CHAPTER 1

EFFECT OF STRUCTURAL CHANGES ON THE CONFORMATION OF DYESTUFFS AND RELATED COMPOUNDS
BRIEF OUTLINE OF THE QUANTUM MECHANICAL METHODS USED FOR
CONFORMATIONAL STUDIES.

Introduction:

The investigations on the conformational properties of molecules involve experimental studies by a large variety of physicochemical and biophysical techniques, and theoretical investigations by different computational methods. The computations involve the use of both 'classical', so-called empirical, and quantum mechanical procedures. Broadly speaking, the theoretical studies may be classified into three categories.

(i) **Empirical computations in the Hard Sphere Approximation**: Developed originally in connection with the conformations of proteins and other biological molecules, in which the atoms are considered as hard spheres of a radius equal to their atomic Van der Waals radii.

(ii) **Empirical Computation in the Partitioned Potential Energy Approximation**: This consists of (a) decomposing the total potential energy into several discrete contributions - such as...
non-bonded interactions, electrostatic interactions, barriers to internal rotations, hydrogen bonding etc., (b) expressing these interactions with the help of empirical formulas based generally on the study of simple model molecules and (c) finally summing these contributions in order to obtain the general evaluation of the potential energy. These methods have two obvious drawbacks. First, although the partitioning of the total potential energy into a series of components has practical justification, the procedure involves an element of arbitrariness and incompleteness. In fact, different authors have considered different sets of only selected components in different work. Secondly, the fundamental formulae and parameters used to define the components differ from one author to another.

(iii) The Quantum Mechanical Computations: Contrary to the partitioned potential energy method, the quantum mechanical computations aim at a direct evaluation of the total molecular energy associated with the different configurations of the system and thus a direct prediction of the preferred molecular conformation.

Quantum mechanical methods may broadly be divided into two categories.

I. Ab-initio Methods

II. Semi Empirical Methods
A. \( \pi \)-Electron Methods

(a) Huckel Molecular Orbital (HMO) Method

(b) Pariser – Parr – Pople (PPP) Method

(c) Variable Electronegativity SCF (VESC) Method

B. All-Valence Electron Methods.

(a) Extended Huckel Theory (EHT)

(b) Complete Neglect of Differential Overlap (CNDO) Method\(^6,7\)

(c) Intermediate Neglect of Differential Overlap (INDO) and Modified Intermediate Neglect of Differential Overlap (MINDO) Methods\(^8,9\)

(d) Perturbative Configuration Interaction over Localized Orbital (PCILO) Method\(^10,11\).

From their very nature, it is evident that the \( \pi \)-electron methods (HMO and PPP) will have only limited applicability. Among the All-valence electron methods, which have been most extensively used for conformational studies are the EHT, CNDO, PCILO and SCF-Ab initio procedures.

The Quantum Mechanical Methods:

In the Schrödinger equation (1) the Hamiltonian, \( H \), includes the kinetic operator for each electron and the electron-nucleus, electron-electron and nucleus-nucleus potential. Since

\[
H \Psi = E \Psi \quad \ldots \ (1)
\]
this can not be solved exactly for systems with more than one electron, approximate solutions are employed. One basic approximation, molecular orbital approximation, consists of constructing the total wave function from molecular orbitals. Each molecular orbital $\Phi_i$ is a one-electron function which depends on the space coordinates $x_i, y_i, z_i$ and spin coordinate $\sigma_i$ of the electron $i$. The simplest wave function built from molecular orbitals is a product of orbitals (the Hartree Product):

$$\Psi(1,2, \ldots, n) = \Phi_1(1) \Phi_2(2) \ldots \Phi_n(n) \quad (2)$$

$\Psi(1,2, \ldots, n)$ is an approximate wave function and stands for $\Psi(x_1, y_1, z_1, \sigma_1, \ldots, x_n, y_n, z_n, \sigma_n)$. Similarly $\Phi_1(1)$ stands for $\Phi_1(x_1, y_1, z_1, \sigma_1)$. To satisfy the antisymmetry requirement with respect to the exchange of two electrons (Pauli principle), the wave function is written as an antisymmetrized product of spin-orbitals in the form of a determinant called slater determinant. For a system of $n$ electrons the approximate wave function will be

$$\Psi(1,2, \ldots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \Phi_1(1) & \ldots & \Phi_1(n) \\ \Phi_2(1) & \ldots & \Phi_2(n) \\ \vdots & & \vdots \\ \Phi_n(1) & \ldots & \Phi_n(n) \end{vmatrix} \quad (3)$$

Such a determinant would, in fact, be the correct wave function for a system of non-interacting electrons. However, electrons do interact in real molecular systems. Thus, in order to obtain a
satisfactory representation preserving the convenient one-electron model, one has to determine the individual orbitals \( \Phi \), so as to take into account the presence of the other electrons.

The total energy of the system can be expressed by the standard quantum mechanical expression,

\[
E = \frac{\int \psi^* H \psi \, dr}{\int \psi^* \psi \, dr} \tag{4}
\]

in terms of the individual orbitals \( \psi \), by using the determinantal expression of \( \psi \). According to the variation principle, the energy calculated by the above expression using an appropriate wave function always lies higher than the exact energy. Thus, the best possible molecular orbitals \( \Phi_i \)'s are obtained by minimizing the total energy with respect to the orbital \( \Phi_i \).

For a closed-shell system of \( 2n \) electrons with paired spins, the best molecular orbitals are obtained from the solutions of the Hartree-Fock or Self Consistent Field (SCF) equations,

\[
F \Phi_i = \epsilon_i \Phi_i \tag{5}
\]

Where \( F \) is an operator called the Fock operator and \( \epsilon_i \) is the orbital energy associated with the orbital \( \Phi_i \).
An essential characteristic of the Fock equation is that each individual operator $F$ depends on all the orbitals that are occupied in the system (on account of the explicit inclusion of the interaction term); thus each $\phi$ is given by an equation that depends on all the $\phi$'s. The Fock equations are solved through an iterative procedure. Initially an arbitrary set of $\phi$'s are chosen and used to calculate the $F(i)$'s. Then the Fock equations are solved for a new set of $\phi$'s. This process is repeated until consistency is attained, hence the name 'self consistent field' given to the method.

The classical choice of the starting orbitals is based on the following idea: considering a chemical bond formed between two monovalent atoms $A$ and $B$ by the pairing of their valence electrons, one on $A$, the other on $B$, it is natural to assume that when one electron in the molecule is close to the nucleus $A$, its molecular orbital will resemble the atomic orbital that it would occupy in $A$, and a similar situation would occur in the vicinity of $B$. Thus the molecular orbital may be approximated by a linear combination,

$$\phi = c_1 \chi_A + c_2 \chi_B \quad \ldots \quad (6)$$

where the $\chi$'s are the atomic orbitals. For a polyatomic molecule, the extended form will be

$$\phi_i = \sum_k c_{ki} \chi_k \quad \ldots \quad (7)$$
This is the classical and general LCAO approximation (linear combination of atomic orbitals) of the molecular orbital method.

The LCAO-MO-SCF orbitals ($\psi_i$'s) for a closed-shell system are determined by solving the Roothan equation

$$ \sum_{l=1}^{n} C_{lk} (F_{kl} - E_p S_{kl}) = 0 \quad (\text{for each index } k) \quad \ldots (8) $$

where $n$ is the number of basis set functions used and $E_p$ are the orbital energies of each one of the MO's $\psi_p$ through the determinant

$$ \begin{vmatrix} F_{kl} - E_p S_{kl} \end{vmatrix} = 0 \quad \ldots (9) $$

where the overlap integral $S_{kl}$ is defined as

$$ S_{kl} = \int \chi_k^* \chi_l \, dz \quad (\equiv \langle \chi_k | \chi_l \rangle) \quad \ldots (10) $$

The Roothan equations may be written in the matrix form as

$$ FC = SCE \quad \ldots (11) $$

Where $E$ is the diagonal matrix of the energy $E$. 
The terms $F_{kl}$, called matrix elements of the Fock operator, or simply the constituent matrix terms. When only one configuration is considered as an approximation of the total wave function, $F_{kl}$ is given by the expression,

$$F_{kl} = H_{kl} + G_{kl} \quad \ldots \quad (12)$$

$H_{kl}$ represents the kinetic and nuclear attraction energy of an electron residing in the $k-1$ overlap region and is defined as,

$$H_{kl} = \int \chi_k(i) \, \nabla_i \chi_1(i) \, \, d\tau_i \quad \ldots \quad (13)$$

The operator $\nabla_i$ includes all single electron terms, nuclear attraction operators and kinetic energy operators, i.e.,

$$\nabla_i = - \sum_A \left( \sum \frac{Z_A}{r_{Ai}} + \frac{1}{2} \nabla_i^2 \right) \quad \ldots \quad (14)$$

The two-electron parts $G_{kl}$ is defined as

$$G_{kl} = \sum_m \sum_n p_{mn} \left[ \langle kl | mn \rangle - \frac{1}{r_{ij}} \langle kn | lm \rangle \right] \quad \ldots \quad (15)$$

$$\langle kl | mn \rangle \equiv \iint \chi_k(i) \chi_m(i) \, \frac{1}{r_{ij}} \chi_1(i) \chi_n(j) \, d\tau_i d\tau_j$$

and
\[ \langle k_n | l_m \rangle = \iint \chi_k(i) \chi_m(j) \frac{1}{r_{ij}} \chi_l(j) \chi_n(i) \, d\tau_i \, d\tau_j \quad \cdots \quad (17) \]

\[ \langle k_l | m_n \rangle \] is the coulomb repulsion between two electrons residing in the overlap regions \( k-l \) and \( m-n \) respectively. \( \langle k_n | l_m \rangle \) is called the exchange integral.

\[ P_{mn} = 2 \sum_{p} \text{occ} \, C_{mp} \, C_{np} \quad \cdots \quad (18) \]

the summation being over all occupied molecular orbitals (p's). \( P_{mn} \) represents the total electron population (bond-order matrix) existing in the overlap region of the basis functions \( \chi_m \) and \( \chi_n \). The factor 2 indicates that each MO is doubly occupied. Thus we find that the Fock-matrix \( F_{kl} \) are functions of the coefficients \( C_{mp} \) and \( C_{np} \). Consequently the Hartree-Fock model requires that a preliminary guess at the values of the matrix terms \( P_{mn} \) be made previously. These values are used to calculate the matrix elements \( F_{kl} \) and thus the secular equation is resolved. This provides a better approximation of the wave function, \( \Psi \), and consequently, leads to an improved set of values of \( P_{mn} \). This process is repeated as many times as may be necessary to reach self consistency (hence the name of the theory as Self Consistent Field).

