

# **Computational Modeling of Physical Properties in Liquid Crystalline Polymer Systems**

Kevin D. Monajati

Advisor: Kenneth Marshall

Summer High School Research Program 2001

Laboratory for Laser Energetics

University of Rochester

## **Abstract:**

New software is available to aid in the modeling of liquid crystalline polymer systems. Oligomers with nine repeat units can be modeled successfully using MOPAC 2000. Programs have been written to aid in solving for the birefringence and dielectric anisotropy of the molecule, thus allowing all numerical analysis to take place on the UNIX platform. This numerical analysis will allow for a reduction in laboratory investigations with polymer synthesis.

## 1. Introduction

Between solid and liquid, there is a state of matter known as a liquid crystal. The properties exhibited by the molecules are very different from either solids or liquids. Because of the rod-like shape of these molecules, the values of their dielectric constants and refractive indices depends on their orientation to an electromagnetic field or light source, respectively (Fig. 1) . The maximum and minimum values of these two properties are found to be parallel and perpendicular to the molecular axis. The dielectric anisotropy is the difference between the maximum and minimum dielectric constants for the molecule, and the birefringence is the difference between the maximum and minimum refractive indices. These properties provide for many applications of liquid crystals in optical devices.

Liquid crystalline systems can be either main chain polymers or side chain polymers. Main chain polymers result when the mesogens are aligned head to tail in the polymer backbone, with spacers between each molecule normally made up of several alkyl groups. Side chain polymers are polymers attached to a backbone of made up of combinations of carbon, silicon and oxygen atoms or other repeating groups. Spacer groups, made up of chains of carbon atoms, are at the head of each mesogen, which attaches to the side of the backbone. Due to their structure, polymeric liquid crystals have advantages over single mesogens (Fig. 2). They are much more robust, and able to form freestanding films. However, because of the protrusion of the mesogens from the backbone, polymeric systems are much more viscous and thus have slower electro-optic response times.

The measurement of the properties of liquid crystals in the laboratory environment can be time-consuming and often inaccurate. Computer modeling has come to the forefront of the scientific world recently because (1) of its remarkable predictive ability, and (2) graphically

assembling molecules and evaluating their structure/property relationships computationally is much easier and less time-consuming than synthesizing compounds with every possible structural permutation and combination in the lab. With the advent of modern, high-speed, multi-processor machines and advanced software, calculations that previously took months can now be done in only a few hours. When compared to the time it may take to synthesize, purify and characterize a single sample of a new liquid crystal, the advantage is obvious.

## 2. Method

Candidate mesogens were first constructed graphically using Wavefunction, Inc.'s Spartan v.5.1.3, a computational chemistry software package running on a DEC Alpha Server under the UNIX operating system (Fig. 3). Merck energy minimization was performed before optimizing the geometry at 0° K using the AM1 semiempirical method and parameter set. Mesogenic groups were constructed and duplicated, and then attached to a carbon-carbon polymer backbone structure. The output file generated by Spartan was graphically viewed using the XMO visualizer (Fujitsu Ltd, Fig. 4), the polymer was checked for any possible errors, and any of these errors were corrected using Spartan if required. The corrected output file was imported into MOPAC 2000 (Schroedinger, Inc) for the polarizability calculations after viewing with XMO, and the resulting data was input into a C++ program that was used to calculate the dielectric anisotropy and birefringence of the candidate polymer.

### 2.1. Using MOPAC 2000 and XMO

MOPAC 2000 is designed to efficiently compute and analyze macromolecular structures in a short period of time. However, the program is entirely text-based and requires the use of external data files that cannot be edited from within the program. Hence the XMO viewer is

used to view the polymers and check for overall structural correctness before importing into MOPAC. XMO uses MOPAC 2000's algorithm for detecting bonding sites, but displays the molecule graphically, making it easy for the user to do error-checking. In order for MOPAC 2000 to understand what the user is requesting, a line of keywords is used at the beginning of a text file.

## 2.2. Using *deltaEdeltaN.cpp*

DeltaEdeltaN is a new C++ program developed during this project (K. Monajati) that allows the user to take data directly from either Spartan or MOPAC output files and enter it into the program. The C++ code does all of the calculations for the user, returning the values for the dielectric anisotropy and birefringence of the molecule. A sample output screen from the program can be found in Fig. 5.

