A Molecular Orbital Approach to Molecular Design

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GOALS
The project goal is two fold: 1) To demonstrate the utility of molecular orbital (MO) theory as a viable approach to designing state-of-the-art dyes, fibers and chemical auxiliaries that will enhance the competitiveness of the U.S. textile industry; and (2) to pool the heretofore individual efforts and knowledge of several NTC investigators interested in the use of MO-based computational chemistry, to jointly set in place a fundamental approach to the design of a variety of organic compounds of commercial importance to the textile industry.

ABSTRACT
Rigorous testing of many commercial and experimental dyes and a number of polymeric systems has facilitated the development of MO-based methodologies for the design of novel organic materials. Although the prediction of multiple properties of organic compounds using a single semi-empirical modeling system is not feasible with models currently available, optimum results can be achieved by employing a model that has been developed to predict a specific chemical or physical property. For azo dyes, the semi-empirical method AM1 is preferred for geometry prediction, and a geometry optimization methodology has been developed. PISYSTEM is the best method for prediction of hue and color strength of azo, anthraquinone, diarylide, and cyanine dyes and pigments. Models based on Newtonian mechanics (MM2) are preferred for the modeling of polyatomic systems, including interactions between polymer chains. Semi-empirical MO models (AM1) are useful for the prediction of polymer properties only when local interactions are considered. AM1 was used to predict the torsional potentials for biphenyl analogs of PBO and PBZT. In this case, calculations using the AM1 Hamiltonian provided predictions of single chain stress-strain curves for axial tension and compression, and provided the basis for the design and synthesis of monomers for new PBO and PBZT analogs. Molecular mechanics was used to calculate solubility parameters and thermodynamics of mixing for organic compounds evaluated as model systems for promoting dissolution of PET trimer as a basis for preventing machine fouling during pressure dyeing of PET fiber.

INTRODUCTION
The development of a common systematic methodology for the design of dyes, fibers and auxiliary chemicals would provide a unified ‘language’ for industrial and academic textile scientists working in these areas. The benefits of such an approach would include a reduction of the number of organic compounds requiring synthesis before a commercial product is derived, thereby providing more efficient use of R&D resources.

One approach to the development of such a methodology is to utilize the recent advancements in computational chemistry as a predictive tool in the molecular design process. Over the past year, research in our laboratories has focused on determining the scope and limitations of hardware and MO software that preclude prohibitive costs but meet the demands of the quantum mechanical calculations required for complex organic compounds. Until very recently (i.e. within the last three years), quantum mechanical methods based on theory alone, for example
**ab initio and** density functional theory (DFT), **required** exorbitantly expensive hardware and software. Semi-empirical methods, however, while being less **theoretically** pure, simply **require** the use of a high powered desk top computer, and the basic **software** needed is available at relatively low cost. Hence, semi-empirical MO **modeling** at the present time offers a good **compromise** between **predictive** accuracy and cost and efficient use of computer time. Rigorous testing of many commercial and experimental textile dyes, polymers and various chemical agents has enabled the development of methodologies for **predicting** key **properties** of organic compounds that are essential to the textile industry. **Ideally,** a single MO method would be derived that could be employed as a molecular design tool by organic, physical and polymer textile chemists alike. However, results from our studies over the past year have shown that such a method has not **been** perfected at the **semi-empirical** level. Rather, it has been found that optimum **results** are **produced** by employing a model that has been developed to **predict** a specific chemical or physical property. Thus, a combination of selective **parameterization** and development of a systematic approach to predict a specific property of a particular chemical class (e.g. azo dyes), or even chemical sub class (e.g. heterocyclic azo dyes), **currently** is the most reliable approach. MO methods have been developed in our laboratories that **predict** to a good level of accuracy:

(a) a minimum energy geometry of common azo and nitro diphenylamine disperse dyes,
(b) hue, color strength, UV **absorption**, and transition dipoles of most dye classes,
(c) solubilities of common azo and anthraquinone dyes,
(d) a minimum energy geometry of PBO, PBZT and selected analogs,
(e) stress/strain data for PBO, PBZT and selected analogs,
(f) thermodynamics of mixing for binary mixtures of solvents and PET trimer.