Semi-empirical methods: The methods used to simplify the Hartree-Fock model can be divided into two groups: (a) full-overlap methods and (b) neglect of differential overlap (NDO) or zero differential overlap (ZDO) methods.
The underlying approximation for many approximate SCF methods is the zero-differential overlap approximation which assumes that

(i) the overlap integral \( S_{kl} = \langle \chi_k | \chi_l \rangle \) = 1 if \( k = l \)

= 0 if \( k \neq l \)

(ii) nuclear electron attraction integrals

\[
Z_A \int \chi_k(i) \frac{1}{A_i} \chi_l(i) = 0 \quad \text{unless} \quad k = 1
\]

(iii) the electron-electron repulsion integrals \( \langle kl | mn \rangle = 0 \) unless \( k = l \) and \( m = n \); and the exchange integrals

\( \langle kn | lm \rangle = 0 \) unless \( k = n \) and \( l = m \). This assumption is particularly important because it removes all three- and four-centre integrals and many of the one- and two-centre integrals. This approximation was introduced first by Pariser, Parr and Pople for \( \pi \)-electron systems.

Different approximate SCF methods have evolved depending on the condition imposed on the orbitals \( \chi_k \) and \( \chi_l \) for the zero differential overlap approximation.

A popular semi-empirical SCF method is the CNDO (complete neglect of differential overlap) method, with all the valence electrons of the molecule treated explicitly and the assumption of zero differential overlap for any set of
orbitals. The coulomb integrals are approximated as coulomb integrals over the spherically symmetric s Slater functions in order to ensure the invariance with respect to a rotation of the molecular axis. The method incorporates a number of parameters which are either derived from observed atomic energy levels (for the atomic ionization potentials or electronegativities) or fitted with ab initio calculations (for some bonding parameters). Two versions labelled CNDO/1 and CNDO/2 differ slightly in the procedures used for obtaining the matrix elements of the Fock matrix. A CNDO/s version, developed by Del Bene and Jaffe\textsuperscript{13} to interpret electronic spectra, retains many features of Pariser-Parr-Pople method for the $\pi$-electron.

Less severe approximations for the use of the zero differential overlap correspond to the INDO (intermediate neglect of differential overlap) procedure\textsuperscript{8}. In order to take some account of exchange terms, the INDO approximation retains the monoatomic differential overlap in one-centre integrals $(k_{A}^{1A} | k_{A}^{1A})$; but is otherwise closely related to the CNDO/2 method.

A MINDO (modified INDO) method\textsuperscript{9}, based on the use of thermochemical data rather than the results of ab initio calculations to fix the bonding parameters, has been developed by Dewar and collaborators. Several parametrizations have been proposed successively in order to overcome some shortcomings of the method.
Perturbative Configuration Interaction over Localized Orbitals (PCILO) method\textsuperscript{10,11}.

By far the most complete and abundant computations in the study of conformation have been carried out by the PCILO method.

This method is based on the expansion of the molecular orbitals, not as linear combination of atomic orbitals but in terms of localized bond orbitals constructed from pairs of hybrid orbitals. The excited state is built from a set of antibonding orbitals which are used to obtain a configuration interaction matrix. The energy and wave functions are produced by perturbation theory, avoiding the necessity of matrix diagonalization. A series of terms just have to be summed to give contributions to the energy up to third order.

Configuration Interaction (CI): The purely theoretical SCF one-electron model, even when carried out exactly, yields, a molecular wave function which contains a 'built-in' error, the correlation error, due to the model itself in which two electrons of different spins may occupy the same molecular orbital. This allows for the possibility of finding two electrons in the same place at the same time, which contradicts the fact that similarly charged particles avoid each other as much as possible because of their coulomb repulsion. One classical device to avoid this error is the following:
When the SCF-LCAO equations are solved, one obtains more molecular orbitals than are needed to build the determinant (which is constructed on the orbitals of lowest energies). The remaining orbitals (the virtual orbitals) can be used for constructing other determinants, $\Psi_k$, of the same type, in which one of the initial $\Phi$'s is replaced by one virtual orbital. These determinants correspond to 'excited' configurations of the system, in the sense that one electron has been 'excited' to an orbital of higher energy. Configurations may be singly-, doubly-, triply- etc., excited. All these configurations are mixed in an appropriate manner to correct the correlation error inserted in a single-determinantal wave function. This is to compute the best possible linear combination of all the $\Psi_k$'s:

$$\Theta = d_k \Psi_k$$

... (20)

This is called configuration mixing or configuration interaction (CI). The classical CI technique uses a variational procedure for obtaining the coefficients $d_k$ which minimize the total energy corresponding to $\Theta$.

**Perturbative Configuration Interaction (PCI):** For solving the configuration interaction problem, the most appropriate and convenient method is to apply perturbation techniques. The single configuration determinants $\Psi_k$ may be considered as the eigenvectors of an unperturbed Hamiltonian $H_0$, which differs
To get faster convergence of the perturbation process, the following definitions of $H_Q$ and $V$ are adopted, which does not require the explicitation of the operators themselves but only of their matrix elements over the $\psi_k$'s.

$$H = H_o + V$$  \hspace{1cm} \ldots (21)$$

with $(H_o)_{kk} = E_k$

The wave function and energy corresponding to the exact solution may thus be developed into Taylor expansions in the neighborhood of $\lambda = 0$,

$$\xi = E_k + \lambda E_1' + \lambda^2 E_2' + \ldots$$  \hspace{1cm} \ldots (22)$$

$$\theta = \psi_k + \lambda \phi_1' + \lambda^2 \phi_2' + \ldots$$  \hspace{1cm} \ldots (23)$$

for a given $k$. Taking $k = 0$, the first, second, third etc. order corrections $E_1'$ and $\phi_1'$ are given in terms of the matrix elements of $V$ and the eigenvalues of $H_o$. For instance,

$$E_1' = V_{00}$$  \hspace{1cm} \ldots (24)$$

$$E_2' = \sum_{k \neq 0} \frac{|V_{0k}|^2}{E_o - E_k}$$  \hspace{1cm} \ldots (25)$$

$$E_3' = \sum_k \sum_{l \neq 0} \frac{V_{ko} V_{10} V_{0k}}{(E_o - E_k)(E_o - E_l)}$$  \hspace{1cm} \ldots (26)$$

To get faster convergence of the perturbation process, the following definitions of $H_o$ and $V$ are adopted, which does not require the explicitation of the operators themselves but only of their matrix elements over the $\psi_k$'s.
\[ H_{ij} = V_{ij} \text{ for } I \neq J \quad \cdots (27) \]

\[ H_{ii} = (H_0)_{ii} \text{ for all } Is \quad \cdots (28) \]

where \( H \) is the known exact Hamiltonian. In this way, the \( E_k \) values of the denominators are the energies of the single determinants computed with \( H \), all \( V_{ii}'s \) are zero (so that the first-order correction is zero) and the other necessary matrix elements of \( V \) are the usual elements of the CI matrix computed with \( H \). Since \( H \) contains only one- and two- electron operators, only single and double excitation terms interact with \( \Psi_0 \) in the CI matrix. Hence the perturbation up to third-order requires only the double excitation terms.

**Localized Orbitals:** It is well known that the relatively delocalized canonical SCF molecular orbitals can be transformed through a matrix transformation into an equivalent set of orthogonal localized orbitals (over the chemical bonds) leaving the SCF energy invariant.

The configurations contributing most strongly to the correlation energy are constructed by localizing the SCF orbitals on the chemical bonds and the virtual orbitals into 'antibonding' orbitals in the corresponding regions. This property of localized orbitals may be utilized in side a perturbative configuration treatment.
PCIL0 Method: Perturbative configuration interaction over localized orbitals is the general framework of the PCIL0 method. The originality of this method lies in the particular choice of the localized orbitals. The sole restriction is that of using an orthonormal set of orbitals rather than SCF molecular orbitals. On the other hand, best convergence is to be expected from the use of occupied and virtual orbitals localized in the same region of space, hence the idea of using a set of bond orbitals and their antibonding counterparts defined a priori on the chemical bonds.

PCIL0 method is an all-valence-electron method which incorporates the following simplifications: (a) the use of the full ZDO approximation, (b) the adoption of the CNDO/2 integral approximation both for the coulomb integral and for the core matrix elements.

The starting molecular orbitals are constructed as bond orbitals, $i$ or lone pair orbitals from pairs of hybrid orbitals.

$$i = \alpha \chi_1 + \beta \chi_2 \quad \ldots \quad (29)$$

The corresponding antibonding orbitals is given by

$$i^* = -\beta \chi_1 + \alpha \chi_2 \quad \ldots \quad (30)$$

(for lone pairs $\chi_2$ is rejected to infinity: $\beta$ and $i^* = 0$)
The appropriate hybrids are constructed from the usual slater atomic orbitals so as to ensure maximum overlap on the chemical bonds and orthogonality between bonds by a procedure due to Del Re.

The ZDO condition makes the starting set of bond orbitals automatically orthogonal. The zeroth-order ground state determinant is constructed over all the \( i \)'s and all possible excited determinants are constructed using the \( i^* \)'s. This and the total Hamiltonian define entirely both the \( E_k \) and the necessary perturbation matrix elements \( V_{ok} \) according to the Eqs. 24-26.

The second order correction to the energy comprises

(a) single excitations \( i \rightarrow i^* \) (polarization term) or \( i \rightarrow j^* \) (delocalization term), (b) double excitations reduced by ZDO to

\[
\begin{align*}
i \& \rightarrow i^* i^* \text{ (intrabond correlation)} \\
i \& \rightarrow i^* j^* \text{ (interbond correlation)}
\end{align*}
\]

The third order terms \( E_3 \) involve interaction between the following configurations; single excitations with single excitations; single excitations with double excitations; double excitations with double excitations. The first combination is made up of polarization and/or delocalization corrections, the second and third involve again 'correlation'. 

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In the PCILO method, the starting orbitals not being self-consistent, the single excitation terms do not cancel out as in a conventional CI over an SCF determinant. The SCF level lies somewhere in the neighbourhood of the zero-order + single excitation correction level and is not identical to it. Further inclusion of the double excitation terms in PCILO roughly corresponds to what would be obtained by adding double excitations by perturbation to an SCF determinant, but again is not identical to it.
A REVIEW ON THE CONFORMATIONAL STUDIES RELATED TO BENZYLIDENE-ANILINES AND ORGANIC DYESTUFFS.

