

# IBM ACADEMIC INITIATIVE HUNGARY

## PROJECT REPORT

1991 - 1993



Edited by

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## **ACKNOWLEDGEMENTS**

All participants of the research and educational projects as well as the authors of the selected publications express their thanks to IBM for providing the basic hardware and software tools within the framework of the IBM Academic Initiative Programme in Hungary.

All data processing work for the educational activities and all or most work in the various fields of research were carried out on the IBM 3090 170J mainframe computer operated by the IBM Competence and Development Center, Budapest.

AULA Kiadó kft. Budapesti Közgazdaságtudományi Egyetem  
A kiadásért felel: dr. Halász Géza, az Aula Kiadó igazgatója.  
Készült a BKE házi sokszorosító üzemében  
Nyomdavezető: Ifkovits Józsefné

## Full Geometric Optimization of $\alpha$ -Phenyl Cinnamic Acid Isomers

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### Introduction

Cinnamic acids and its derivatives are important compounds in several aspects. They are key compounds in the shikimic acid pathway of secondary metabolism [1], and they offer the possibility of studying hydrogen bonding *and* aromatic packing in the liquid and solid phases. Their formation through condensation reactions are also of interest, since usually geometric isomers form and the isomeric ratio may depend on several not fully explored factors. Finally, experimental *and* theoretical investigations concerning their geometric isomerization reactions may resolve some controversies related to the thermodynamical stability of the isomers.

A particularly useful candidate for these sort of studies is the isomer pair of  $\alpha$ -phenyl cinnamic acid. An  $\alpha$ -phenyl cinnamic acid molecule contains one phenyl group attached to each pillar atom of the double bond. Since another bulky group, the carboxyl group is also bonded to one of the olefinic carbon atoms, (when one phenyl and the carboxyl groups are on the same side the configuration is **Z** when they are on different sides it is **E**) the molecule becomes very crowded and the optimal spatial arrangement cannot be predicted just by viewing e.g. a stick-and-ball model of the compound.

The final goal of the project is to attack and possibly solve each problem outlined in the first section of the paragraph. Firstly, a relatively simple system was studied experimentally as well as theoretically. This was the isomerization reaction in the liquid phase. Experiments revealed that an almost 50-50 % isomeric distribution could be achieved either starting from the pure **Z** or the **E** isomer. This observation clearly shows that the thermodynamic stability of the isomers are nearly identical. This contradicts to earlier finding [2], i.e. Zimmerman *et al.* reported 4 for the **E/Z** ratio, which is the sign of significant difference in thermodynamic stability. In order to provide additional information, theoretical calculations on the optimal conformation and stability of the molecules seemed desirable. These calculations may give support to one of the experimental findings and at the same time may point to experimental artifacts in one of the experimental studies.

## Methods

Since *semiempirical* and *ab initio* methods are suitable for studying the properties of isolated molecules, they seemed to be good choices for modelling molecules in dilute solvents, especially if the solvent is inert in the sense that van der Waals interactions are negligible.

Initial optimization was started by *semiempirical* calculations. AM1, MNDO as well as PM3 methods were applied. Full geometric optimization was done by the BFGS algorithm [3].

The output of the *semiempirical* calculations served as the input for *ab initio* computations. Initially, a small basis set was used (STO 3G) but calculations with other larger sets are also planned.

## Results

*Semiempirical* calculations revealed that the thermodynamic properties of the molecules are very close to each other. The standard enthalpies of formation by the AM1 method are as follows:  $\Delta H_E^\circ = -23.48$  kcal/mol,  $\Delta H_Z^\circ = -23.33$  kcal/mol. The PM3 method gave very similar results ( $\Delta H_E^\circ = -23.26$  kcal/mol,  $\Delta H_Z^\circ = -23.37$  kcal/mol), while the MNDO method provided with higher standard heats of formation ( $\Delta H_E^\circ = -27.27$  kcal/mol,  $\Delta H_Z^\circ = -26.25$  kcal/mol). It is to be noticed that the stabilities of the isomers are practically equal by each method. These results clearly coincide with our experimental observation i.e. in equilibrium the mixture contains equal amounts of E and Z isomers.

It is also uncovered that the Z isomer is more polar than the E ( $\mu_E = 1.88$  and  $\mu_Z = 2.53$ ) which predicts that this isomer may be more abundant in protic solvent.

As far as the optimized geometries are concerned, the plane of the phenyl groups are perpendicular to each other for the E isomer, while they are almost parallel in the Z. The carboxyl group is near perpendicular to the phenyl group attached to the same olefinic carbon atom in both isomers. These features are to be seen in Figures 1 and 2

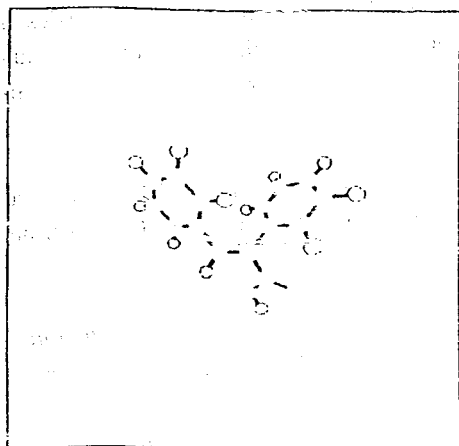


Figure 1 The AM1 optimized structure of the E isomer

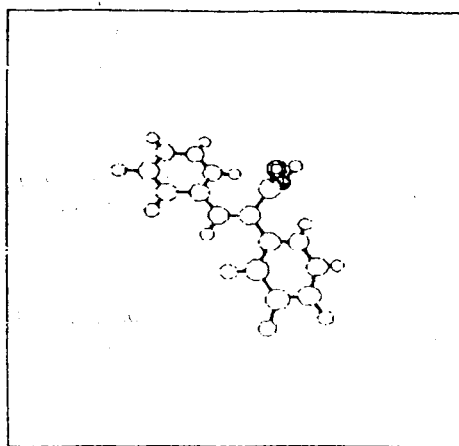


Figure 2 The AM1 optimized structure of the Z isomer

As mentioned above *ab initio* calculations were also performed on a STO 3-G basis. Full geometric optimization without geometric constraints could be performed only for the Z isomer. The procedure did not converge for the E isomer. The *ab initio* optimized structure is displayed in Figure 3.

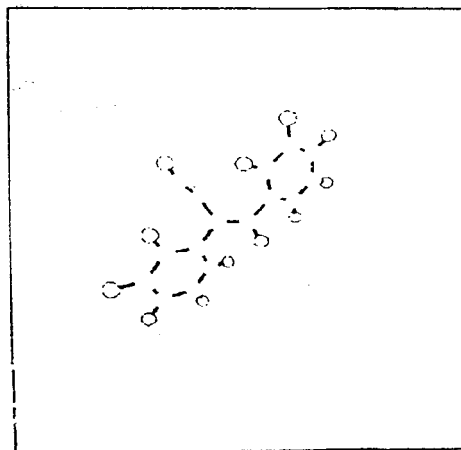


Figure 3 The *ab initio* optimized structure of the Z isomer

### Further work

After having the *ab initio* optimized structure of the E isomer, the pathway of the isomerization will be studied and the saddle point geometry will be determined. Then the *semiempirical* as well as the *ab initio* optimized geometries of the hydrogen bonded dimers will also be calculated to model structures in more concentrated solutions and as a first step to obtain a deeper insight into the crystalline form of these molecules.

### Acknowledgement

This work has been supported by the IBM Academic Initiative Program and the National Science Foundation of Hungary through grant F4297/1992.

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