**Progress** in the last 12 months has culminated in four publications [1-4]. The present report contains examples of some of the more interesting method developments **during** the last twelve months, and is supplemental to the 1995 annual report.

**Computations**

For modeling dyes, two molecular modeling systems were used. PISYSTEM, which is based upon the **π** only SCF MO **approach** of Parker, Parr and **Pople** (PPP) was executed on a 133 MHz Pentium-based P.C. system with 16MB of RAM. Atoms contributing to the **π** system of the dye are entered into a graphical editor, which then subjects the structure to a 2-D geometry optimization **routine** before the PPP SCF calculation is started. This is a fast process, normally **requiring** less than 60 seconds on our Pentium processor. Spectroscopic predictions were made based upon the results of a limited **configuration** interaction calculation involving the 36 lowest energy singly **excited** configurations.

**CAChe** Worlcsystem (Oxford Molecular) running on an Apple Macintosh Quadra 950 equipped with a 40 MHz CXP RISC coprocessor card, 64 MB RAM, and a 3-D stereoscopic monitor was used for the remaining dye calculations. **CAChe** implementations of MOPAC 6.0 and ZINDO were used for all-valence **electron** quantum mechanical calculations.

Geometry optimizations of dye **structures** were effected using a mechanical force field (Augmented MM2) to obtain a tough geometry, followed by the use of one of the quantum mechanical methods implemented in MOPAC (MNDO, MINDO/3, AM1, PM3) or ZINDO (CND0/1, CNDO/2, INDO/1, INDO/2). Normally an Eigenvector Following energy **minimizer** **routine** was employed, and the structure was deemed to be a minima when the conjugate gradient value fell below 2. In the case of ZINDO calculations, the Newton-Raphson **minimizer** was used,
unless convergence problems were encountered, in which case an Augmented Hessian converger was employed.

Spectroscopic data for all-valence electron studies involving dyes were obtained from the ZINDO package, using INDO/S parameters and in a configuration interaction computation of the first 81 singlet configurations.

For modeling polymers, MOPAC was utilized using BIOSYM software on silicon graphics workstation. AM1 calculations were employed for all geometry optimizations and for the prediction of stress-strain curves.

For modeling the solubility of PET trimer in various solvents, molecular mechanics was utilized using BIOSYM and Cerius 11 software on a Silicon Graphics computer.

Dyes

Geometry Optimization

The most effective method for optimizing the structure of azo and nitrodiphenylamine dyes is to use a mechanical method (MM2) followed by the AM1 or PM3 semi-empirical method. Earlier methods such as MINDO/3 and MNDG compromised the planarity of the structure, and often omitted hydrogen bonding interactions essential to the stability of the chromophore. Prior to optimization, it has been found that a number of routine adjustments to the initial planar starting geometry of azo dyes facilitates faster and more accurate prediction of a minimum energy geometry. Examples of such adjustments are outlined below.

Routine Geometry Adjustments Prior to Optimization

The outcome of geometry optimizations are highly dependent upon the starting geometry. Consequently, an optimized methodology for azo dyes includes a number of routine manual adjustments that can be made to the dye structure, to give better final, optimized geometries.

a) treatment of amino donor groups

If the alkyl chains of amino donor groups in aminoazobenzene-based dyes are co-planar in the starting structure, in most cases the optimizer will retain this co-planarity, at the cost of pyramidalization of the amino nitrogen in order to relieve steric strain. A lower energy final structure is returned if one of the alkyl groups is rotated out of plane before the optimizer is started, as shown in Figure 1. The energy difference between the two rotomers is of the order of 10 kcal mol$^{-1}$.