A. BENZYLIDENEANILINES:

Crystallographic Studies.

The marked dissimilarity in the electronic spectra of benzylideneanilines (BA) and the isoelectronic trans-stilbene (S) and trans-azobenzene (AB) molecules has led to many theoretical and experimental studies on their crystal and molecular structure. S and AB have been reported to be almost planar, centrosymmetric molecules in the solid\textsuperscript{14} and nearly so (rotation $\sim30^\circ$) in the gas phase\textsuperscript{15} and are assumed to be such in solution. BA has a nonplanar conformation in solid and gas phases\textsuperscript{15,16}. The close correspondence between its diffuse reflectance spectrum and solution spectra support the conclusion that it is also nonplanar in solution\textsuperscript{17}. The difference in the spectral behaviour of BA on one hand and S and AB on the other, is attributed to this fact.
In order to define the actual molecular geometry and to investigate the effect of substituents, various authors have reported the structures of 4,4'-derivatives of BA(I) obtained from crystallographic, spectroscopic and theoretical studies. The relevant literature are summarized in Table-I.

Table-I: Substituted Benzylideneanilines

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Reference</th>
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<tbody>
<tr>
<td>BA</td>
<td>H</td>
<td>16,17,18,21,23,25-31,57</td>
</tr>
<tr>
<td>a</td>
<td>NO₂</td>
<td>23,25,26,28</td>
</tr>
<tr>
<td>b</td>
<td>NMe₂</td>
<td>23,28b,28c</td>
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<tr>
<td>c</td>
<td>H</td>
<td>23,30,28b,28c</td>
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<tr>
<td>d</td>
<td>H</td>
<td>NMe₂</td>
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<tr>
<td>n</td>
<td>NMe₂</td>
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* In the following review, the nomenclatures used in the original literature are retained, though in many cases they do not conform to the IUPAC system.
A large number of studies which employ a variety of means for forcing BA into planar conformation have been reported in the literature. The most stable nonplanar conformation is generally considered to be due to a competition between two factors:

(i) The repulsive interaction of the orthohydrogen on the aniline ring and the hydrogen on the bridge carbon, which is relieved by an out of plane rotation about the N-phenyl bond.

(ii) Two different electron delocalization processes—
(a) the delocalization between \(-\text{CH} = \text{N}^{-}\) double bond and the aniline phenyl ring or in case of 4,4'-substituted benzylideneanilines with a donor and acceptor, this delocalization may extend over the whole molecule, i.e., between the substituents. Nakai et al. have termed this intramolecular charge transfer as CT-1 that is facilitated for a planar conformation, (b) on the other hand, there could also be an overlap of the lone pair electrons on the bridge nitrogen atom and the pi-electron system of the aniline ring, which increases with increasing nonplanarity. This has been termed as CT-2.

Several different molecular conformations of trans-benzylideneanilines have been observed in the crystalline state; (i) first, there is a conformation with considerable torsion of ring A about C1-N bond, but with limited torsion
about the C\textsubscript{7} - C\textsubscript{1}' single bond. The values in the parent compound (BA) are 55°, -10°\textsuperscript{16,21} respectively, and similar values are obtained for the 2',4'-dichloro, 4-nitro-4'-methyl, 4-bromo and the 4-carboxylic acid derivatives\textsuperscript{20}, (ii) planar conformation observed in the metastable form of 4,4'-dichloro, 4,4'-dibromo and 4-dimethylamine -4'-nitrobenzylideneanilines\textsuperscript{22,23}, (iii) nonplanar conformation with significant torsion about C-N bond C-C single bonds (\sim 25°) as in the stable modification of 4,4'-dichlorobenzylideneaniline.

**Spectroscopic Studies:**

The reported nonplanar structure of benzylideneanilines from crystallographic studies is supported by the electronic absorption spectra. Since the crystal reflectance spectra are most of the cases similar to the solution spectra, it seems likely that the stable conformation in the solution and the crystalline state are not too different from each other\textsuperscript{17}.

El-Bayoumi et al.\textsuperscript{24} have reported the electronic absorption spectra of various benzylideneanilines (I\textsubscript{h}, I\textsubscript{i}, I\textsubscript{j}) at room temperature in different media. Spectral changes due to substitution, change of solvent, and protonation support a nonplanar structure in which the nitrogen lonepair is conjugated to the phenyl group of the aniline part of the molecule. These spectra have been adequately interpreted in terms of two weakly interacting moieties of the molecule, namely the benzal
and the aniline parts. States have been identified as either locally excited or predominately charge-transfer states. This classification has been used in the assignments of various electronic transitions.

Skrabal et al.\textsuperscript{23} studied the UV absorption spectra of BA, Ia - Id, Im, and In along with the corresponding 3H-indoles as planar model compounds. It is concluded that 4-dimethylamino 4'-nitrobenzylideneaniline (In) has a planar or nearly planar conformation. The twist angle in 4-dimethylaminobenzylidene aniline (Ib) is considerably reduced. This is to be expected if it is assumed that delocalization of the nitrogen lone pair into the aniline ring partly compensates the loss of pi-electronic energy in the twisted benzylideneaniline; the dimethylamino group in aniline ring has the major effect, since the delocalization of the nitrogen lone pair is impeded. When the nitro group is also present as the substituent, obviously an additional increase in the slope of pi-electronic energy with increasing twist angle occurs and the potential minimum is further shifted to smaller twist angle. The electronic spectra of 4'-nitro benzylideneaniline (Ic) and 4-nitro benzylideneaniline (Ia) reveal that substitution by the nitro group alone has only a minor effect. However, when the dimethylamino group is also present (Ic,Id), partial planarization is observed.

In an investigation performed by means of photoelectron spectroscopy, Bally et al.\textsuperscript{17} came to the conclusion that for BA, the twist of the aniline ring is close to 36°, a value
lower than the one obtained by X-ray analysis. Akaba et al. have also reported their studies on electronic structure and molecular conformation for benzylideneaniline and its 2-methyl, 2,6-dimethyl, and 4-nitro derivatives (all in the aniline ring) by electronic absorption on photoelectron spectroscopy combined with CNDO CI calculations. In all the compounds studied, the aniline ring is found to be twisted, the most twisted conformation being 4-nitrobenzylideneaniline.

Maeda et al. have reported the results of the proton NMR and optical spectroscopic studies on the conformations of cis- and trans- isomers of benzylideneanilines. They have drawn two conclusions that are different from earlier reports:
(a) Effects of trans-cis isomerism on diamagnetic shielding in NMR spectra suggest only a limited deviation of the aniline ring from the plane containing the central atoms in the trans-isomers in the absence of steric hindrance due to methyl substitution. This has been corroborated from the intensity lowering effects of trans-cis isomerism and of methyl substitution of the first electronic absorption band, (b) the first electronic transition extends over the whole molecules as in stilbene and rule out the possibility that the aniline ring is perpendicular to the above plane in either isomer of benzylideneaniline.

Recently, Akaba et al. have reported the results of their NMR (Proton and $^{13}$C) studies on mono and di (in the two aromatic rings) substituted benzylideneanilines. The non-additivity of
substituent effect observed for $4\text{-}Y\text{C}_6\text{H}_4\text{CH} = N\text{C}_6\text{H}_4\text{NMe}_2-$ and $4\text{-}\text{NO}_2\text{C}_6\text{H}_4\text{CH} = \text{NC}_6\text{H}_4 X-$ is interpreted in terms of substituent-substituent interactions accompanied by conformational changes with substituents in these benzylideneanilines. It was found that for benzylideneanilines carrying the variable substituent $X$ on the anilino-benzene ring the azomethine protons undergo upfield shifts with increasing electron-drawing property of $X$, whereas those for benzylideneanilines carrying the variable substituent $Y$ on the benzylidene benzene ring exhibited the expected low field shifts with increasing electron withdrawing property of $Y$. This anomalous upfield shifts of the azomethine proton has been attributed to the increase in the twist angle of the aniline ring from the molecular plane containing $-\text{C}=\text{N}-$ bond.

Theoretical Studies:

One of the earliest applications of molecular orbital theory to the electronic absorption spectra of benzylideneanilines was reported by Smith. The energy levels, electron densities and bond orders were calculated by using LCAO-MO method with the inclusion of overlap. The results were applied for the interpretation of the electronic absorption spectra of benzylideneanilines and some of its derivatives. It was concluded that the anomalous spectrum of benzylideneanilines could be explained on the basis of twisting of the aniline ring out of the plane of the molecule.
Minkin et al. investigated the interaction of electronic and steric factors in benzylideneaniline molecules. The theoretical calculations predicted that the molecule exists as a stable nonplanar conformation, in which, the dihedral angle between the aniline ring and the rest of the molecular plane is 40° - 60°, and that substituents in the aryl nucleus have little effect. These were in conformity with experimental observations. The nature of electronic transitions and their connection with molecular conformation was investigated by ASMO-CI method. It was concluded that the effect of competing conjugation, coupled with demands of stereofactors are responsible for the nonplanar conformations of benzylideneaniline molecules and some of their peculiar properties.

Within the framework of Huckel molecular theory, Burgi and Dunitz proposed a simple model, which takes into account the dependance of pi-electronic energy and non-bonded interactions on molecular conformation. The model consistently reproduced the twisted conformation of benzylideneanilines and almost planar conformation of azobenzene and stilbene. The calculated pi-electronic energy plus the calculated nonbonded interactions favour the twisted benzylideneaniline over the planar conformation by 8.4 kJ/mol (2 kcal/mol). For azobenzene and stilbene the nonbonded interactions are relatively small and the potential curves are dominated by pi-electronic energy. In BA these two factors contribute roughly equal amounts to its
potential. This has been rationalized as due to the compensation of the pi-electronic energy in the twisted benzylideneaniline, partly, by delocalization of the nitrogen lone pair into the aniline ring. If non-bonded interactions are neglected, pi-electronic energy has been found to favour the planar conformation of BA over the perpendicular conformation by a small amount.