### 2.3.1 Calculation of $\Delta\epsilon$

The dielectric anisotropy is calculated using the Maier – Meier theory, given by<sup>1</sup>

$$\Delta\epsilon = \frac{NFh}{\epsilon_0} \left( \Delta\alpha - \frac{F\mu^2}{3k_bT} (1 - 3\cos\beta) \right)$$

where

$$F = \frac{1}{(1 - f\alpha)}$$

$$f = \frac{\epsilon - 1}{2\pi\epsilon_0 a^3 (2\epsilon + 1)}$$

$$h = \frac{3\epsilon}{2\epsilon + 1}$$

and  $\epsilon_0$  is the permittivity of a vacuum,  $k_b$  is Boltzmann's constant, N is the molecular density, T is the absolute temperature,  $a$  is the radius of the spherical cavity surrounding the molecule,  $\mu$  is the magnitude of the dipole moment., and  $\beta$  is the angle made between the

director and the dipole moment. The values of N, and T, were taken to be 1000 kg/m<sup>3</sup> and 293° K, respectively. The static permittivity,  $\epsilon$ , is derived algebraically from the Onsager theorem<sup>1</sup>,

$$\epsilon - 1 = \frac{NFh}{\epsilon_0} \left( \alpha + \frac{F\mu^2}{3k_bT} \right)$$

where  $\alpha$  is the mean polarizability.

### 2.3.2 Calculation of $\Delta n$

The birefringence,  $\Delta n = n_e - n_o$ , was calculated from values from the Vuks equations<sup>1</sup>

$$\frac{n_e^2 - 1}{n^2 + 2} = \frac{N}{3\epsilon_0} \left( \alpha + \frac{2\Delta\alpha S}{3} \right)$$

$$\frac{n_o^2 - 1}{n^2 + 2} = \frac{N}{3\epsilon_0} \left( \alpha - \frac{\Delta\alpha S}{3} \right)$$

where S is the order parameter of the liquid crystal compounds (a value of 0.7 was assumed for all calculations). The Lorentz – Lorenz equation

$$\alpha = \frac{3\epsilon_0(\epsilon - 1)}{N(2\epsilon + 1)}$$

gives values for  $\epsilon$  at optical frequencies, where  $\epsilon = n^2$  as above.<sup>2</sup>

## 3. Modeling of Polymeric Systems

A total of 24 side-chain polymers were modeled to determine the properties of polymer mesogens with high  $\Delta\epsilon$ . However, only 20 models were successful, because MOPAC 2000 was unable to recognize the electronic configuration of nitrogen atom in the carbazole group (Fig 6) due to its aromatic structure. Other molecules that were modeled were made of three carbon spacers followed by either a benzene, naphthalene, or anthracene structure, followed by an ether group, and then another cyclic structure. This system allowed for a small  $\beta$ , giving the molecule a larger dipole. Although all of the 20 systems have been computationally modeled by

MOPAC 2000, data analysis and final calculations of  $\Delta\epsilon$  and  $\Delta n$  for these systems using deltaEdeltaN.cpp remains to be completed.

#### **4. Summary**

The use of computational modeling for prediction and analysis of polymeric systems is a valid method that can reduce laboratory time and increase accuracy. Experimental systems analyzed showed interesting trends, although final analysis still needs to be completed.

Although MOPAC 2000 shows great potential for prediction of structure/property relationships in macromolecules, great care must be taken to insure that the structures created represent valid compounds. The availability of XMO to visually error-check structures prior to processing in MOPAC 2000 is a significant improvement, and will be a great tool in the further investigation of larger liquid crystalline systems.

