the order MNDO>AM1>PM_3. This is indeed what is observed in general cases, but still on specific cases the ordering will be different.

2.2 *Ab initio* Implementation of Hatree-Fock Molecular Orbital Theory

The fundamental assumption of HF theory that each electron sees all of the others as an average field, allows for tremendous progress to be made in carrying out practical MO calculations. Early developers of the so-called 'ab-initio' HF theory, however tended to be less focused on making short-term predictions and more focused on long-term development of a rigorous methodology that would be worth the wait. Of course the ultimate rigor is the Schrödinger equation, but that equation is insoluble in a practical sense for all but the most simple systems. Thus, HF theory, in spite of it's fairly significant fundamental assumption, was adopted as useful in the ab initio philosophy because it provides a very well defined stepping stone on the way to more sophisticated theories.

The HF wave functions are constructed from mathematical functions, which are called basis-sets. The full HF wave function is expressed as a Slater determinant formed from the individual occupied MOS. In the abstract, the HF limit is achieved by use of an infinite basis set, which necessarily permits an optimal description of the electron probability density. In the absence of additional simplifying approximations like those present in semi empirical theory, the number of two electron integrals increases as N^4 where N is the number of basis functions. So keeping the total number of basis functions to a minimum is computationally attractive. In addition, however, it can be useful to choose basis set functional forms that permit the various integrals appearing in the HF equations to be evaluated in a computationally efficient fashion. Finally the basis functions must be chosen to have a form that is useful in a chemical sense. The functions should have large amplitude in regions of space where the electron probability density is also large and small amplitudes where the probability density is small. The simultaneous optimization of these factors is the heart of basis set development.

Slater type orbitals (STOs) have a number of attractive features. However, they suffer from a fairly significant limitation in ab-initio HF theory. Nevertheless, high quality STO basis sets have been developed for atomic and diatomic calculations, where such limitations do not arise. This was achieved in a way that the radial decay of the STOs be changed from e^{-r} to

e^{-r^2} that is, the AO (Atomic Orbital) like functions are chosen to have the form of a Gaussian function. The general function form of a normalized Gaussian type orbital GTO is

$$G_{nlm}(r,\theta,\phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta,\phi) \quad \textbf{(2.14)}$$

where G_{nlm} is the Gaussian as a function of radial and angular components, α is an exponent controlling the width of the GTO, N_n is a normalizing factor r is orbital radii, and $Y_l^m(\theta,\phi)$ is the spherical harmonics.

Although they are convenient from a computational standpoint, GTOs have specific features that diminish their utility as basis functions. One issue of key concern is the shape of the radial portion of the orbital. In order to combine the best feature of GTOs (computational efficiency) with that of STOs (proper radial shape), most of the first basis sets developed with GTOs used them as building blocks to approximate STOs. That is, the basis functions used for SCF calculations were not individual GTOs, but instead a linear combination of GTOs which coefficients C fit to reproduce as accurately as possible a STO. When a basis function, is defined as a linear combination of Gaussians, it is referred as a ‘contracted’ basis function, and the individual Gaussians from which it is formed are called ‘primitive’ Gaussians. Thus, in a basis set of contracted GTOs, each basis function is defined by the contraction coefficients C and exponents of each of its primitives. The following equation shows this

$$\varphi = \sum_{a=1}^{M} c_a \phi \quad \textbf{(2.15)}$$

where ϕ are series of Gaussians while φ is the Slater type form linear combination of the M Gaussians. A series of different basis set were constructed for different number of Gaussians in the linear combinations (M) as equation 2.14. In particular M=2 to 6 were considered and named as Slater-Type orbital approximated by M Gaussians (STO-MG). Obviously, the more primitives that are employed the more accurately a contracted function can be made to match a given STO. However, as M gets larger the equation becomes increasingly complicated to evaluate. It was discovered that the optimum combination of speed and accuracy was achieved for M=3. The other limitation of using GTOs is that they fail to exhibit radial nodal behavior, use of a contraction scheme, however alleviates this problem, contraction coefficients can be chosen to have either negative or positive sign, and thus fitting to functions having radial nodal behavior poses no special challenges.