![Figure 1](image)

(a) Adjustment of pendant side chains from (a) to (b) to generate a good starting conformer for geometry optimizations.

b) treatment of substituents in azo dyes

In the case of azo dyes possessing a substituent ortho to the azo moiety, lower energy structures are returned from the optimizer if the geometry of the substituent is adjusted such that it
is situated in line with the direction of the lone pair of the α-azo nitrogen. In this way, steric repulsion between the substituent and the lone pair electrons on the β-azo nitrogen is avoided (Figure 2). An exception to this manual adjustment rule occurs when the ortho substituent is an acylamido group, which forms an intramolecular hydrogen bond with the β-azo nitrogen atom.

In the case of heterocyclic azo dyes, the situation is further complicated by lone pair orbitals of the heteroatoms steric interactions with the azo group lone pair orbitals (Figure 2). If the wrong (strained) isomer is used as the starting structure, then it is possible that the optimizer will attempt to relieve the strain in the molecule by compromising molecular planarity.

![Figure 2](image)

Figure 2 Adjustment of azo dye conformation before optimization to relieve unfavorable lone pair orbital interactions involving heterocyclic azobenzenes (left) and ortho-substituted azobenzenes (right)

**Spectroscopic Predictions**

The position and intensity of the longest wavelength absorption band of a dye are two of the most important properties associated with a commercial dye. The most reliable semi-empirical method for predicting color and the extinction coefficient is the PPP molecular orbital method. However, there are shortcomings to the original PPP method, most notably its inability to accommodate non-planar systems. Thus, alternative semi-empirical methods, such as the INDO/S method, were investigated for predicting spectroscopic data. For simple cyanine and polyene dyes, the INDO/S method gave excellent correlation with experimentally determined values [1]. However, in cases such as azo dyes, the PPP SCF CI method outperformed the INDO/S method. Despite advances and refinements incorporated into more recent spectroscopic MO methods (e.g. INDO/S), our studies showed that PPP SCF MO methods generally provide more accurate predictions. However, the PPP method is restricted in that no consideration is given to d-orbitals, and also the atomic parameters available for the PPP method do not include transition metals. Due to the commercial importance of transition metal-complexed dye molecules in textiles, INDO/S remains an important parameter set for spectroscopic predictions involving these compounds.

**Position of maximum absorption band**

Dye structures la-h were optimized in MOPAC (AM1) according to the protocols described above. These structures were then fed into ZINDO for configuration interaction calculations, to predict the position of the longest wavelength absorption band (lambda max). Structures la-h were also fed into the graphical interface of PISYSTEM, which performed a 2-D geometry optimization. A PPP SCF CI calculation was then used to generate absorption maxima. In all cases, the wavelength recorded was that corresponding to the first allowed transition. The results are displayed in Figure 3.

Although the data in Figure 3 suggest that there is a correlation between the observed absorption maximum and that predicted by the INDO/S method (coefficient of determination \(R^2=0.79\), the wavelength predictions were too hypsochromic to be useful. The PPP method provided a good correlation, with a coefficient of determination of 0.86. These results are consistent with experimental data reported in the literature.
Quantum mechanical calculations can be used to assess the probability of a light absorption event occurring by estimation of the transition dipole moment, \( \mathbf{M} \). The oscillator strength is proportional to \( \mathbf{M}^2 \) multiplied by the average frequency, \( \nu \), of the light being absorbed. Spectroscopists wishing to characterize a colored substance record the extinction coefficient of a dye. While this particular quantity is difficult to predict from the oscillator strength without knowledge of the shape of the absorption curve, this is the form most published spectroscopic data take. The INDO/S method gives a value for the transition dipole moment for the longest wavelength allowed transition, and from this, a value proportional to the oscillator strength is calculated using the frequency of light corresponding to the transition, also calculated using the INDO/S method. PISYSTEM predicts a value for the oscillator strength directly. Figure 3 displays the \( r^2 \) values for the oscillator strengths of dyes \( la-h \) for both INDO/S and PPP when compared with experimental \( \varepsilon \) max. Although it appears from the data that the INDO/S oscillator strengths correlate with the experimental values, if the outlying point due to structure 2f is removed from the data set, the graph turns into almost random scatter, and the \( r^2 \) value drops from 0.8625 to 0.621. In the case of values predicted by the PPP method, removal of the two outlying points due to structures 1f and 1h increased the coefficient of determination to 0.971.