#### **5. Acknowledgements**

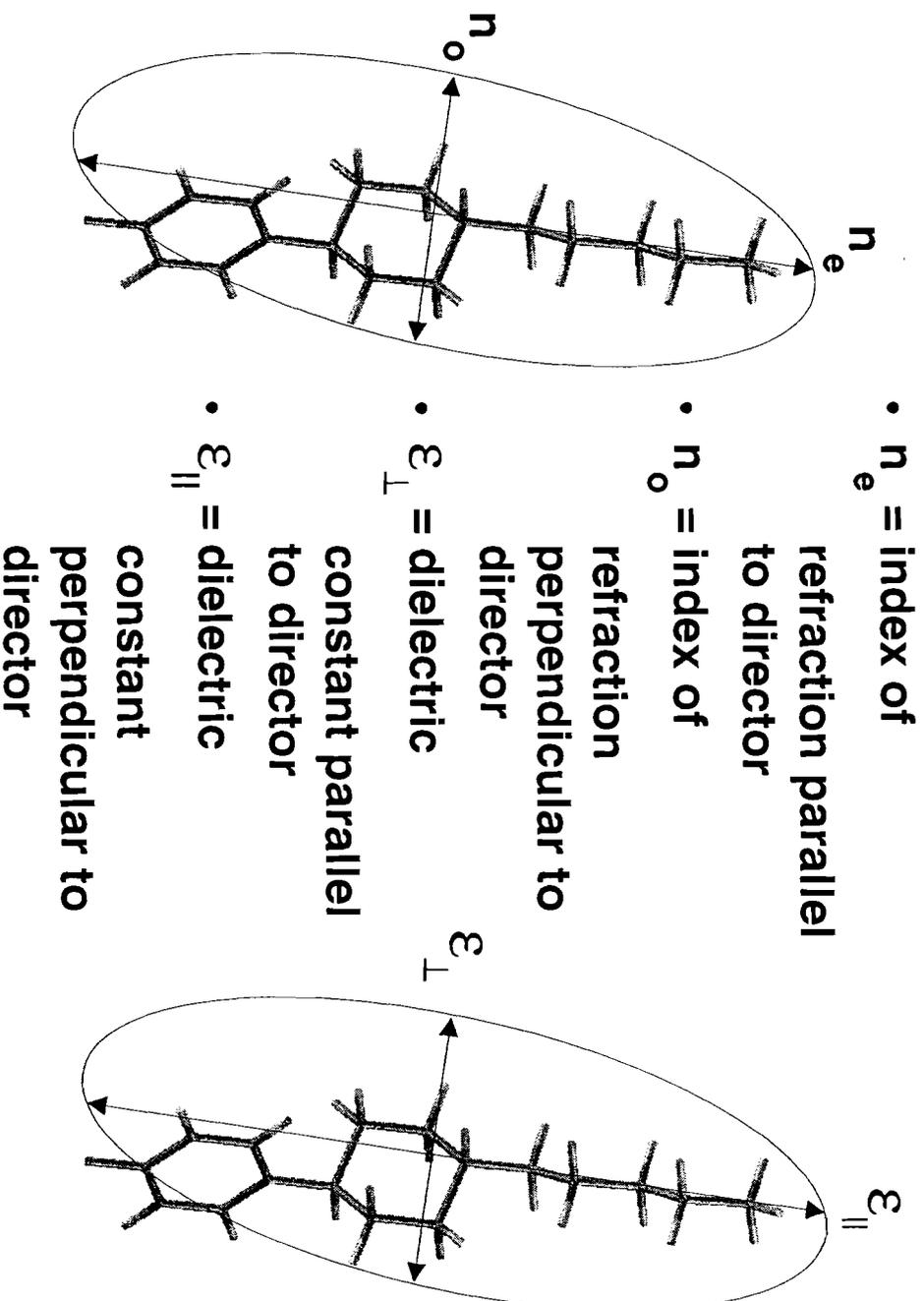
I would like to extend my sincerest thanks to Dr. R. Stephen Craxton for providing my fellow students and I the opportunity to conduct research over the summer. I would also like to thank my project advisor, Mr. Kenneth Marshall, for his help and guidance throughout my time at LLE. My thanks also go out to M. Gao, C. Piro, M. Fiedler, and other students who worked in the IAL with me. Finally, I would like to acknowledge L. Stein for his helpfulness in working me through the intricacies of the UNIX system.

References:

- 
1. M. Klasen, et al., "Calculation of Optical and Dielectric Anisotropy of Nematic Liquid Crystals." *Jpn. J. Appl. Phys.*, 37, 945 (1998).
  2. J. VanLare, "Predicting the Optical and Dielectric Anisotropy of Liquid Crystalline Systems," 1999 Summer Research Program for High School Juniors at the University of Rochester's Laboratory for Laser Energetics, Laboratory for Laser Energetics Report No. 311, NTIS document No. DOE/SF/19460-338 (1999).