Warren et al. have reported the ground state conformation of the trans- and cis- isomers of benzylideneanilines and the mechanism and energetics of their interconversion by CNDO method. The prediction of the CNDO calculations that the minimum energy trans conformation of BA in nonplanar, agrees with the results obtained by HMO theory. The minimum energy conformation of the trans-isomer was shown to be the one in which the aniline and the aromatic rings are twisted by 90° and 53° respectively as compared to the X-ray results of 55° and 170°. Both the calculated and experimental conformations show the C-N-C angle to be close to that for sp² hybridization at the nitrogen atom. It has been calculated that the conversion of the minimum energy form to the experimental structure requires an energy of about 1 kcal/mol and is suggested that an energy difference of this magnitude could be accounted for by stabilization accruing from the preferred packing arrangement in the crystal. Their calculations tend to confirm the proposal that the conformation of the free molecule is not too different from that in the crystal.
By comparing the photoelectron spectral results of benzylideneaniline with analogous compounds including stilbene and azobenzene Bally et al. have concluded that semi-empirical methods (MINDO/2, CNDO/2, MINDO/3) are not applicable to the systems of this type and suggested that, in general, these methods are not reliable for treating torsional energies about essential single bonds which connect pi-systems. However, Jacques and Faure have reported that semi-empirical studies employing geometry optimization with PCIL, does produce a minimal energy conformation close to that observed in the photoelectron spectroscopic method. Besides, this method provides outstanding results for dipole moment values and the correct order of stability for the trans- and cis-forms.

From an ab initio study of conformational energetics of benzylideneaniline using STO-4G basis set, Bernstein et al. have found that the aniline and the benzene rings in BA are twisted by 45° and 0° respectively.
B. DYESTUFFS:

Synthetic dyestuffs these days have found a wide range of applications. Besides the classical use as photographic sensitizer, they find use in laser technology for the production of tunable dye lasers, thermochromic and photochromic substances in information retrieval systems, as potential photoconductive and photovoltaic materials and in liquid crystal display systems. Though not entirely, all these applications or potential applications depend largely on their structural features and hence the conformational studies related to dyes have now acquired a good deal of importance. But surprisingly a survey of literature reveals that such information are extremely scarce. Most of the limited information that are available, are related to crystal structure determination by X-ray and the structure of dye aggregates. The paucity of experimental data is possibly due to the difficulties involved in growing single crystals, solvation and subsequent disintegration of the dyes. But the extremely limited theoretical studies is more surprising.

Crystal Structure Studies:

One of the earliest crystallographic studies on cyanine dyes was made by Wheatley who elucidated the structure of the unsolvated 3,3'-diethylthiacarbocyanine bromide(III). The cation was found to be planar with the conjugated chain in
the extended form. The sulphur atoms are cis with respect to this chain. Subsequently in a brief note, Nakatsu et al.\textsuperscript{35} have confirmed these observations. The sulphur atoms which lie in the same side of the cation are only 2.99 Å apart, implying a bonding interaction between them. The bond lengths in the two halves of the cation are equivalent, which indicates that the resonance between the extreme structures is complete. The ethyl groups apparently project on the same side of the plane.

Potenza and Mastropaolo\textsuperscript{36} have studied the crystal structure of thiacarbocyanine dyes to examine the geometric factors which could affect the attachment of such dyes to silver halide surfaces. The dye 5,5'-dichloro-3,3',9-triethyl-thiacarbocyanine bromide (IV) shows significant deviations from planarity. Atoms from each half of the cation show an average deviation of approximately $\pm 0.05$ Å from planarity; the dihedral angle of 8.6° between these planes suggests a limited bowing of the cation. Bond distances in the central carbon chain are equivalent; their magnitude indicates partial
double bond character and suggest electron delocalization between the two halves of the cation. They have also reported the crystal structure of 3,3'-diethylthiatricarbocyanine iodide by a single crystal three dimensional X-ray diffraction method. The cation has long been considered as a model long wavelength (near infrared) sensitizer. Previous crystallographic studies of thiacarbocyanine dyes, with three carbon atoms in the central chain have revealed the all-trans configuration in a number of cases (including the structures with no alkyl substituents on the central chain, and with a bulky 9-ethyl substituent). In case of 3,3'-diethyltricarbocyanine, steric strain associated with atoms on the central chain is minimal and the all-trans structure is favoured energetically. Deviations of the cation from planarity are large. Atoms on the central chain show an average deviation of 0.04 Å from the plane with a maximum deviation of 0.06 Å. Atoms towards the centre of the chain show positive deviation, while those towards the end show negative deviations. This indicates that the central chain is bowed slightly. The cation is best described as S-shaped,
with the heterocyclic groups bent from the central chain in opposite directions. Lastly, both heterocyclic planes are also twisted slightly from the central chain, and to different degrees.

From the X-ray crystallographic study of 3,3'-diethyl-9-phenyl thiacarbocyanine iodide, Nakai et al.\textsuperscript{38}, have elucidated the influence of a meso-phenyl substituent on the molecular structure and the stacking of dyes in the crystals.

The crystal structure of 1,1'-diethyl-2,2'-thiazoline-carbocyanine iodide has been reported\textsuperscript{39}. An apparent alternation in bond lengths led the authors to conclude that there is localization of the positive charge on one of the nitrogen atoms. The sulphur atoms lie on the same side of the cation and the ethyl groups protrude from the cation plane in one direction. Because of the saturated carbons, the thiazoline rings depart somewhat from planarity.

The simplest cyanine whose structure has been determined is the streptocyanine 1,3-bis(dimethylamino) trimethinium perchlorate(V)\textsuperscript{40}. This dye is not known to aggregate or sensitize, but Kobischke and Dahne\textsuperscript{41} have shown that the heptamethine

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H} & \quad \text{CH}_3 \\
\text{H}_2\text{C} & \quad \text{N} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{CH}_3 \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{ClO}_4^{-} 
\end{align*}
\]
analog possesses these properties. The cations are approximately planar and the bond lengths indicate complete delocalization of the pi-electrons. The crystal structure correlates very well with polarized reflection spectra and is consistent with the transition moment parallel to the long axis of the polymethine chain.

Yoshioka and Nakatsu\textsuperscript{42} have briefly reported the crystal structure of the photographic sensitizer, 1,1'-diethyl-4, 4'-cyanine bromide. Steric interference of the hydrogen atoms at the 3 and 3' positions causes the angle at the bridge carbon to enlarge and the quinoline rings to be twisted with respect to the plane of the three central carbon atoms. The bond lengths indicate complete delocalization of the pi-electrons over the chromophore.

Two structure determinations have been reported for the classic sensitizing and aggregating dye, 1,1'-diethyl-2, 2'-cyanine (VI) - a low precision structure briefly reported by Yoshioka and Nakatsu\textsuperscript{42}, for the bromide, and subsequently a refined
structure by Nakatsu, Yoshika and Morishita\textsuperscript{43} and a high-precision structure reported in detail by Dammeier and Hoppe\textsuperscript{44} for the chloride monohydrate. The dye cation is found to assume a skewed conformation and the dihedral angle between the roughly planar quinoline rings was found to be 41°. In the crystals each quinoline ring of the dye cation is stacked in a face-to-face manner. The intense, sharp $J$ absorption band observed on a powder sample is ascribable to the linear array. A charge-transfer interaction between the dye cation and the iodide anion is suggested to be present from an SCF-MO calculation on the dye cation; this is evidenced by the crystal structure.

Tanaka et al.\textsuperscript{45} have measured the reflection spectra of single crystals of 1,1'-diethyl-2,2'-cyanine iodide, bromide and chloride in order to find the origin of the $J$-band. The $J$-band was found along particular crystalline direction in which the dye molecules are stacked face-to-face showing importance of interplanar pi-electron interaction.

Related to the 2,2'-cyanines is 1-ethyl-2-[(1-ethyl-1,2-dihydroquinolin-2-ylidene) phosphino] quinolinium perchlorate (VII) in which phosphorous has replaced the bridging CH group\textsuperscript{46}.

\vspace{4cm}

\begin{center}
\includegraphics[width=0.5\textwidth]{structure}
\end{center}

(VII)
This molecule is distorted unsymmetrically, with the quinoline rings rotated by 40° and 24° around the C-P bonds. The normals to the plane enclose an angle of 60°. Another phosphacyanine whose structure has been reported is N-ethyl-2-(N-ethyl benzothiazolin-2-ylidene)-phosphino benzothiazolium perchlorate(VIII)⁴⁷. The molecule is relatively planar; the two benzothiazole systems enclose an angle of only 6.1°. The two sulphur atoms lie on the same side of the cation and are separated by only 2.95 Å, which indicates an attractive S ... S interaction. The ethyl groups are oriented approximately perpendicular to the cation plane and protrude in opposite directions from this plane.

Allman⁴⁸ has reported the structure of 1,4-bis(N-ethyl-1,2-dihydrobenzothiazol-2-ylidene) tetrazene(IX). In this neutral
molecule, there are four nitrogen atoms in the conjugated chain connecting the benzothiazole rings instead of the odd number of CH's found in cyanines. The definite alternation of bond length in the chain is consistent with the fact that only one simple uncharged valence bond picture can be drawn for the molecule. The sulphur atoms are cis to the tetrazene chain and thus are on opposite sites of the molecule because of the even number of atoms in the chain. The ethyl groups protrude to opposite sites of the molecular plane. The molecules lie on centres of inversion so the benzothiazole planes are parallel but inclined 4.8° to the plane of the tetrazene chain.

The structure of a 2-propanol solvate of 1,1',3,3'-tetraethylimidazo[4,5-b]quinoxalino cyanine iodide (X) has been determined by Smith and Barrett. Because of the steric interference between the ethyl substituents, the cation is not planar but can be divided into three planes - a central plane consisting of the methine carbon and its adjacent carbon atoms.
and two end planes consisting of the fused ring systems but excluding the 2-carbon atoms. The dihedral angles are 55.4° between the end planes and 35.3° and 21.0° between the central and end planes. Several angular distortions of about 5° help to relieve the strain. Bond lengths show that the pi-electrons are largely delocalized in spite of the molecular distortion.

Smith and Luss\textsuperscript{50} have determined the crystal structures of a 2:1 methanol and a 1:1 acetonitrile solvate of 1,1',3,3'-tetrachloro-5,5', 6,6'-tetraethyl benzimidazolo - carbocyanine iodide(XI). The bond lengths and angles of the carbocyanine dye

\[
\begin{align*}
\text{(a). } & 2\text{CH}_3\text{OH} \\
\text{(b). } & \text{CH}_3\text{CN}
\end{align*}
\]

(XI)

are equivalent in the two structures and indicate complete delocalization of the positive charge. The cations are nearly planar but do exhibit systematic distortions.

All the merocyanine dyes (XII - XV), whose crystal structures have been published\textsuperscript{33} contain the rhodanine nucleus. Bond lengths indicate the molecules to be largely in the uncharged state. Shibaeva et al.\textsuperscript{51a} have briefly reported the structure
of 1:2 complex of 3,3'-dimethylthiacyanine and 7,7,8,8-tetracyanoquinodimethane. The dihedral angles between the planes of the benzothiazole rings was found to be 9.7°.