It is not altogether surprising that the PPP method surpasses the INDO/S method for the prediction of lambda max as the atomic and bond parameters used in the former method are not generalized. Different electronic configurations, and oxidation states of the same atom are given different parameters, and these parameters have been refined many times to reproduce the spectra of moderately sized dye structures. The INDO/S method, on the other hand, uses generalized atomic parameters, which are derived from spectroscopic data from small molecules or \textit{ab initio} calculations. Thus, one might expect that the INDO/S method would be applicable to a more diverse range of compounds than the PPP method. The PPP method, however, can be used as a
highly specialized tool for predicting the absorption maximum of moderately sized, non-metallized dyes.

In addition to the spectroscopic properties discussed above, semi-empirical methods have been used to model and visualize thermal activation processes such as proton transfer events in photoexcited nitrodiphenylamines, hydroxybenzotriazoles and hydroxybenzophenones, by plotting potential hypersurfaces of the ground and photoexcited states of dye and photostabilizer structures. Photochemical investigations in progress involve modeling azo dyes which have been shown to photoisomerize readily. INDO/S is the preferred method for predicting such properties, since the PPP SCF MO method cannot be utilized in this way at the present time.

**Polymers**

Prediction of stress-strain curves for PBO and PBZT

Molecular modeling was used to predict the torsional potentials for the biphenyl analogs of PBO and PBZT shown in Figure 4. AM1 was used to calculate single chain stress-strain curves for axial tension and compression. After an equilibrium geometry was calculated, the translation vector representation for the polymer chain was allowed to vary, thereby representing tensile or compressive strain, and the resulting geometry was optimized. In this way, the relationship between heat of formation and molecular strain was determined by rotation of the dihedral angle at the biphenyl linkage, and prediction of heat of formation at each conformation, as shown in Figures 5 and 6. As a result of these calculations, two biphenyl analogs of PBZT have been synthesized for 3-D crosslinking studies. The derivatives synthesized were ortho-ortho’-dinitro, dimethyl PBZT and ortho-ortho’-tetramethyl PBZT. Groups in the ortho-ortho’-positions of the biphenyl moiety increase the energy barrier to rotation for low energy noncoplanar conformations and also increase the probability of forming thre-dimensional cross-links on heating.

Experimental analogs of PBZT and PBO modeled using AM1.

It is well known that high performance fibers such as poly(1,4-phenylene terephthalamide and poly(p-phenylene-2,6-benzobisthiazole) have compressive strengths which are an order of magnitude less than their tensile strengths. Attempts to improve the compressive properties of PBZT by thermally cross-linking poly(2-chloro-1,4-phenylene terephthalamide) were unsuccessful
Figure 5  Graph of heat of formation versus dihedral angle for compounds M1-MS

Graph of heat of formation versus dihedral angle for compounds M6-M10

because of the formation of one-dimensional cross-linked materials. Preliminary MO calculations on 2,2',6,6'-tetramethyl biphenyl analogs of PBO and PBZT indicate that the benzene rings would preferentially adopt a noncoplanar conformation which would be ideal for 3-D cross-linking. We believe that 3-D cross-linking in a relatively strain-free system will lead to substantially improved compressive properties. Improvements in the optical and electronic properties are expected as well for these modified polymers. The synthesis of poly(p-2,2'-dinitro-6,6'-dimethylbiphenylene bisbenzthiazole) is described elsewhere [5]. However, a brief summary of the synthesis of the tetramethyl analog is presented below.