Figure 1

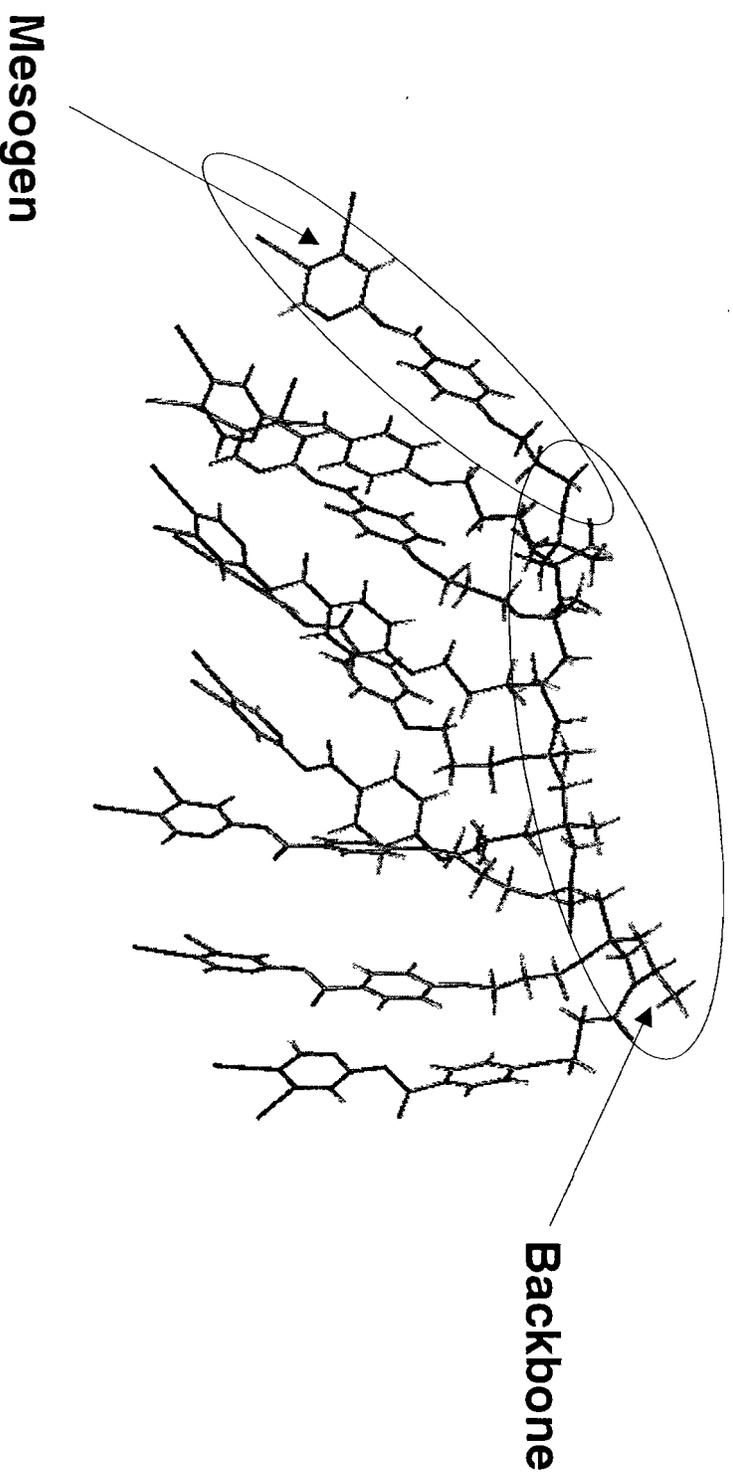
# LC mesogens have two dielectric constants and two indices of refraction



- Maximizing  $\Delta n$  and  $\Delta \epsilon$  is the aim of modeling LC polymers