Etter et al.\textsuperscript{51b} have reported the structures of a new class of mixed dyes - the chloroform solvate of a cyanine - oxonol complex of 3,3'-dimethylthiacarbocyanine(IIIa) and 3,3',5,5'-tetramethyltrimethineoxanol(IIIb). It has been demonstrated that cyanine dyes can form mixed aggregate stacks with oxonol dyes and the two can interact with favourable configurations, leading to many crystalline forms. Many of the crystal forms undergo thermal phase changes involving thermochromic desolvation and polymorphic transformations, which perturb the electronic structures of the complexes.
Conclusions from the evidence already available from crystal structure determinations may be summed up as following: bond lengths indicate that the symmetrical cyanines have their positive charge delocalized symmetrically over the chromophore to form an aromatic resonance system, even when the dye deviates considerably from planarity. Strong dispersion forces between the planar aromatic molecules cause the molecules to pack plane to plane on edge to form polymeric chains and sheets in the crystals and thus probably in aggregate too. Molecular substituents determine the lateral displacements of adjacent rows and hence slip angles.
Conformational analysis today has acquired a good deal of importance in chemistry due to the fact that chemical and physical properties of the molecules are intimately related to their conformations not only in their ground state but also in their transition and excited states. With respect to the dyestuffs, it may be stated that besides spectra, many of their properties which are of practical importance like photosensitization, laser efficiency, photoconducting and photovoltaic properties, thermochromic and photochromic behaviour etc. are also conformation dependent.

The present work consists of theoretical computations, using quantum mechanical PCIL0 method, on the conformations of:

(a) Some substituted benzylideneanilines and some of their stilbene and azobenzene analogues. These compounds may be considered as merocyanine-type donor acceptor chromogens,
(b) p-dimethylaminostyryl dyes derived from some heterocyclic nuclei, their $\alpha$- and $\beta$- aza derivatives which may be considered as the heterocyclic analogues of stilbene and benzyledeneaniline respectively.

Besides reproducing some data already obtained experimentally, the theoretical approach to conformational analysis has many additional advantages. Most of the experimental techniques yield information about the most stable conformation only, whereas a theoretical method can usually produce a complete potential function. Theoretical methods deal with the molecules in the gas phase, which is most appropriate for studying conformational problems because it is the only phase in which the intramolecular forces exclusively determine the molecular conformations. In a pure liquid or in a solution, intermolecular forces compete with the intramolecular forces, for the subtle equilibrium responsible for the assumed conformation. The solvent effects are though, of practical importance, can hardly be described quantitatively unless the behaviour of the free molecule is properly understood, and this can be achieved only by theoretical methods.

The theoretical and experimental facts accumulated so far, indicate that the substituents in the ring play an important role in determining the benzyledeneaniline conformation and most spectroscopists seem to emphasize that the origin of non-planarity can be attributed to the delocalization of the
azomethine lone pair. In order to get a deeper insight into the substituent effects on the mechanism responsible for the noncoplanarity of the aniline ring and/or the phenyl ring, we have attempted to investigate the effect of strong electron-donating and strong electron-withdrawing substituents on the conformation of benzylideneanilines. Specifically, conformational studies on the following benzylideneanilines have been undertaken.

1. Monosubstituted benzylideneanilines
   (a) N-benzylidene-4-nitroaniline (Ia)  
      (4-Nitrobenzylideneaniline)
   (b) N-benzylidene-4-dimethylaminoaniline (Ib)  
      (4-Dimethylaminobenzylideneaniline)
   (c) N-(4-nitrobenzylidene) aniline (Ic)  
      (4'-Nitrobenzylideneaniline)
   (d) N-(4-dimethylaminobenzylidene) aniline (Id)  
      (4'-Dimethylaminobenzylideneaniline)

2. Disubstituted benzylideneanilines
   (a) N-(4-dimethylaminobenzylidene)-4-nitroaniline (Im)  
      (4-Nitro-4'-dimethylaminobenzylideneaniline)
   (b) N-(4-nitrobenzylidene)-4-dimethylaminoaniline (In)  
      (4-Dimethylamine-4'-nitrobenzylideneaniline)

3. Stilbene (IIa) and azobenzene (IIb) analogues of Im and In.

![Diagram](II)

\( a : P = CH = Q \); \( b : P = N = Q \)
Conformational studies on (i) p-dimethylaminostyryl dyes (XVIa-XXa) derived from the condensation of p-dimethylaminobenzaldehyde with five different heterocyclic bases, quinoline-4, quinoline-2, pyridine-4, pyridine-2, and benzothiazole, (ii) their α-aza (XVIb-XXb) and (iii) β-aza (XVIc-XXc) analogues, were undertaken with several objectives in mind. Some of the dyes of this series (e.g., XVIIa, XIXa, XXa) are reported to be quite powerful sensitizers, while some other (e.g., XVIa) do not possess any sensitizing property at all, although apparently all of them bear quite close structural resemblance to each other. This, in itself, is an interesting theoretical problem, whose solution, we think, may lie in the difference in their conformation. Besides, a vast amount of experimental and theoretical work on the stilbenes, azobenzenes and the closely related benzylideneanilines, indicate a non-planar structure for some of these compounds. Since, the styryl and azastyryl dyestuffs, are quite similar to stilbenes and benzylideneanilines (the phenyl ring in stilbene or benzylideneanilines is substituted by a heterocyclic ring), we intend to find out whether similar interactions also operate in case of styryl dyes to determine their most stable conformations.
XVI
a : X = CH = Y 
b : X = N, Y = CH 
c : X = CH, Y = N 

XVII
a : X = CH = Y 
b : X = N, Y = CH 
c : X = CH, Y = N 

XVIII
a : X = CH = Y 
b : X = N, Y = CH 
c : X = CH, Y = N 

XIX
a : X = CH = Y 
b : X = N, Y = CH 
c : X = CH, Y = N 

XX
a : X = CH = Y 
b : X = N, Y = CH 
c : X = CH, Y = N
Method:

Among the main theoretical methods dealing with all valence electrons, the PCILO (Perturbative Configuration Interaction using Localized Orbitals)\textsuperscript{11} method is extensively used for conformational studies because of its proven success with quite diverse types of molecule\textsuperscript{32,52-54}. This method is based on the expansion of the molecular orbitals in terms of localized bond orbitals constructed from pairs of hybrid orbitals. The excited state is built from a set of antibonding orbitals, which are used to obtain a configuration interaction matrix. The lower eigenvalues of the CI matrix are calculated by a Rayleigh-Schrodinger perturbation expansion.

Difficulties, that may arise, in the use of PCILO method involving delocalized bonds have been discussed in some detail by Martin et al.\textsuperscript{55} in connection with conformational studies on phenyethylamine. By employing three different criteria to perform computations on both Kekule structures, viz. (i) use of multiconfigurational zeroth-order wavefunction, (ii) use of the arithmetical mean of the third-order energies of the two Kekule structures, (iii) use of best third order (final) energy, they have obtained a satisfactory agreement between all the three conformational results. Jacques and Faure\textsuperscript{32} have reported the conformational study of benzylideneaniline by the PCILO method. Although not explicitly mentioned, evidently there is no significant falsification of the results by an arbitrary choice of any one of the localized bond structures.
As a further check of this hypothesis, calculations were carried out with two canonical structures of 1(b) and β-aza styryl dye (XVIIIc) and all the four structures of α-azastyrly dye (XVIIIb) derived from pyridine-4. It can be seen from the results that the lowest energy corresponds to identical conformations.

\[ \text{Emin at } \phi = 30^\circ, \ \theta = 180^\circ \quad \phi = 30^\circ, \ \theta = 0^\circ \]

\[ \text{Emin at } \phi = 150^\circ, \ \theta = 180^\circ \quad \phi = 150^\circ, \ \theta = 0^\circ \]
The dihedral angles of the phenyl and the heterocyclic rings with respect to the central methin chain are measured in terms of torsion angles $\phi$ and $\theta$ which are defined as,

\[
\phi = C_2 - C_1 - N - C_7 \\
\theta = N - C_7 - C_1' - C_2' 
\]

For I

\[
\phi = C_2 - C_1 - P - Q \\
\theta = P - Q - C_1' - C_2' 
\]

For II

and

\[
\phi = C_3 - C_4 - X - Y \\
\theta = X - Y - C_{12} - C_{13} 
\]

For p-Dimethylamino styryl dyes and their aza analogues

The clockwise direction being positive. The cis and trans-dihedral angles have been taken as 0° and 180° respectively.
Input geometries:

For substituted benzylideneanilines, stilbene and azobenzene analogues, the standard geometries (bond lengths and bond angles) from Pople and Beveridge$^7$ have been adopted as the input data. All bond angles involving $sp^2$ and $sp^3$ hybrid orbitals, have been taken as $120^\circ$ and $109.47^\circ$, respectively.

In case of p-dimethylamino styryl dyes and their aza analogues, since no crystallographic values are reported, the input geometries have been taken from certain related molecules,

(i) The dimethylamino benzene part from the crystallographic studies of Nakai et al.$^{19}$ on p-dimethylamino benzylidene-p-nitroaniline.

(ii) Geometry of the quinoline-4, from the crystallographic studies of Yoshioka and Nakatsu$^{42}$ on 1,1'-diethyl-4,4'-cyanine bromide.

(iii) Quinoline-2 geometry from Nakatsu et al.$^{43}$ on the structure of 1,1'-diethyl-2,2'-cyanine iodide.

(iv) Pyridine-2 and Pyridine-4 geometries from the crystallographic results of Rerat$^{56}$ on pyridine hydrochloride.

(v) Benzothiazole geometry from the crystallographic studies on 3,3'-diethylthiatricarbocyanine iodide by Potenza et al.$^{37}$. 
In conformity with the reports of the above crystallographic studies, the phenyl and the heterocyclic rings (excluding the side chain Me or Et substituents) have been taken to be planar.

The PCIL0 energies have been computed as a function of $\Phi$ and $\Theta$ at 30° intervals with preselected values of the other geometrical parameters. The presentation of the results on the conformational energy maps is restricted to 5 kcal/mol isoenergy over the global minimum.
4A. BENZYLIDENEANILINES, STILBENE AND AZOBENZENE DERIVATIVES.