In the STO-3G as the naming implies there is one and only one basis function defined for each type of orbital core through valence and hence is a single zeta (where zeta is the Greek alphabet used as an exponent in the Gaussian function). From a chemical standpoint, then there is more to be gained by having flexibility in the valence basis functions than in the core; and recognition of this phenomenon led to the development of so-called. ‘Split-valence’ or ‘Valence-multiple zeta’ basis sets. In such basis sets core orbitals continue to be represented by a single (contracted) basis function; while valence orbitals are split into arbitrarily many functions, i.e. are ‘deconstructed’. The most widely used split-valence basis sets are, 3-21G, 6-21G, 4-31G, 6-31G and 6-311G. The nomenclature is a guide to the contraction scheme. The first number indicates the number of primitives used in the contracted core functions. The number after the hyphen indicates the number of primitives used in the valence functions. Older basis sets use a segmented contraction scheme, which implies that the primitives used for one basis function are not used for another of the same angular momentum. An alternative method to carrying out a segmented contraction is to use a so-called general contraction scheme. In a general contraction, there is a single set of primitives that are used in all contracted basis functions, but they appear with different coefficients in each.

A variety of molecular properties prove to be sensitive to the presence of polarization functions, which is almost always added in the form of basis functions corresponding to one quantum number of higher angular momentum than the valence orbitals. Thus, for a first row atom the most useful polarization functions are d-GTOs, and for hydrogen p-GTOs which are symbolized as 6-31* (6-31G (d)) and 6-31G** (d,p) respectively. Introduction of polarization functions into basis-set functions improve description of chemical bonds and may recover electron correlations. These and other approaches are active areas of research today.

2.3 Density Functional Theory

The basis for Density functions theory (DFT) is the discovery that the ground-state electronic energy is determined completely by the electron density ρ. The wave function itself is essentially un-interpretable, it is an inscrutable oracle that returns valuably accurate answers when questioned by quantum mechanical operators, but it offers little by way of sparking intuition.

The Hamiltonian depends only on the positions and atomic number of the nuclear and the total number of electrons. The dependence on total number of electrons immediately suggests that a useful physical observable would be the electron density ρ, since when integrated over all space it gives the total number of electrons N, i.e.

$$N = \int \rho(r) dr \tag{2.16}$$

while the complexity of a wave function increases with the number of electrons, the electron density has the same number of variables, independently of the system size. The goal of DFT methods is to design function connecting the electron density with the energy. A function is a prescription for producing a number from a set of variables (coordinates).

Different models were developed by different scholars at different times. Early attempts at deducing functionals considered the Born-Openheiner approximation for potential energy parts and for the kinetic and exchange energies considered a non-interacting uniform electron gas. (Thomas Fermi DFT). This assumption of a non-interacting uniform electron gas does not hold very well for atomic and molecular systems. (TF theory does not predict bonding and hence no molecule.)

Later on Hohenberg and Kohn developed an existence theorem. The Hohenberg-Kohn theorem was provocative with potential but altogether unhelpful in providing any indication of how to predict the density of a system. Just as with MO theory we need a means to optimize our fundamental quantity. Hohenberg-Kohn showed a second theorem that, also just as with Mo theory the density obeys a variation principle. Thus in Principle one can keep on choosing different densities and those that provide lower energies closer to correct. This again would be frustrating due to two reasons, one is that there is no prescription for how to go about choosing improved candidate densities and second basically DFT aims to avoid solving the Schrödinger equation and computing the energy as the expectation value of the Hamiltonian is no advance. The difficulty lies in the nature of the functional itself, to determine the energy directly without recourse to the wave function was important, an approach first appeared in 1965. The introduction of orbitals by Kohn and Sham paved the way for DFT methods to be used in computational chemistry.

