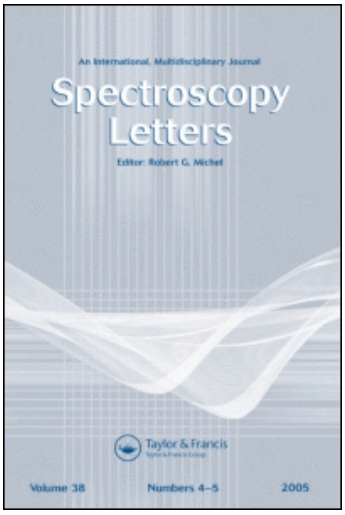

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Geometry Optimization in Molecular Structure Calculations: Vinylcylopropane and Vinyloxirane

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GEOMETRY OPTIMIZATION IN MOLECULAR STRUCTURE CALCULATIONS : VINYLCYLOPROPANE AND VINYLOXIRANE

Key Words: Geometry Optimization, INDO, EHMO

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ABSTRACT

The necessity of geometry optimization within the framework of a particular molecular orbital technique is demonstrated using the INDO and EHMO semiempirical methods. The difficulty of finding the global minimum and the proper choice of technique is also discussed. The choice of molecules demonstrates that structure optimization can completely reverse the prediction of which conformer has the lowest energy.

INTRODUCTION

The importance of complete structure optimization in molecular structure calculations has been appreciated for some time[1]. However since the procedure of optimization can be rather time consuming, it is not always performed. The importance can be realized by remembering that unless structure optimization is performed, one can not know where on the potential energy

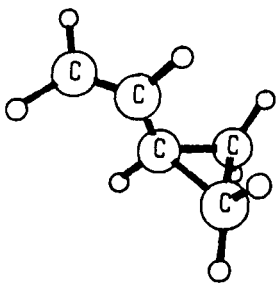
surface the calculated energy is located. Each method of structure calculation will have different values of molecular parameters which will locate the energy at the minimum of the potential energy surface according to that method. If those particular structure parameters are not used then one could be anywhere on the energy surface and conclusions based upon such calculations could be in considerable error. Structure parameters from experimental techniques can be utilized as starting values from which a search for optimum values can proceed, but such experimental values should not be used as the parameters of choice. One also must be careful about which technique to apply in structure calculations for if one is using an inappropriate technique then structure optimization will not be of benefit for the source of error is more fundamental. To demonstrate these cautions, the energy curves predicted by bond rotation in vinylcyclopropane and vinyloxirane by two methods will be presented.

Vinylcyclopropane has been studied by ab initio molecular orbital techniques using STO-3G and 4-31G basis sets[2] using geometries obtained by optimizing the structures of cyclopropane, planar cyclobutane, and ethylene in the STO-3G basis. This method of optimizing structures in representative molecules and transferring the structure parameters to a more complicated molecule is commonly used and most certainly a better approach than using experimental data; but it can still lead to errors, particularly when different basis sets are used for the calculations even though the basic method of calculation is the same. Methods of structure optimization have improved considerably in the past ten years but, for large molecules, a complete study can still be quite expensive. The author did allow two

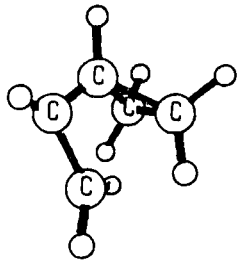
internal angles to vary which allowed some flexibility of structure. We will present an example of the importance of structure optimization in ab-initio calculations later but for this study two approximate techniques will be demonstrated. The methods used will be INDO[3], and EHMO[4]. The EHMO method has been previously shown not to be a method of choice in studying rotational barriers[1] so the futility of structure optimization will be demonstrated. The INDO method does sometimes lead to acceptable results in rotational studies[6] and the importance of structure optimization in an appropriate method of choice will also be demonstrated. All structure optimizations were performed with the Simplex method[5] and all bond lengths and bond angles were optimized at all angles of rotation considered.

RESULTS AND DISCUSSION

Considering first vinylcyclopropane, the likely minimum energy structures are the s-trans (considered the zero degree rotation structure) and the s-cis (the 180 degree rotation structure) forms which are indicated as structures I and II, respectively, below:



I



II

Another possible structure would be the gausch structure which would be obtained by a rotation of 60 degrees from II. A three-fold rotational potential has been indicated by electron diffraction analysis, but the NMR studies favor a two-fold barrier.