The global minima as well as the low energy regions (upto 1.0 kcal/mol above the global minimum) for the four monosubstituted molecules (Ia - Id), the disubstituted compounds (Im and In) and the stilbene (IIa) and azobenzene (IIb) derivative are presented in Table - II, with their energies by taking the lowest global minimum of each molecule as zero. Figures 1-4 represent the conformational energy maps (restricted to 5 kcal/mol isoenergy over the global minimum) of Im, In, IIa and IIb.

N-Benzylidene-4-nitroaniline, (Ia): There are four reports on the conformation of I(a). Skrabal and collaborators\(^\text{23}\) from a comparison of its electronic absorption spectra with benzylideneaniline have proposed that the twist angle of the aniline ring (\(\Phi\)) should be of the same order as that in case of benzylideneaniline, which is 55°. Theoretical calculations (CNDO / S) and UV spectral studies by Akaba et al.\(^\text{25}\) indicate that in Ia the twist of the aniline ring in solution and gas phase is more than benzylideneaniline itself, and
Table-II: Preferred conformations of substituted Benzylideneanilines, Stilbene and Azobenzene.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy of the planar conformation (kcal/mole)</th>
<th>Global Minimum</th>
<th>Low-Energy Regions</th>
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<tr>
<td></td>
<td>Φ(deg)</td>
<td>Θ(deg)</td>
<td>Φ(deg)</td>
</tr>
<tr>
<td>Ia</td>
<td>1.96</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td></td>
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<td>90</td>
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Table-III: Interatomic distances

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<thead>
<tr>
<th>Molecule</th>
<th>(\text{HC}(3) - \text{HC}(7)) ((A))</th>
<th>(\text{H}(C7') - \text{H}(C2')) ((A))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Planar</td>
<td>Nonplanar</td>
</tr>
<tr>
<td>Im</td>
<td>1.67</td>
<td>2.7</td>
</tr>
<tr>
<td>In</td>
<td>1.67</td>
<td>2.0</td>
</tr>
<tr>
<td>IIa</td>
<td>1.74</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table-IV: Absorption Spectra \((\lambda_{\text{max}})^{62}\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Molecule</th>
<th>(\lambda_{\text{max}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>325</td>
<td>Im</td>
<td>446</td>
</tr>
<tr>
<td>Ib</td>
<td>374</td>
<td>In</td>
<td>400</td>
</tr>
<tr>
<td>Ic</td>
<td>346</td>
<td>IIa</td>
<td>431</td>
</tr>
<tr>
<td>Id</td>
<td>342</td>
<td>IIb</td>
<td>475</td>
</tr>
</tbody>
</table>
Figure 1. Conformational energy map of N-(4-dimethylamino-benzylidene)-4-nitroaniline, (Im)

Figure 2. Conformational energy map of N-(4-nitrobenzylidene)-4-dimethylaminoaniline, (In)
Figure 3. Conformational energy map of 4-Dimethylamino-4'-nitrostilbene II(a)

Figure 4. Conformational energy map of 4-Dimethylamino-4'-nitroazobenzene II(b)
$\Phi = 70^\circ - 85^\circ$. This contention was further confirmed from the photoelectron spectra\textsuperscript{26}. From NMR measurements on substituted benzylideneanilines, it was proposed that the introduction of the electron-withdrawing nitro group at the 4-position of the aniline ring enhances the delocalization of nitrogen (of $-N = CH -$ ) lone pair electrons into the ring that leads to an increase in the value of $\Phi$ in solution, which in turn changes the ring current effect by the aniline ring exerted on $H(C7)$ resulting in an anomalous upfield shift\textsuperscript{28}.

Results of the present computations show that the aniline ring in I(a) is twisted by $60^\circ$ in either directions. The rotational energy barrier with respect to the planar conformation is $1.96$ kcal/mol. It is seen from the results described in Table-II that $\Phi = 30^\circ$ to $90^\circ$ through $60^\circ$, represents low energy regions indicating that the molecule has a good deal of conformational flexibility in this region. This situation is similar to the value of $\Phi = 70^\circ - 85^\circ$, proposed by Akaba et al.\textsuperscript{25}. PCILO calculations on benzylideneaniline itself give value of $36^\circ$ of $\Phi$\textsuperscript{32}. Thus, it is seen that theoretical computations and spectral measurements (UV, PES and NMR) lead to the same conclusion that the aniline ring in I(a) is more twisted than benzylideneaniline.
N-Benzylidene-4-dimethylaminoaniline, (Ib): UV absorption spectra by Skrabal et al.\textsuperscript{23} reveal only a small torsion angle for the aniline ring in I(b). Although the NMR is not very explicit about the conformational state of this particular molecule, it appears by implication that two opposing factors will operate here—(a) in the absence of any electron-attracting substituent at the 4-position, the through-conjugative interaction is obviously impaired leading to less planarity and (b) on the other hand, presence of the electron-donating dimethylamino group would lead to a smaller twist angle.

The present computational results indicate the aniline ring to be twisted out of the plane by $\pm 30^\circ$. This conformation is of 1.53 kcal/mol higher energy than the planar conformation. The low energy region is confined to $\pm 60^\circ$ with an energy barrier of 0.82 kcal/mol. These results clearly indicate that there must, at least, be one more factor contributing to nonplanarity, besides the delocalization of the nitrogen lone-pair.

N-(4-Nitrobenzylidene)aniline, (Ic): For I(c), a torsion angle similar to BA is predicted from UV results\textsuperscript{23}, which means $\phi \sim 55^\circ$. HMO calculations by Minkin\textsuperscript{30} give $\phi = 44^\circ$. We find the value of $\phi = \pm 30^\circ$ from present calculations. The energy barrier with respect to the planar structure is 1.51 kcal/mol. However, it is seen from Table-II that the region,
\( \Phi = \pm 60^\circ \) is only of 0.06 kcal/mol higher energy. Since an energy barrier of this magnitude can easily be overcome in the solution or solid state, it may be concluded that the experimental (UV) and the theoretical conformations lead to the same result.

\[ \text{N-}(4\text{-dimethylaminobenzylidene) aniline, (Id): From the UV spectral study, I(d) is found to be more or less planar. The results are, however, not unambiguous. The present calculation shows that the aniline ring is twisted out of plane by } \pm 30^\circ \text{ with a rotational energy barrier of } 1.54 \text{ kcal/mol. The low energy region is indicated by } \Phi = \pm 60^\circ , \text{which is only of } 0.16 \text{ kcal/mol higher energy.} \]

\[ \text{N-}(4\text{-dimethylaminobenzylidene-4-nitroaniline, (Im): The results with regard to I(m) are close to the crystallographic data}^{19} \text{ in which the aniline and the benzylidene rings are reported to be twisted out of the } C - N = C - C \text{ plane by about } 50^\circ \text{ and } 7.7^\circ , \text{ respectively. The calculated values are } 60^\circ \text{ and } 0^\circ . \]

\[ \text{N-}(4\text{-nitrobenzylidene-4-dimethylaminoaniline, (In): Contrary to the earlier crystallographic and spectral results}^{19,23} , \text{ we find in the present work that the aniline ring in I(n) is expected to be twisted out of the plane by } 30^\circ . \text{The difference in the crystallographic and the calculated conformations in case of I(n) be due to some distortion of the molecule which} \]
occurs when incorporated into a crystal, particularly since the energy requirement is quite small (1.5 kcal/mol). An energy difference of this magnitude may easily arise from the stabilization due to preferred packing arrangements in the crystal.

4-Dimethylamino-4'-nitrostilbene (IIa): It is seen to be nonplanar, the aromatic rings being twisted out of the plane containing the central atoms by 30° in opposite directions. This is, however, in conformity with the reports of Trattenberg and coworkers on the conformation of stilbene in the gas phase.

4-Dimethylamino-4'-nitroazobenzene (IIb): It is found to be planar.

To explain the noncoplanarity of 4,4'-disubstituted benzylidenanilines with electron donor and acceptor, Nakai et al. have involved the concept of intramolecular charge transfer between the substituents (CT-1) and that from the bridge nitrogen lone-pair to the substituent in the aniline ring (CT-2). They suggest that the contribution of CT-2 to the stabilization of the molecule increases with increasing twist angle. The smaller the twist angle, the larger is the contribution of CT-1. The molecules of Ie, Ik, and Im thus result in a twist conformation of the aniline ring. Since CT-2 force is not likely to operate to any appreciable extent in In, in which CT-1 is evidently quite dominant, it is expected to be planar and that is what they observe crystallographically,
supported by the UV spectral finding of Skrabal, and co-workers. This interpretation, however, does not seem to be adequate to accommodate all the present observations: (a) II(b), in which CT-2 is expected to make a significant contribution, is planar, (b) In and Ila, in which CT-2 will make none or very weak contribution, are nonplanar. A similar line of argument by El-Aasser et al. that the azomethine group acts as an electron acceptor or donor, depending upon whether linked to a phenyl group at its carbon or nitrogen end, has also been questioned by Cimiraglia and Tomasi from ab initio calculations of benzaldimine and N-phenylformaldimine. Bernstein, and coworkers have examined the electronic spectra and structure of a polymorph of I which was nonplanar in solution. The chlorine substituents donot significantly perturb the electronic spectrum with respect to that of benzylidene aniline.

From the above discussions, we are inclined to believe that the present results can best be accommodated by considering that besides the stabilization of the nonplanar structure due to an interaction of the bridge nitrogen lone pair and the aromatic $\Pi$-system, there is repulsion between the hydrogen on the $-\text{CH} = \text{N}-$ and one of the ortho hydrogens on the aniline ring, which is relieved by a twisting of the N-phenyl bond (Fig.5a). Since there are two bridge hydrogens in Ila, each is capable of steric interaction with one of the ortho
hydrogens of both the aromatic rings (Fig. 5b) and consequently both the rings are puckered. These conclusions are borne out from the appropriate interatomic distances described in Table-III.

Bernstein et al., from an ab initio study of the benzylideneaniline have arrived at similar conclusions with regard to the factors determining its conformation. Both, the ortho hydrogen interaction and the delocalization of nitrogen lone pair are found to be responsible for the noncoplanarity of benzylideneaniline.

The above arguments are further corroborated by the results of PCILO calculations on the monosubstituted benzylideneanilines, viz., Ia - Id. It can be seen from Table-II that the results with respect to Ib, Ic, Id are strikingly similar. This implies that perhaps there is a common mechanism that determines the conformational characteristics of these molecules and it appears most rational that this mechanism is
the interaction between the ortho hydrogens \( H(C2) \) and \( H(C7) \), since in all the three cases, CT-1 (\( \pi \)-delocalization between the substituents) and CT-2 (delocalization of the nitrogen lone pair to the substituent in the aniline ring) will either be extremely weak or altogether absent. This hypothesis is supported by the results obtained with respect to Ia. In this molecule there can be a substantial overlapping of the \( N \)-lone pair with the aniline ring bearing the strongly electron-withdrawing \( \text{NO}_2 \) group (CT-2) which reinforces the nonplanar structure due to orthohydrogen interaction leading to a greater twist angle \( \Phi \) (= 60°).