Kohn and Sham basically considered a. Hamiltonian for a non-interacting system of electrons. The crucial bit of cleverness then is to take as a starting point a fictitious system of non-interacting electrons that have for their overall ground-state density the same density as some real system of interest where the electrons do interact. The energy functional can be divided into specific components to facilitate further analysis

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + V_{ee}[\rho(r)] \qquad \textbf{(2.17)}$$

where the terms on the r.h.s refer, respectively, to the kinetic energy of the non-interacting electrons, the nuclear-electron interaction, the classical electron-electron repulsion, the correction to the kinetic energy deriving from the non-interacting nature of the electrons and all non-classical corrections to the electron-electron repulsion energy. If orbitals χ that minimize E are found, they should satisfy the pseudo eigen value equations

$$h_i^{ks}\chi_i = \varepsilon_i \chi_i \qquad \textbf{(2.18)}$$

where Kohn and Sham one electron operator is defined as

$$h_i^{ks} = -\tfrac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{z_k}{|r_i - r_k|} + \int \frac{\rho(r^1)}{|r_i - r_k|} + V_{xc} \qquad \textbf{(2.19)}$$

$$V_{xc} = \frac{\partial E_{xc}}{\partial \rho} \quad \text{and} \quad E_{xc} = \Delta T + \Delta V_{ee} \qquad \textbf{(2.20)}$$

Note that as long as E that is being minimized is exact, the orbital χ must provide the exact density (i.e. the minimum must correspond to reality). Further note that it is these orbitals that form the Slater determinantal eigen function for the separable non-interacting Hamiltonian defined as the K-S operators. So there is internal consistency in the Kohn-Sham-approach of positing a non-interacting system with a density identical to that for the real system. For the determination of the KS orbitals the same line followed for the MO theory will be followed. At this stage DFT needs to know E_{xc} as a function of ρ. As a result; considerable research effort has gone into finding functions of the density that may be expected to reasonably that may be expected to reasonably approximate E_{xc}. DFT methods have the potential of including the computationally difficult part in wave mechanics, the correlation energy, at a computational effort similar to that for determining the uncorrelated HF energy.

The difference between DFT methods is the choice of the functional form of the exchange-correlation energy. There is little guidance from theory how such functionals should be chosen and consequently many different potentials have been proposed. Functional forms are often designed to have a certain limiting behavior and fitting parameters to know accurate data. Which functional is the better will have to be settled by comparing the performance with experiments or high-level wave mechanics calculations.

2.4 Excited State Calculation

Ground state wave functions can very often be expressed in terms of a single Slater determinant formed from variationally optimized MOs with possible accounting for electron correlation. Such orbitals are determined in the SCF procedure. However the problem of variation collapse typically prevents an equivalent SCF description for excited states. That is any attempt to optimize the occupied MOs with respect to the energy will necessarily return the wave function to that of the ground state. Variational collapse can sometimes be avoided, however, when the nature of the ground and excited states prevents their mixing within the SCF formalism. This situation occurs most commonly in symmetric molecules where electronic states belonging to different irreducible representations do not mix in the SCF, and also in any situation where the ground and excited states have different spin.

Most basis sets are optimized for ground state atoms and molecules, so to the extent basis-set limitations affect the calculation they should affect excited states. For many singly excited states, ΔSCF calculations are not an option under any circumstance. Within the context of using the orbital of the ground state to describe the excited state, the simplest way to evaluate the energy of the excited state would be to evaluate the Hamiltonian for the determinant formed after promotion of the excited electron. A significant draw back of these singly excited single-configuration wave functions is that, although each one will be orthogonal to the ground state, they are unlikely to be orthogonal to one another. However if limited only to singly excited states orthogonality can be introduced. This orthogonalization is known as configuration interaction singles (CIS) because a configuration interaction matrix is formed restricting consideration to only the HF reference and all singly excited configurations. The matrix is essentially of size MXN, where M is the number of occupied orbital from which excitation is allowed, and N is the number of virtual orbitals into which excitation is considered. If excitation results in a spin-flip then the size increases.

Orthogonalization of the CIS matrix takes place only in spaces of the excited states, since they don't mix with the HF reference. The orthogonalization provides energy eigen values each of which has associated with it an eigen vector detailing the weight of every singly excited determinant in the state. That is, the CIS wave function for each excited state is written as

$$\psi_k = \sum_{i}^{occupied} \sum_{a}^{vitual} C_{iak} \psi_i^a \tag{2.21}$$

where the coefficients C are the components of the eigenvector for state K. With large enough basis sets, even the CIS matrix may grow cumbersomely large with which to work, and iterative methods designed to locate only lower energy roots are employed, just as in CI treatments considering higher excitations. Analytic gradients are available for CIS wave functions, so it is possible to optimize the geometry of a particular state, making CIS a useful method for obtaining excitation energies. The ground state functions are important only to the extent of determining the orbitals, and the configuration interaction is carried out to orthogonalize the singly excited states. Since this process does not involve any orbital re-optimization for any particular state, it provides a wave function that is roughly equivalent in quality only to an HF wave function for the ground state. To improve the CIS results beyond their roughly HF quality, various options may be considered, such as semi-empirical parameterization and others. Therefore, based on this background the present work focuses on the following objectives.