Figure 2

## Liquid crystal (LC) polymers have basic structural similarities



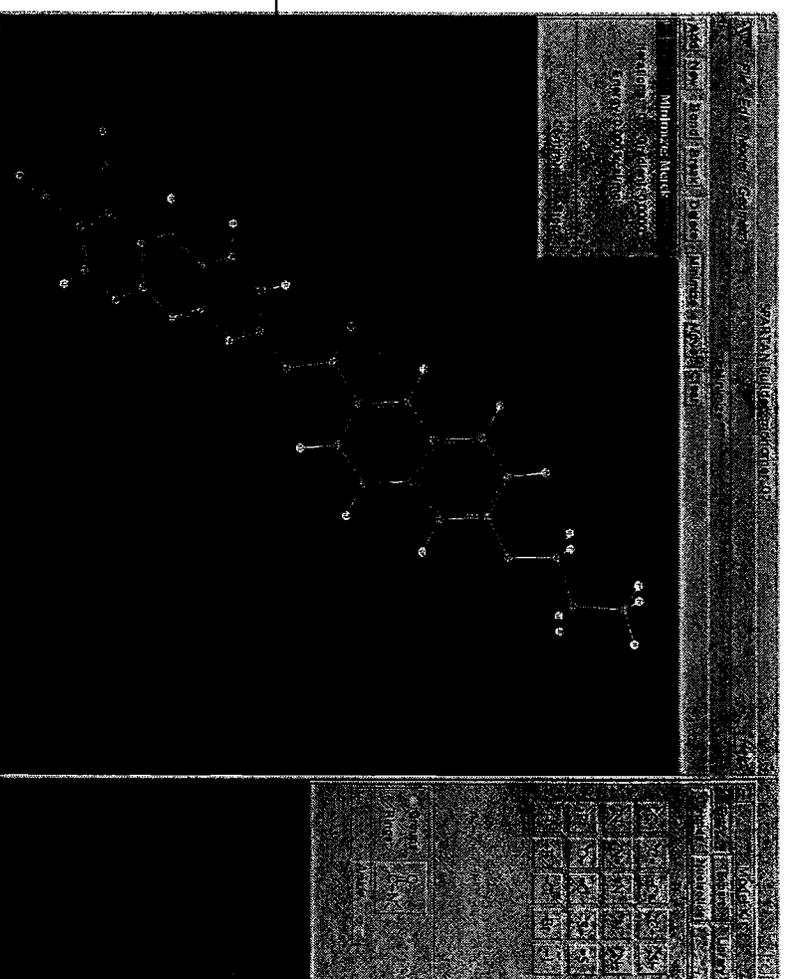
- Liquid crystal polymers are more environmentally robust than mesogens
- Larger molecules are more viscous, making alignment harder

Figure 3

# Spartan v.5.1.3<sup>1</sup> is used to graphically build initial mesogens



- A mesogen is constructed using Spartan's graphical interface
- Energy is optimized using Merck MMFF94 force field minimization
- Mesogens are repeated, and bonded to a common backbone structure
- The oligomer is then minimized again to prevent misplacement of atoms
- The file is exported and formatted



<sup>1</sup> Spartan. v.5.1.3.  
Wavefunction, Incorporated:  
Irvine, CA. 1993.

Figure 4

**XMO<sup>1</sup> is used to visually check the oligomer before being sent to MOPAC 2000<sup>2</sup>**



- Polymer is checked for mistakes in data file, including misbonded, incorrect, or missing atoms
- Once file is inspected, it is read by MOPAC 2000, and a data file is created by the program using the AM1 semiempirical method
- From this file, values are gathered to be used for determination of the physical properties of the molecule

---

<sup>1</sup> XMO. v.4.0. Fujitsu, Limited: Nakase, Japan. 2000.

<sup>2</sup> MOPAC 2000. Schrödinger, Incorporated: Nakase, Japan. 2000.