Polymer Synthesis

The required monomers include 2,5-diamino-1,4-benzenedithiol dihydrochloride, which was prepared as described by Wolfe [5], and 2,2',6,6'-tetramethylbiphenyl-4,4'-dicarboxyl chloride. The latter was prepared in three steps: 1) Oxidation of mesitylene (1,3,5-trimethylbenzene) with
ferric chloride at room temperature, yielding 28% of chloromesitylene, 30-38% of bimesityl (2,2',4,4',6,6'-hexamethylbiphenyl), and small quantities of oligomer, with bimesityl being separated from the mixture by a reduced fractional distillation and further purified by recrystallization from acetone, 2) further oxidation using molecular oxygen to give a mixture of the biphenyl para monoacid and the biphenyl 4,4'-diacid, with separation of biphenyl monoacid and biphenyl diacid achieved by dissolving the mixture in diethyl ether and extracting the solution with 5% aqueous sodium bicarbonate, followed by precipitating the diacid with HCl solution, and 3) formation of the diacid chloride using SO₂Cl₂.

Polycondensation reactions (including copolymerization) were carried out in PPA, as shown in Scheme 1. A solid content of 16 - 28% by weight was employed. Final concentrations of the solutions were designed as 15 wt. % and 10 wt. % of polymers, respectively. A nematic liquid crystalline phase was observed while the polymerization reaction was conducted. The 10 wt. % polymer solutions were found to be more appropriate for fiber spinning than those having higher concentrations, since the former are more homogenous and have less defects.

\[
\begin{align*}
\text{CH}_2\text{N} & \quad \text{SH} \\
\text{HS} & \quad \text{NH}_2\text{Cl} \\
\end{align*}
\]

\[
\begin{align*}
(1-n) \text{ClOOC} & \quad \text{COCl} \\
\text{nClOOC} & \quad \text{COCl} \\
\end{align*}
\]

\[
\begin{align*}
\text{PPA} \\
\end{align*}
\]

![Scheme 1](image.png)

Synthesis of tetramethylbiphenyl analog of PBZT.

**Thermal Properties of Polymers**

The tetramethylbiphenyl-based polymers began to degrade at 500 °C, 100 °C lower than the degradation temperature of parent PBZT. The polymers exhibited two degradation temperatures, one at 500 °C and the other at 900 °C. The low degradation temperature has been attributed to methyl decomposition, using the TG-Mass spectroscopy. Once the methyl groups degrade at 500 °C, cross-linking reaction occurs between the polymer chains, due to radical species produced from the fragments of methyl groups. Thus, cross-linking resulted in an increase in degradation temperature of the polymer backbone. Furthermore, the cross-linked structure caused an 80% weight retention at 900 °C.

So far, as a result of modeling studies using the AM1 parameterization, several fibers have been produced from the tetramethylbiphenyl PBZT dope by a dry-jet wet spinning. Morphology and structure-property relationships will be investigated, to confirm the viability of the modeling studies.

**Surface-Active Agents**

The accumulation of oligomer from PET fiber during the pressure dyeing process is known to be detrimental to uniform dyeing and also leads to frequent equipment servicing. Consequently, the initial objective of this work is to identify surfactant systems which will promote dissolution and micellar solubilization of PET oligomers and to prevent redeposition or nucleation of oligomer on the fiber and process machinery surfaces.
Two different approaches have been used to investigate the solubility of the cyclic trimer in different solvent solvent models. The first approach involved calculating the solubility parameter (δ) using bulk atomistic simulations on 3-D models under periodic boundary conditions. System energies were obtained by averaging results from 10 individual dynamics calculations for each system. Table 1 contains some of the initial results for the predicted (calculated) δ value of selected halogen and oxygen-containing solvents, the cyclic trimer, and PET along with the literature value. The calculated values were in good agreement with those reported in the literature. The calculated solubility parameter for the cyclic trimer was found to be significantly larger than that for amorphous PET. This is in agreement with experimental data since the cyclic trimer is known to phase separate from PET. Trichlorobenzene, known to be useful as a carrier in atmospheric dyeing of PET, afforded a predicted solubility parameter very close to that predicted for PET.

Table 1. Calculated and experimental δ values for model compounds.