Objectives

The objective of this project is to:

-make a theoretical investigation on the electronic ground state conformation of selected chromophores, which show unusual spectroscopic behavior.

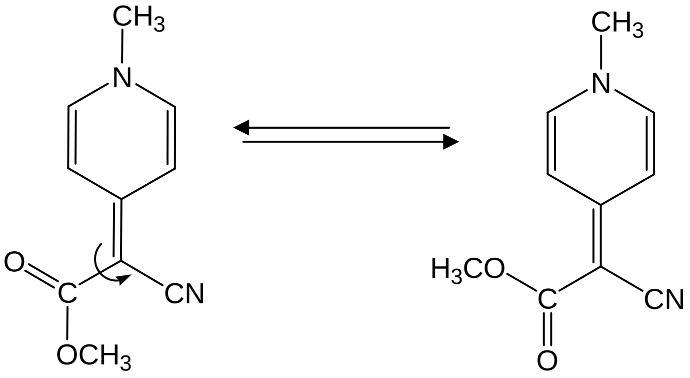
-Confirm experimental results obtained from electrooptical measurements by quantum mechanical calculation results after selecting an appropriate method.

-Give a conclusion based on the results.

3. Calculation Part

The calculation was performed using the Gaussian 03 package to study the ground state isomeric structures of the two compounds MCPA and MCPN shown.

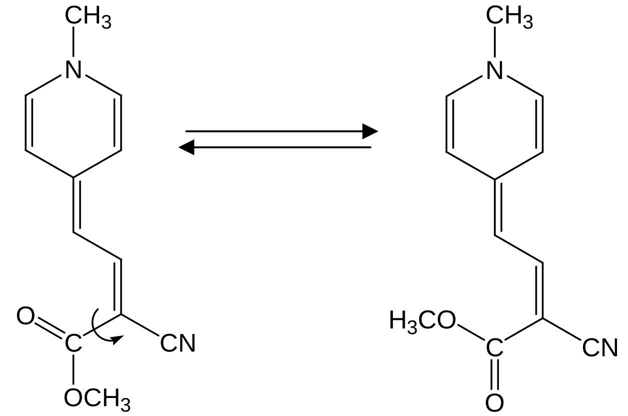
I



IA **IB**

methyl 2-cyano-2-(1-methyl pyridine-4(1H)-ylidene)acetate **(MCPA)**

II



IIA **IIB**

(2Z)-2-acetyl-4-(1-methylpyridin-4(1H)-ylidene)but-2-enenitrile **(MCPN)**

Fig. 3.1- Calculation done for structure I and II using DFT/B3LYP method.

The selected method was a DFT B3LYP with either 3-21G or 6-31G(d) basis set. From literature it is found that the 6-31G(d) basis set gives better results for more or less related compounds. [1,7]. The calculations run were in the order shown below

1- Optimization of both Structure I (MCPA) and II (MCPN)
2- Potential energy calculation for every 15^0 rotation of the acetate group (This was done for both MCPA and MCPN).
3- Frequency calculation for both MCPA and MCPN in order to obtain the free energy values.

On our case PE curves were calculated using the 6-31G(d) for the ground states. However, our system failed to use the 6-31G(d) CIS for the excited state calculations. Thus the ground and excited states were calculated using the 3-21G basis set after optimizing the structure by DFT/B3LYP/3-21G method. Rather it was possible to apply the 6-31G(d) in the TD-DFT system for calculating potential energies of the excited states. However, our main concern goes to the ground state results. Thus results of both basis sets will be reported.

In addition to the PE curves for the structure I and II above, free energies were calculated for the two isomeric structures, which will be discussed on the next section. The same was done in solvents (cyclohexane and THF) in addition to the gaseous state.