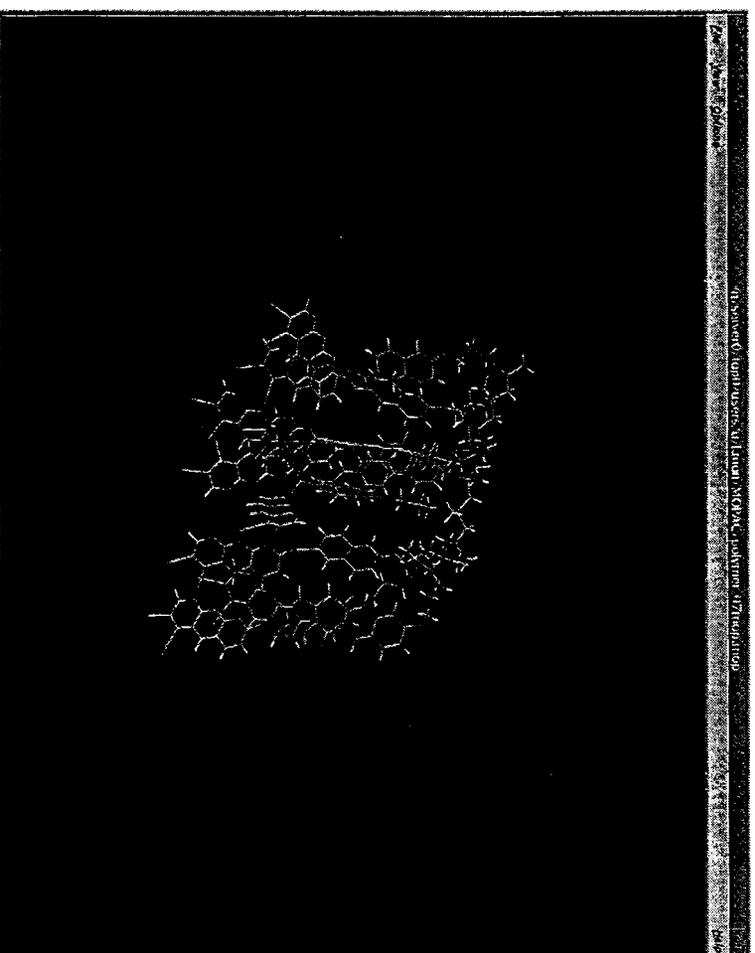


Figure 5

"deltaEdeltaN" is used to calculate the dielectric anisotropy and birefringence of the oligomer



- Using data such as molecular mass, dipole moment, and anisotropy of molecular polarizability, deltaEdeltaN analytically solves for the following values using the Maier-Meier theory:

$$\left[ \Delta \epsilon = \frac{NFh}{\epsilon_0} \left( \Delta \alpha - \frac{F\mu^2}{2k_b T} (1 - \cos^2 \beta) \right) S \right]$$

- $\Delta \epsilon$
- $n_e$
- $n_o$
- $\Delta n$
- $\epsilon$  – the static permittivity of the molecule
- $\beta$  – the angle between the director and the dipole

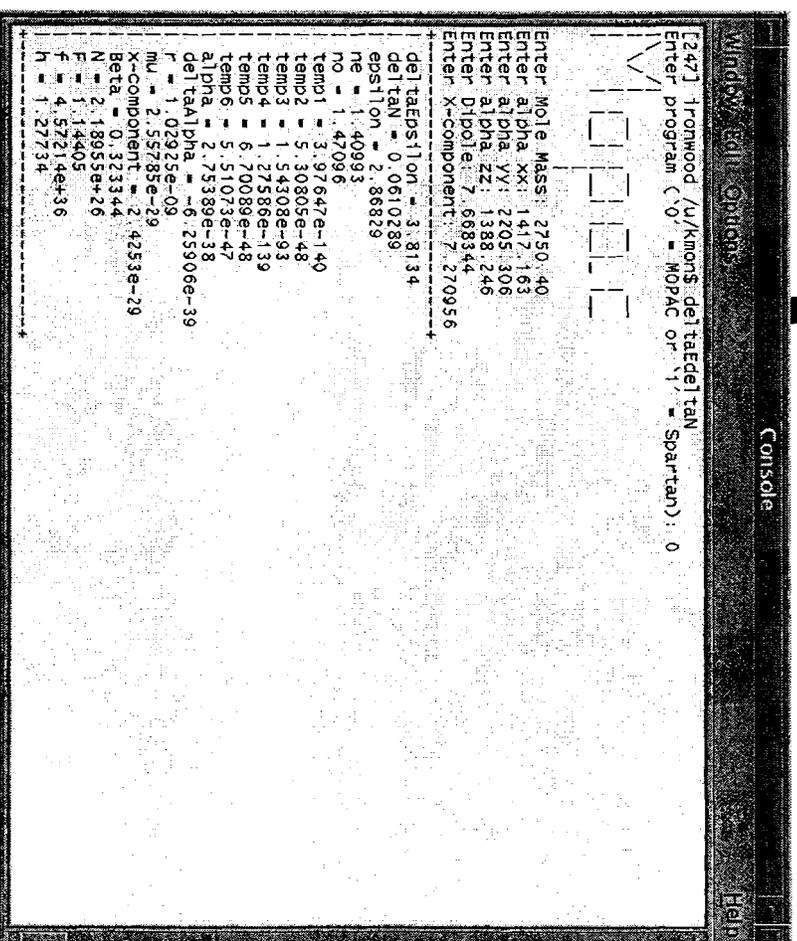


Figure 6

## Carbazole heterocyclic functional group was unable to be recognized by MOPAC2000

- Due to aromatic heterocyclic ring structure, MOPAC was consistently unable to analyze the configuration of the nitrogen atom