The EHMO method predicts that the s-trans structure is the stable structure and it does not indicate any other orientation to be stable. Structure optimization does not improve the predictions of this method. The INDO method using standard geometric parameters and without structure optimization predicts only one stable structure and that is the s-cis structure. The energy vs dihedral angle of the vinyl group with respect to the ring, as indicated in the figures above, is shown in Figure 1. With complete structure optimization, the INDO method predicts two minima in the rotation energy curve which is shown in Figure 2. The s-trans structure and the s-cis structure are both indicated as minima. The two forms are separated by an energy barrier of 3.0 kcal/mol with the s-trans structure more stable by .40 kcal/mol. Notice that structure optimization completely reversed which structure was energy preferred. This twofold barrier to rotation is consistent with the experimental work of Luttke and de Meijere[6] who predicted the s-trans structure to be more stable by 1.1 kcal/mol. The theoretical predictions of Hehre also showed the s-trans to be the more stable with the 4-31G basis set predicting the existence of the s-cis minima also with the s-trans more stable by about 2 kcal/mol and a barrier of about 2.2 kcal/mol. The STO-3G calculations also show a third energy minima which is a gausch structure but this is suspect.

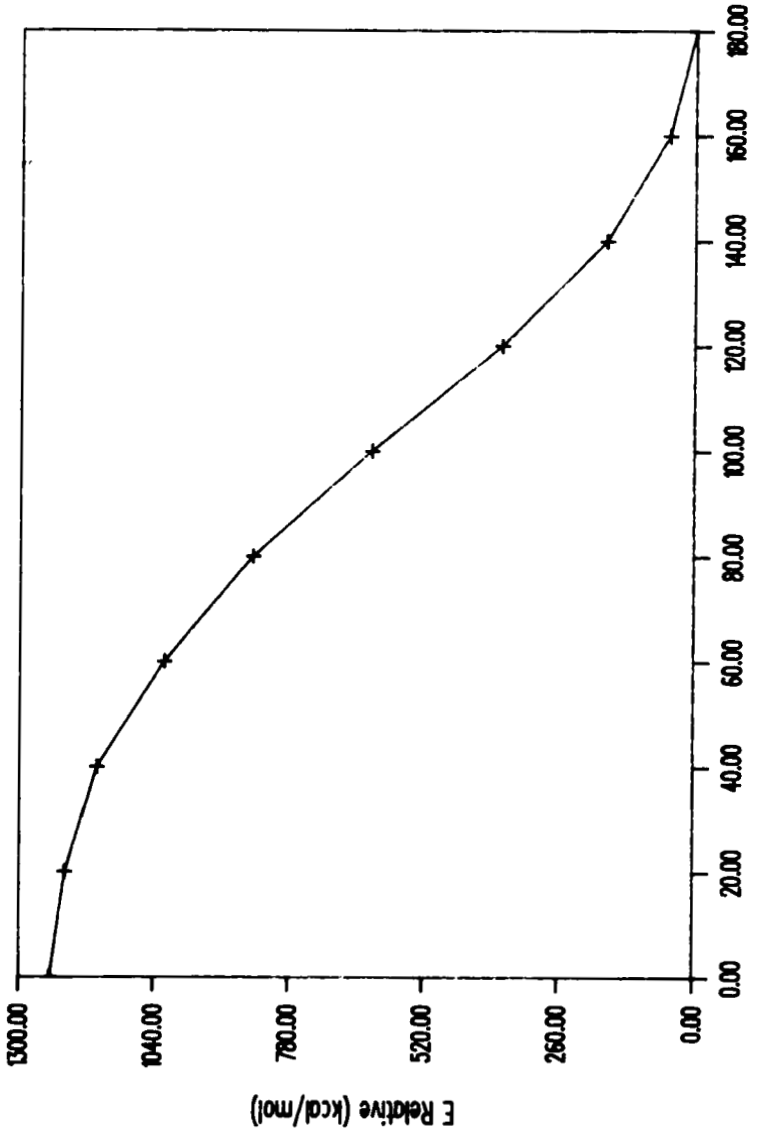
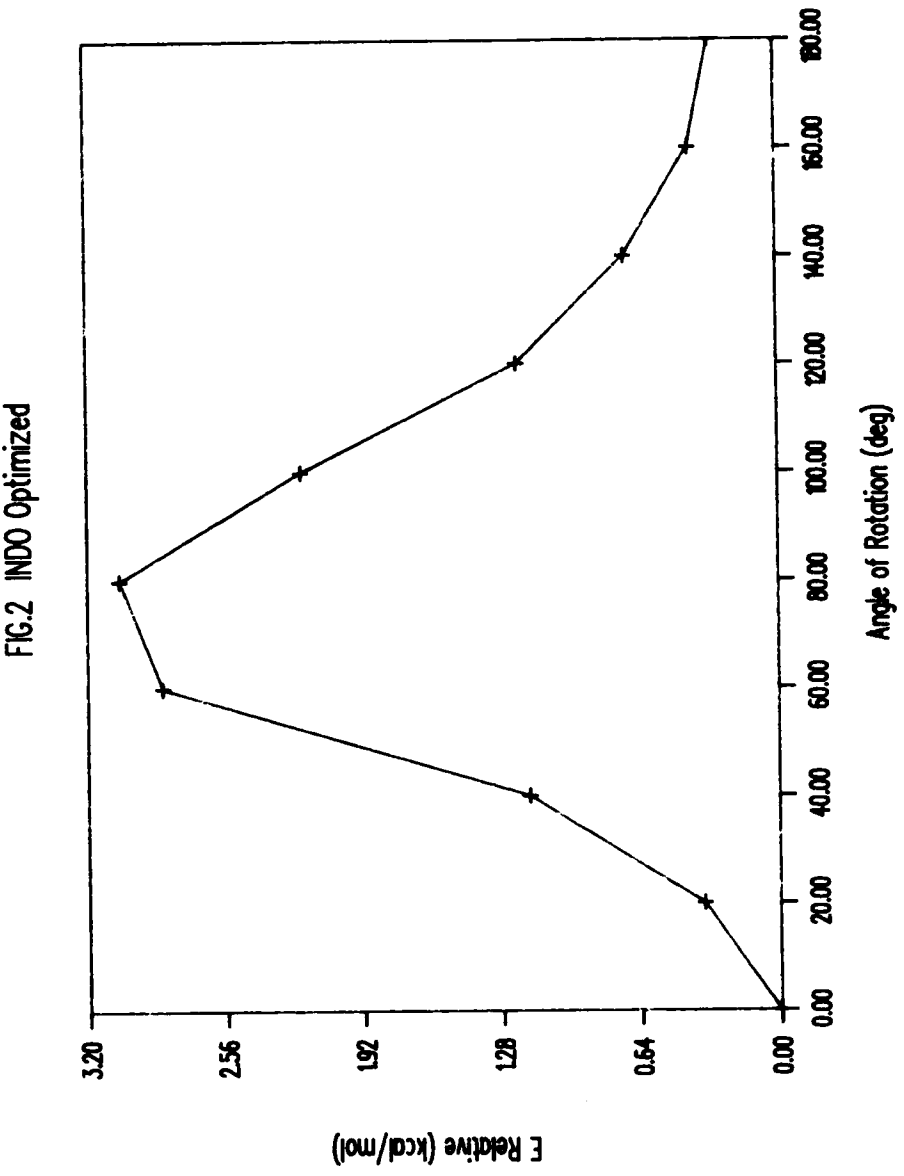