For further comparison dipole moments in gaseous state and in solvents (cyclohexane and THF) were calculated for ground states of the following two structures using the DFT/B3LYP/6-31G(d) system.

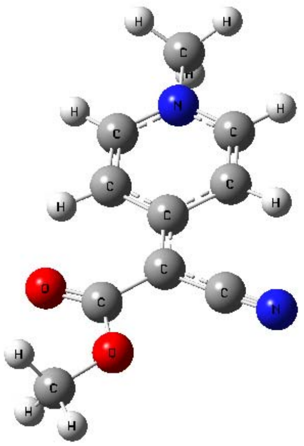
4. Results and discussions

The ultimate goal of this project was to give confirmation and evidence on the existence of the ground state isomeric structures in equilibrium and support earlier experimental findings with computational results. These structures have been studied previously for electrooptical absorption experiments but their ground state isomeric structures are still left open for further study [6]. The results obtained are summarized as follows.

4.1 Investigation of molecular properties of MCPA

4.1.1 Optimization

Both isomeric structures of MPCA (IA and IB) are optimized using the DFT/B3LYP/6-31G(d) method. The resulting structures were planar for both isomeric structures IA and IB. In addition structure IA was optimized using DFT/B3LYP/3-21G method. The result was consistent with the result obtained with the 6-31G(d) basis set.



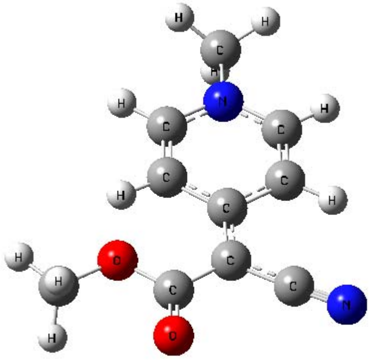


Fig. 4.1 Optimized structure of MCPA IA and IB

For the IB structural isomer and 90° rotated isomer of MCPA further optimization was performed. The results indicate that the 90° structure optimized to the IA isomeric structure while the IB structure remained as it was. This gives an indication that the MCPA IB isomer is more stabilized than the 90° rotated isomer. The degree of stabilization cannot be predicted with this optimization result alone, but this can deliver a starting information for further investigation.

The experimental value of the dipole moment for the di-cyano counter part of MCPA, structure III in Fig 1.2 is 12.29 D in dioxane solution. In the same paper it is reported that the dipole moment of MCPA is 9.29 D in dioxane solution. Such a lowering of dipole moment cannot be explained as the change of the nitrile group by an acetate group. It was suggested that the reason to be due to the stable isomer of the IA structure of MPCA [6]. How ever there was no high level computational investigation to support their assumption.

According to our result the dipole moment of structure III is 15.71 D in THF solvent. The dipole moment of MCPA IA is calculated to be 11.60 D and that of IB is calculated to be 14.63 D in THF solvent.

This result confirms the suggestion made in the literature. The experimental measurement was carried in dioxane while in our theoretical calculation we used THF. This is because in Gaussian 03 package dioxane is not implemented as a solvent. However, THF and dioxane have comparable degree of polarity, expressed in their dielectric constants THF = 7.6 [16] and Dioxane = 6 [17]. This may have contributed to the difference in the results expected and obtained. Since the comparison between experimental and theoretical results will always have deviation by some factor. In our case the factor is calculated to be 1.26 (theoretical/experimental). This factor is consistent through out and multiplication of the results resulted good agreement with the experimental data including the μ_g of MCPA IA and structure III, thus our result gives theoretical justification for the dipole moment of MCPA IA and structure III.

4.1.2 Potential Energy Curves

For MCPA potential energies were calculated for every 15^o rotations of the acetate group as shown in Fig 3.1 above. The results obtained are summarized on Table 4.1 and Figures 4.2 and 4.3.