Visible Spectra, Failure of the simple HMO Theory:

In useful extension of the HMO theory, called perturbative molecular orbital (PMO) theory, Dewar has made certain generalizations regarding the effect of \(-N=\) substitution in place of \(-CH=\) on the electronic spectra of odd alternant systems. According to the PMO theory, replacement of a \(-CH=\) group by \(-N=\) at a starred position will result in a hypsochromic shift and an opposite effect will be found for the same perturbation at an unstarred position.

On examining the four molecules I, In, IIa, and IIB, we find that if the stilbene derivative, IIa, is considered as the parent molecule, \(-N=\) replacement has taken place at a
starred and an unstarred position, respectively, in $I_m$ and $I_n$. The shifts in the wavelength in the visible absorption spectra are in conformity with the PMO prediction. But when both positions are replaced by two $-N=$ as in $II_b$, there is a large bathochromic shift, contrary to the expectations from PMO arguments (Table-IV).

The spectral observations can perhaps be explained by considering the present computational results. As is well known, nonplanarity causes a reduction in the overlap of the adjacent p-orbitals, which, in turn, will affect the wavelength of absorption. The order of acoplanarity of the four molecules approximately correspond their wavelength of absorption. Thus we see that the transition energy is lowest for the planar molecule $II_b$, and it increases steadily with increasing twist angle of the aniline ring.

A similar trend is also observed in case of the mono-substituted derivatives. The transition energy is maximum ($\lambda = 325$ nm)$^{23}$ in case of the most nonplanar compound $I_a$, while it is the minimum in case of $I_b$ ($\lambda = 374$ nm)$^{23}$. The other two $I_c$ and $I_d$ have intermediate values ($\lambda = 346$ nm and 342 nm, respectively)$^{23}$. 
In the following discussion, we shall refer the 'b' molecules (nitrogen adjacent to the dimethylaminobenzene ring) as \( \alpha \)-aza and the 'c' molecules (nitrogen adjacent to the heterocyclic ring) as \( \beta \)-aza styryl dyes. The relevant data are described in Table-V and VI. Figures 6-15 represent the conformational energy maps (restricted to 5 kcal/mol isoenergy over the global minimum) of the aza styryl dyes (XVIb - XXb and XVIc - XXc).

**Conformation of p-Dimethylaminostyryl Dyes (XVIa - XXa).**

XVIa: The most stable conformation for dye XVIa is obtained with \( \phi = 30^\circ \) and \( \theta = 120^\circ \) which is stabler than the planar structure \( (\phi = 0^\circ , \theta = 0^\circ ) \) by an amount of energy 1.13 kcal/mol. The two quinoline rings in 1,1'-diethyl-4,4'-cyanine bromide have been reported to be twisted out of plane due to steric interaction between the two ortho (with respect to -CH=) hydrogen atoms. In case of dye XVIa the twisting of the quinoline ring is perhaps due to the steric interaction between H(C10) and H(C13) and possibly due also to some extent, the interaction between H(C11) and H(C18). This argument is borne out from the appropriate interatomic distances, which are 1.87 and 2.00A, respectively, for the planar structure and 4.13 and 3.38A for the nonplanar structure. A weak interaction between H(C3) and H(C11) is indicated by the fact that the \( 0^\circ \), 120 conformation is only of 0.16 kcal/mol higher energy.
### TABLE V: Preferred conformations of styryl dyes (XVIa - XXa; X = CH = Y)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Energy of planar conformation*</th>
<th>Global Minimum</th>
<th>Other Energy Regions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>φ°</td>
<td>θ°</td>
<td></td>
<td>φ°</td>
</tr>
<tr>
<td>XVIa</td>
<td>1.13</td>
<td>30</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>XVIIa</td>
<td>3.39</td>
<td>-30</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-30</td>
</tr>
<tr>
<td>XVIIIa</td>
<td>4.66</td>
<td>30</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>XIXa</td>
<td>4.73</td>
<td>30</td>
<td>-60</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>XXa</td>
<td>0.02</td>
<td>-30</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-30</td>
</tr>
</tbody>
</table>

* The planar conformation corresponds to both the values of torsion angles, 0°(Cis) and 180°(trans). In the above table, 'Planar conformation' refer to the one, whichever has the lower energy.
### TABLE - VI: Preferred conformations of Azastyryl Dyes (XVIb - XXb; XVIc - XXc)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Energy of planar conformation*</th>
<th>b. $X = N$; $Y = CH$</th>
<th>Energy of planar conformation*</th>
<th>c. $X = CH$; $Y = N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi^\circ$</td>
<td>$\theta^\circ$</td>
<td>$\phi^\circ$</td>
<td>$\theta^\circ$</td>
</tr>
<tr>
<td>XVI</td>
<td>0.9</td>
<td>30</td>
<td>180</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>180</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>XVII</td>
<td>2.83</td>
<td>-30</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>0</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-30</td>
<td>10.01</td>
<td></td>
</tr>
<tr>
<td>XVIII</td>
<td>0.92</td>
<td>30</td>
<td>180</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>180</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>XIX</td>
<td>2.68</td>
<td>-30</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-30</td>
<td>-30</td>
<td>0</td>
</tr>
<tr>
<td>XX</td>
<td>0.73</td>
<td>-30</td>
<td>0</td>
<td>-30</td>
</tr>
</tbody>
</table>

*The Planar conformation corresponds to both the values of torsion angles, $0^\circ$(cis) and $180^\circ$(trans). In the above table, 'planar conformation' refers to the one, whichever has the lower energy.
and sensitization properties of the styryl dyes.

Table - VII: Absorption spectra (\( \lambda_{max} \)) molar extinction coefficient (\( \varepsilon_{max} \)) and sensitization properties (Ref.)

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{max} ) (nm)</th>
<th>( \varepsilon_{max} )</th>
<th>Sensitization properties (Ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XVI</td>
<td>550</td>
<td>31,790</td>
<td>Not a sensitizer (66)</td>
</tr>
<tr>
<td>XVII</td>
<td>530</td>
<td>35,730</td>
<td>Sensitizer (67, 68)</td>
</tr>
<tr>
<td>XVII</td>
<td>480</td>
<td>43,030</td>
<td>Sensitizer (70)</td>
</tr>
<tr>
<td>XX</td>
<td>525</td>
<td>61,580</td>
<td>Sensitizer (71)</td>
</tr>
</tbody>
</table>

* Data from Ref. 69.
Fig. 5. Conformational energy map of XVIb

Fig. 6. Conformational energy map of XVIIb
Fig. 7. Conformational energy map of XVIIIb

Fig. 8. Conformational energy map of XIXb
Fig. 9. Conformational energy map of XXb

Fig. 10. Conformational energy map of XVIc
Fig. 11. Conformational energy map of XVIIc

Fig. 12. Conformational energy map of XVIIIc
Fig. 13. Conformational energy map of XIXc

Fig. 14. Conformational energy map of XXc
XVIIa: The lowest energy conformation for the dye XVIIa is the one in which the p-dimethylaminobenzene and the quinoline rings are twisted by 30° each in opposite directions with respect to the plane containing the central atoms. The energy barrier for the planar structure (ϕ = 0°, θ = 0°) is 3.39 kcal/mol. However, that for the structure in which the phenyl ring is in the same plane with the central atoms and only the quinoline ring is twisted (ϕ = 0°, θ = 30°) is only 0.11 kcal/mol, which can be overcome in solutions or crystal packing. A much higher rotational energy barrier (3.33 kcal/mol) is, however, involved for the quinoline ring to be in plane with the central atoms (ϕ = -30°, θ = 0°). The twisting of the quinoline ring is quite close to the reported crystallographic value of 23.7° and 22.8° for 1,1'-diethyl-2,2'-cyanine iodide. This twisting may be due to a steric interaction between H(C10) and H(C13) (the interatomic distances are 1.78 and 2.09 Å for the planar and the non-planar structures respectively). The low energy rotational barrier for the nonplanarity of the phenyl ring is perhaps due to a weak interaction between H(C3) and H(C11).

XVIIIa: Dye XVIIIa is expected to show conformational characteristics very close to those of dye XVIa derived from quinoline-4. The heterocyclic pyridine ring in XVIIIa is, however, twisted to a greater extent in its most stable conformation (θ = 150°), which has 4.66 kcal/mol less energy than
the planar ($\phi = 0^\circ$, $\theta = 0^\circ$) conformation. This again must be due to steric interaction between $H(C10)$ and $H(C13)$. The interatomic distance increases from 1.69 Å in the planar to 4.47 Å in the nonplanar structure. The phenyl ring is twisted by an angle of 30° involving a small energy barrier with respect to this ring being in plane with the central atoms ($\phi = 0^\circ$, $\theta = 150^\circ$). This is possibly due to a weak interaction between $H(C3)$ and $H(C11)$. The energy barrier for the pyridine ring to be coplanar with the central atoms ($\phi = 30^\circ$, $\theta = 0^\circ$) is 4.61 kcal/mol. The energy for the conformation, which is identical to that of dye XVIa ($\phi = 30^\circ$, $\theta = 120^\circ$) is 2.4 kcal/mol higher. This could be due to the benzosubstitution in XVIa and also because of the difference in N-substitution.