FIG.1 INDO Non-optimized



The nonapplicability of EHMO to rotational barrier calculations has already been demonstrated, and the addition of more electronegative elements usually makes EHMO even less applicable[1]. Thus applying the method to vinyloxirane was not viewed as an appropriate task. However calculations were made and the energies behaved very erratically over the entire range of rotational angles so that no prediction could be made about preferred rotational conformer. As expected, structure optimizations do not improve the predictions. The INDO calculations without structure optimization show that the s-trans structure is the only energy-favored structure similarly to the vinylcyclopropane calculations and in disagreement with experiment. When complete structure optimization is performed at each angle of rotation, a double minimum potential is generated with the s-trans form predicted to be the more stable by .13 kcal/mol with an energy barrier of 1.6 kcal/mol separating the two forms. These optimized results appear in general agreement with the experimental observations[7] in that a double potential is predicted, but the work of Kalasinsky showed that the gauche form is the second stable energy form rather than the s-cis.

Figure 2 demonstrates another problem in structure optimization and that is finding the true global minimum. There are many minima in the parameter space and the finding of the global minimum is a significant problem. The data points of Figure 2 do not present a smooth curve which usually means that the absolute minima have not been found at each rotation angle. Using the Simplex method, one could now do further searches using the parameter values found as starting points in a search for lower energy minima. Donnelly[8] has recently developed a

method which shows promise of finding true minima in parameter optimizations.

CONCLUSIONS

These calculations show that the EHMO method is not suitable for rotational barrier studies, as had been previously shown, so that structure optimization will not improve a method which is not suitable for a particular study. The EHMO method is still useful for other studies even in this age of the ease of application of ab-initio calculations. The INDO method is a method which can be utilized in situations where rotational barriers need be considered, but calculations without structure optimization do not yield acceptable results. When complete structure optimization is performed during all angles of rotation, the results are in better agreement with experimental observations. Within the semiempirical framework, a barrier-parameterized method gives even better results for rotational applications[9] when all structural parameters are allowed to vary. One also has to be very careful to have obtained the true global minimum of energy, for it is not always obvious that such a minimum has not been attained.

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