Table 4.1. The ground state potential energy and dipole moments of MPCA in every 15° rotation of the acetate using 3-21G basis set

Rotation Angle	Ground state energy (eV)	Dipole moment (Debye)	Rotation Angle	Ground state energy (eV)	Dipole moment (Debye)
-180	0.514	11.32	15	0.054	8.80
-165	0.471	11.25	30	0.204	8.86
-150	0.438	11.06	45	0.411	8.94
-135	0.509	10.75	60	0.623	9.07
-120	0.661	10.36	75	0.790	9.25
-105	0.808	9.95	90	0.860	9.54
-90	0.860	9.56	105	0.805	9.93
-75	0.790	9.27	120	0.658	10.35
-60	0.620	9.08	135	0.506	10.74
-45	0.411	8.96	150	0.438	11.05
-30	0.204	8.87	165	0.473	11.25
-15	0.054	8.81	180	0.514	11.32
0	0	8.78			

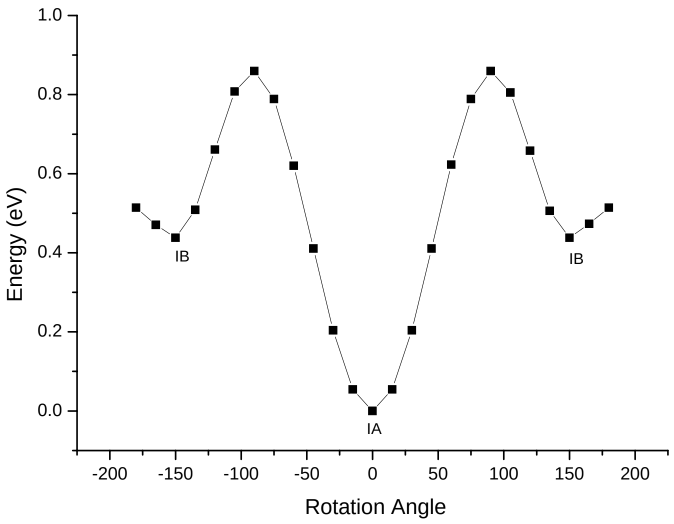


Figure 4.2 – Rotational Angle versus potential energy of MPCA at ground state

As can clearly be seen from Fig. 4.2 there are two stable isomers, while the isomer IA being more stable than isomer IB. For more confirmation similar computation was performed with 6.31G(d) as basis set for the ground state of MCPA. The graph obtained is very much alike to that obtained from the 3.21G basis set (Figure 4.3).

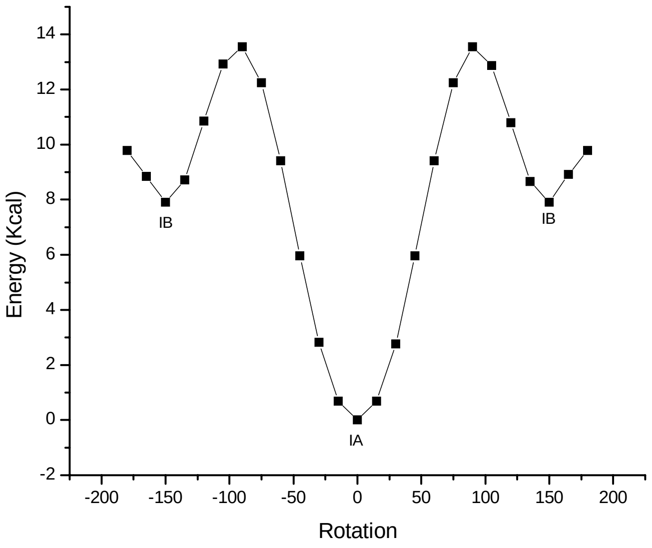


Fig. 4.3. Rotational Angle versus ground state potential energy of structure 1 using DFT/B3LYP/6.31G(d)

Thus, from the PE curve one can conclude that the ground state contains two or more isomers at equilibrium. This conclusion cannot be justified based only on the obtained PE curves. However, these results show that there is a possibility to find equilibrium of the isomeric structures (Fig.3.1) at the ground state instead of only one isomer. Further information needed on the energy barrier between the isomers was found from thermodynamic information. Thus it was mandatory to calculate thermodynamic functions to obtain Gibbs free energy values.

4.1.3 Computation of thermodynamic parameters

For obtaining the Gibbs free energies of the two isomers calculations were run on MCPA. The results acquired are summarized on the Table 4.2.