<table>
<thead>
<tr>
<th>System</th>
<th>δ (Predicted, 25°) (cal/cm³)^(1/2)</th>
<th>δ (Experimental, 25°) (cal/cm³)^(1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchloroethylene</td>
<td>10.6</td>
<td>9.3</td>
</tr>
<tr>
<td>Chloroform</td>
<td>11.3</td>
<td>9.3</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>11.1</td>
<td>9.7</td>
</tr>
<tr>
<td>Dioxane</td>
<td>9.4</td>
<td>10.0</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>10.1</td>
<td>---</td>
</tr>
<tr>
<td>Water</td>
<td>24.3</td>
<td>23.4</td>
</tr>
<tr>
<td>PET (amorphous)</td>
<td>11.0</td>
<td>10.7</td>
</tr>
<tr>
<td>Cyclic Trimer</td>
<td>15.0</td>
<td>---</td>
</tr>
</tbody>
</table>

The second approach used to investigate the solubility of the cyclic trimer involved calculating the thermodynamics of mixing for binary mixtures of selected compounds and cyclic trimer. This calculation, based on a modified (off lattice) Flory-Huggins model, uses a Monte Carlo atomistic simulation to generate different molecular orientations of the molecules employed, and molecular mechanics minimization techniques were then used to calculate the pair interaction energies between molecules. Based on these calculations, compounds found to be miscible with the cyclic trimer between 25°C and 100°C are ethylene glycol, diethylene glycol, propanediol, dioxane, para-(2-hydroxyethyl)toluene, perchoroethylene, perchoroethane, perfluorooctane, 1,1,2-trichlorotrifluoroethane and hexafluoropropylsilanol, while compounds predicted to be immiscible with the cyclic trimer in the same temperature range included ethanol, methanol, phenol, ethylene glycol dimethyl ether, benzene, toluene, naphthalene, trichlorobenzene, silicone, and PET.

Data arising from the thermodynamics of mixing approach were found to agree much better with experimental solubility data than those determined using the solubility parameter approach. For instance, the solubility parameter calculation predicts that the cyclic oligomer should not be very soluble in perchloroethylene, chloroform, methylene chloride and dioxane even through these solvents have been found to dissolve oligomer, while thermodynamics calculations predict these solubilities correctly, and also correctly predict that the cyclic oligomer should phase separate from PET. In addition, the thermodynamics of mixing calculations were found to take less computer time per solvent system studied and to provide more information regarding interactions between the solute and solvent molecules. Consequently, further studies in this area will employ thermodynamics of mixing calculations.
CONCLUSIONS

Molecular modeling protocols have been established for optimizing the geometry of a number of dye classes, thus providing a solid basis for predicting properties such as hue, color strength, solubility, dyeing behavior and fastness. The PPP MO system is the most reliable methodology for predicting the hue and color strength of dyestuffs, despite the development of more theoretically rigorous methods such as INDO/S. The reason for this is likely to be the specialized parameter set that the PPP method utilizes in calculations. Methodologies are also in place for predicting dyestuff solubility.

MOPAC AM1 is the method of choice for localized geometry optimization of PBO and PBZT polymers, and their analogs. Stress-stress strain curves derived from AM1 energy predictions have facilitated the development of polymers that show promise as candidates with high compressibility.

MO calculations involving the thermodynamics of mixing for binary mixtures of solvents and PET trimer suggest that ether-group containing hydrophobes provide a logical "spring board" for the design of surfactant molecules promoting solubilization of PET oligomers.

The results of this investigation demonstrate the utility of MO-based modeling methods for predicting the chemical and physical properties of organic compounds of interest to textile chemists. Thus, in time, by following the requisite optimized method(s), the textile chemist who has limited experience in quantum theoretical models will be able to use an MO approach easily, and with a degree of confidence predict properties of experimental compounds.

FUTURE WORK

Methodologies currently used to predict molecular geometries, hue, color strength, solubility, and genotoxicity of organic dyes will undergo further refinement. In addition, a rigorous analysis of ab initio and DFT based calculations will be initiated on selected dyes, polymers and auxiliaries using recently acquired software and hardware. We are especially interested in modeling dye-fiber interactions and metal-complexed dyes.

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REFERENCES