XIXa: Dye XIXa bears the same resemblance with dye XVIIa as XVIIIa bears with XVIa. The global minimum occurs at $\phi = 30^\circ$, $\theta = -60^\circ$, which is stabler than the planar structure ($\phi = 0^\circ$, $\theta = 0^\circ$) by 4.73 kcal/mol. Here again the $(0, -60)$ conformation is only of 0.04 kcal/mol higher energy while the $(30, 0)$ conformation has an energy barrier of 4.79 kcal/mol, thus indicating a strong steric interaction between $H(C10)$ and $H(C13)$ (the interatomic distance is increased from 1.83 Å in the planar conformation to 2.82 Å in the most stable conformation) and a weak interaction between $H(C3)$ and $H(C11)$. The conformation analogous to that of XVIIa ($\phi = -30^\circ$, $\theta = 30^\circ$) has 1.26 kcal/mol higher energy.
XXa: Although, theoretically the most stable conformation for XXa is found to be the one in which the phenyl and the benzothiazole rings are twisted out of the central plane by 30° each in opposite directions the energy barriers for the planar structure (\( \Phi = 0°, \Theta = 0° \)) or for the structures in which one of the rings is coplanar with the central atoms, are exceedingly low, as can be seen from Table-\( V \). XXa can therefore be thought of as existing more or less in a planar structure. This is understandable because as in case of the other four dyes the interaction between H(C3) and H(C11) is weak, while, there is no ortho hydrogen in benzothiazole ring corresponding to H(C13), to interact with H(C10). The planar conformation of dye XXa is in conformity with all the earlier crystallographic findings on benzothiazole cyanine iodides. The above conclusions may be summarized by stating that the heterocyclic rings in XXa - XIXa are twisted with high rotational energy barriers. Although in the theoretically most stable structures of these molecules, the phenyl ring is twisted by 30°, the energy barriers for the coplanar conformation are very small, so that for all practical purposes, the phenyl ring may be taken to be lying in the same plane as that bearing the central atoms. Again, from energy considerations, XXa may be considered to be planar. The twisting of the heterocyclic rings is possibly due to steric interaction between one of the chain hydrogens and the ortho hydrogen of the heterocyclic ring, a phenomenon similar to stilbenes and benzylideneanilines.
Conformation of α-aza Styryl Dyes (XVIb - XXb):

XVIb: The most stable structure for XVIb has been found to be the one in which the phenyl ring is twisted by an angle 30° in either directions and the heterocyclic moiety is coplanar with the central atoms (C4 - N - C11 - C12) with the 10 - 11 and 12 - 13 bonds trans to each other (φ = 30°, θ = 180°). The twisting of the phenyl ring is possibly due to an interaction between H(C3) and H(C11). That this interaction is weak is evident from the fact that the (0°, 180°) conformation is only of 0.9 kcal/mol higher energy. The trans arrangement of the heterocyclic ring possibly releases the H(C11) and H(C18) interaction. The cis 10-11 and 12-13 conformation has a relatively high energy barrier of 2.3 kcal/mol. The interatomic distances H(C11) - H(C18) which are 3.73 and 2.0 Å in the trans and cis respectively bear out this possibility.

XVIIib: In the most stable structure of XVIIib, both the phenyl and the quinoline rings are out of the (C4-N-C11-C12) plane by 30° in opposite directions. Here again the twisting of the phenyl ring is due possibly to H(C3) and H(C11) interaction with a low energy barrier of 0.83 kcal/mol. The nearly cis 10-11 and 12-13 bonds can perhaps be explained in terms of the release of H(C11) and one of the H(C23) interaction.
XVIIIb: As expected, dye XVIIIb has conformational characteristics similar to those of dye XVIb derived from quinoline-4. The twisting of the phenyl ring by 30° in either directions may be due to a weak steric interaction between H(C3) and H(C11), which is indicated by the fact that (0°, 180°) conformation is only of 0.92 kcal/mol higher energy.

XIXb: The conformational characteristics of XIXb are similar to XVIIb. In its most stable conformation, both the phenyl and the pyridine rings are twisted by 30° each in opposite directions with respect to the plane containing the central atoms. Here also H(C3) and H(C11) interaction results in a twisting of the phenyl ring with an energy barrier of 0.67 kcal/mol.

XXb: The lowest energy conformation for dye XXb is the one, in which the phenyl ring is twisted by an angle 30° whereas the heterocyclic ring is coplanar with the central atoms. The twisting of the phenyl ring is possibly due to the weak interaction between H(C3) and H(C11) as in case of other dyes.

In the systems discussed above, orthohydrogen interaction is the only operating factor. The CT-2 interaction (here the interaction between the N lone pair electrons in the bridge portion and the pi-electrons in the phenyl ring) is not likely to operate to any appreciable extent.
Conformation of β-aza Styryl Dyes, (XVIc - XXc):

XVIc: The lowest energy conformation for dye XVIc is the one in which the phenyl ring is in the same plane with the central atoms and the heterocyclic quinoline ring is twisted ($\phi = 0^\circ$, $\theta = -120^\circ$) with an appreciable energy barrier of 6.7 kcal/mol. The $0^\circ$, $120^\circ$ conformation is almost isoenergetic (0.03 kcal/mol higher energy). Evidently in XVIc, there is a strong possibility of an intramolecular charge-transfer interaction between the bridge nitrogen lone pair and the heterocyclic ring (CT-2). Now the question is what are the relative contributions of the two factors - release of ortho-hydrogen interaction between H(C10) and H(C13) on one hand and CT-2 on the other, towards the twisted conformation of the molecule. Although the twist of the heterocyclic ring in the corresponding styryl dye (XVIa, X = CH = Y) is also $120^\circ$, the energy barrier with respect to the structure, in which the quinoline ring is planar, is only 1.05 kcal/mol, while in case of XVIc it is 6.7 kcal/mol. Since orthohydrogen interaction is only possible operating factor in case of the styryl dye, it seems there is a significant contribution of CT-2 towards the nonplanar conformation of XVIc.

XVIIc: Dye XVIIc, in its most stable conformation ($\phi = 0^\circ$, $\theta = 90^\circ$), is stabler than the planar structure by 3.55 kcal/mol. Here again the ortho hydrogen interaction between H(C10) and
H(C13) and CT-2 interaction are relieved by the nonplanar structure. The energy barrier for \{(-30^\circ), 0^\circ\} (the most stable conformation corresponds to \(\Phi = -30^\circ\) and \(\Theta = 30^\circ\)) conformation of the styryl dye XVIIa \((X = CH = Y)\) is 3.33 kcal/mol which is comparable to that of XVIIc. However, the much larger angle \((90^\circ)\) in XVIIc indicates a significant contribution of CT-2, since the contribution of CT-2 towards the stabilization of the molecule is increased with increasing twist angle\(^{19}\).

XVIIIC: The conformational results of XVIIIC are similar to those of XVIc. Both the energy barrier and the twist angle for the planar structure \((0^\circ, 180^\circ\) conformation) are greater than those of the corresponding styryl dye, suggesting a substantial contribution of CT-2.

XIXC: XIXc is expected to show conformational characteristics similar to those of XVIIIC particularly vis-a-vis their dimethine styryl analogue \((X = CH = Y)\). But the twist of the heterocyclic pyridine ring is same \((60^\circ)\) in both XIXc and its styryl analogue. The energy barrier for the planar structure in XIXc \((3.23\ \text{kcal/mol})\) is also less than that for XIXa \((X = CH = Y, 4.73\ \text{kcal/mol})\) for the conformation \((\Phi = 30^\circ, \Theta = 0^\circ)\). These results suggest the deviation of pyridine ring from coplanarity is essentially due to interaction between H(C10) and H(C13) and CT-2 factor is relatively insignificant.
This situation may arise, when the contribution of the quinonoid structure throughout the whole molecule (CT-1 effect) is significant\textsuperscript{19}, particularly in the bridge portions, in the resonance forms.

The difference in the conformations of XVIIc and XIXc is evidently due to the benzosubstitution in XVIIc and also because of the difference in N-substitution. It is, however, difficult to say why this is not reflected in XVIc and XVIIIc. Besides, the conformation of XIXc, which is same as that of XVIIc, i.e., $\Phi = 0^\circ$, $\Theta = 90^\circ$ is only of 0.85 kcal/mol higher energy. Hence our earlier explanation about the operation of CT-1 and CT-2 should be viewed with caution and not carried too far.

**XXc:** Conformational results of dye XXc shows that the $0^\circ$ $90^\circ$ conformation is the most stable structure and is stabler than the planar structure by an amount of energy 2.98 kcal/mol. Here again both, the energy barrier and the twist angle for the planar structure are very much greater than those of the corresponding styryl analogue XXa ($X = CH = Y$), indicating a significant contribution of CT-2.

The above results may be summarised as following. The $\alpha$-aza styryl dyes derived from quinoline-4, pyridine-4 and benzothiazole are nearly planar; although in the theoretically most stable structures the phenyl ring is twisted by 30$^\circ$ (due
to a weak interaction between the methin hydrogen atom and one of the ortho hydrogen of the phenyl ring), the energy barriers for the coplanar conformation are very small, and energy difference of this magnitude may easily arise from the stabilization due to preferred packing arrangement in the crystal. Hence for all practical purposes, the phenyl ring may be taken to be lying in the same plane as that bearing the central atoms. Dyes XVIIb and XIXb are, however, relatively more strained with both, the phenyl and the heterocyclic rings twisted out of plane by 30° with energy barriers 2.8 and 2.7 kcal/mol respectively with respect to the planar structure. In the β-azastryyl dyes the phenyl ring is coplanar with the central atoms; while there is a substantial twist of the heterocyclic ring with appreciable energy barrier. This situation may be due to the reinforcement of both the factors known to be responsible for the nonplanarity of the benzylideneanilines - the repulsive interaction of the ortho hydrogen and the overlap of the bridge nitrogen lone pair with the π-system of the heterocyclic ring.

Effect on Sensitization and Spectra:

Table-VII describes longest wavelength absorption, the molar extinction coefficient (ε) and photographic sensitization properties of the dyes. A connection between the extent of noncoplanarity and decreased intensity of absorption for dyes XVIa - XXa is
evident. The same is true in case of their sensitization properties since it has been established that nonplanar dyes are nonsensitizers\(^\text{34}\).

The \(\alpha\)-aza styryl ethiodides from quinoline-4 (XVI\(b\)) and benzothiazole (XX\(b\)) have been reported to be powerful desensitizers\(^{63,64}\). Like the sensitizing action, strong adsorption of the dye to the silver halide is an important factor in desensitization, which, in turn, will depend upon the planarity of the dye. Since sensitization and desensitization appear to be complementary properties\(^{65}\), it may be concluded that planarity is also an important criterion for desensitization. The desensitizing action of XVI\(b\) and XX\(b\) are thus in conformity with the present results, as much as correspondence between the sensitization property and the extent of coplanarity obtained from PCIL\(O\) method for the styryl dyes (XVI\(a\) - XX\(a\), \(X = \text{CH} = Y\)). The longest wavelength of absorptions, described in Table-\(VII\), are known to arise due to a \(\pi \rightarrow \pi^*\) transition. It is seen that a replacement of -\(\text{CH}=\) adjacent to phenyl ring by -\(\text{N}=\), causes a bathochromic shift. One of the factors contributing to this phenomenon may be an increased planarity in going from the styryl dyes to aza analogues; since it is quite well known that nonplanarity causes a reduction in overlap with the adjacent p-orbital, which, in turn, will affect the wavelength of absorption.