Table 4.2. Dipole moment and free energy values of the two isomers IA and IIA (0^0 and 180^0 rotations) in gaseous, and THF and cyclohexane solvents

Structure I	0^o Rotation	180^o Rotation
μ_g^a (debye)	8.78	11.32
μ_g^b (debye)	11.60	14.63
μ_g^c (debye)	10.13	12.81
ΔG^a (kcal/mol)	-403686.38	-403673.64
ΔG^b (kcal/mol)	-403781.19	-403777.79
ΔG^c (kcal/mol)	-403778.04	-403774.19

a- in gaseous state ; b- in THF solvent ; c- in cyclohexane solvent

ΔG values can be calculated for MCPA IA and IB assuming the equilibrium on Fig.3.1. ΔG for MCPA IA in THF and Cyclohexane respectively are 3.4 kcal/mole and 3.85 kcal/mol at T=298.15-K. ΔG in the gaseous state is computed to be 12.74 kcal/mol at 298.15-K. In the polar solvent THF the ΔG is smaller than that in cyclohexane, implying that the conformers are still there with different amounts and different stabilities.

In addition the thermal energy of MCPA at 298.15 K is calculated to be 0.59 kcal/mol. The calculated free energy values are larger than the thermal energy of the molecule, indicating that the rotational barrier between the structural isomers is larger than the thermal energy. This implies that free rotation within the molecule is not possible at 298.15 Kelvin or below this temperature. Thus the results obtained show that the isomers do exist at equilibrium i.e. the ground state is not simply the MCPA IA isomer. Instead in the ground state the two isomers exist at equilibrium.

The result obtained above can also explain the unusual dual intermolecular CT band observed in a solution of MCPA and tetracyanoquinone (TCNQ). [5]. TCNQ is a highly charge deficient system, thus when compounds like MCPA and TCNQ are in the same solution an intermolecular charge transfer takes place. This intermolecular charge transfer state results in an intermolecular charge transfer band. Generally a single intermolecular CT band is expected for a single compound. The appearance of two CT bands indicates the presence of two structures. TCNQ has no structural isomer. Thus the MCPA is supposed to be in two structural conformations. If the isomeric equilibrium is accepted as the ground state electronic mode for MCPA then the anomal dual CT band is well explained. Each band should originate from the intermolecular charge transfer between the two isomers and TCNQ.

4.2 Investigation of molecular properties of MCPN

4.2.1 Optimization

Both isomers of MCPN (IIA and IIB Fig1.3) were optimized using the DFT/B3LYP/6-31G(d) method. The result obtained is a planar structure as shown in Fig. 4.3.

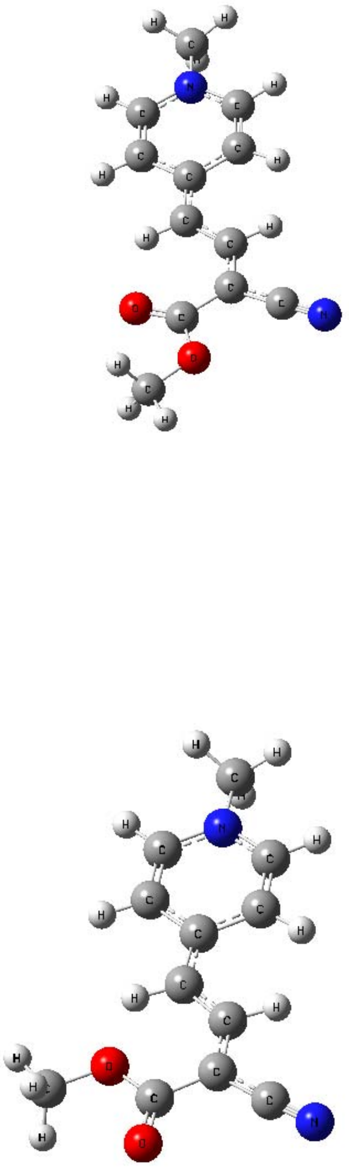


Fig. 4.3- The optimized structure of MCPN IIA and IIB using DFT/B3LYP/6-31G(d)

The optimization of the IIA and IIB structures resulted in two different isomeric structures as shown in the Fig 4.3. This gives an indication that further investigation should be carried out to prove which isomer is more stable.

Dipole moment was calculated for structure IV (Fig.1.2) in THF solvent. The result obtained is 20.55 D, which is comparable to the result obtained from electrooptical absorption experiments, which is 18.89 D [6]. Though the experimental result gave the ground state dipole moment of MCPN it was unable to explain the ground state isomeric configuration as that of MCPA [6]. However, further application of theoretical investigation on the small μ_g could not be carried out as the Gaussian 03 package was unable to calculate dipole moments for MCPN in solvent thus it is not possible to make comparisons for MCPN other than the gaseous state. For MCPN potential energy curve was calculated to further investigate the co existence of the isomers.

4.2.2 Potential energy curve

For MCPN a potential energy curve was calculated using DFT/B3LYP/6-31G(d) method by every 15° rotation of the acetate group as shown in Fig 3.1. The results obtained are presented in Fig 4.4 below.

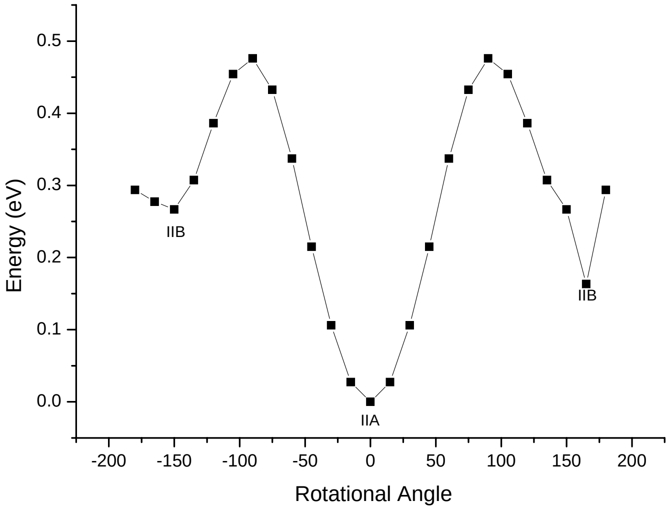


Fig. 4.4. Rotational Angle versus ground state potential energy of structure 1 using DFT/B3LYP/6.31G(d)

As can be seen from the PE curve in Fig.4.4 the IIA isomeric structure should be the most stable, which is in agreement with the experimental result explained above. But still the PE curve shows that the IIB isomer has significant stability. Thus it is mandatory to compute thermodynamical quantities.

4.2.3 Computation of thermodynamic parameters.

For the case of MCPN for both isomers IIA and IIB our system failed to give free energy values in any solvent. Repeated attempts were made with no success. Thus only results obtained for the gaseous sate are presented (Table 4.3 below).

Table 4.3. Dipole moment and free energy values of the two isomers (0^0 and 180^0 rotations) in gaseous state

Structure II	0^o Rotation	180^o Rotation
μ_g in gaseous (Debye)	11.77	14.72
ΔG in gaseous (kcal)	-454466.34	-454458.50

The calculated free energy difference between the two isomers is ΔG =12.73 kcal that is larger than the thermal energy which is 0.592 kcal at 298.15 K . This again shows that free rotation and hence inter conversion between the isomers is restricted. Thus based on the result obtained one can suggest the co existence of the two isomers at equilibrium in the ground state of MCPN.

Conclusion

As a conclusion the over all ground state dipole moment (μ_g**)** is due to the dominance of the isomeric structure MCPA IA and MCPN IIA. From the experimental result it's impossible to make such a conclusion and that's why the experimental report left the isomer structure uncertain [6]. Therefore our computational result is in agreement with experimental data [6]. One of our initial goal was to support electro optical measurement results by computational results, thus the result obtained is in agreement with the experimental data. Further investigation should be made to compare the MCPN structure in solvents.

Based on the obtained result and discussion it can be concluded that the two isomers indeed co exist in equilibrium at ground state. The result obtained gives an explanation for the anomal dual intermolecular charge transfer band seen in charge deficient solvents where intermolecular charge transfer takes place [5].

These result and conclusion pave a direction for further investigation of other unusual spectroscopic behaviors.

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Theoretical investigation on some photophysical phenomenon expressed by isomeric equilibria

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