orbital is present in each bonding region. The molecular orbital description of ethane, analogous to the original formulation, is obtained *via* an SCF calculation but using each of the FSGO as independent basis orbitals in the formation of each molecular orbital (*i.e.*, the linear coefficients of the two CH FSGO are discarded when $C_2H_6$ is formed, and the two FSGO in the CH region are treated as independent basis orbitals). Also given in Table XI is the molecular orbital structure of the ethane molecule, calculated at a C–C distance of 2.907 Bohrs, which is the distance corresponding to the calculated minimum energy.

There are several points of interest to note in Table XI. First, instead of a 9.1% error in the predicted C–C distance that occurred in the initial formulation, it is seen that the error is reduced to 0.3% using the modified fragment description. Next, comparison of the molecular orbital ordering in Table XI with the results of extensive basis set studies[25] in Table VI shows that the molecular orbital ordering remains in exact agreement with the extensive basis set studies. Also, an orbital energy linearity plot results in $a = 0.9122$, $b = -0.1141$, $S = 0.0041$, and $\rho = 0.9999$, indicating the improved balance of the modified basis set in another manner. The barrier to rotation using this fragment is calculated to be ~5.1 kcal/mol, roughly the same as in the initial formulation, where a 5.6 kcal/mol barrier was found.[58]

It should be emphasized that these are preliminary investigations of an improved molecular fragment description. However, they illustrate clearly the ease of analysis and improvement of the approach. In addition, the substantial improvement observed in geometric and electronic structure characteristics at relatively small computational expense provides considerable encouragement that an "analytical tool" that is applicable to large molecular systems and which also possesses acceptable accuracy for a variety of properties of interest to chemists and biologists can be achieved. Additional efforts are currently underway to develop a general approach for obtaining optimized fragments, similar to the one just described, that will allow for large molecules not only improved accuracy of molecular properties such as those just discussed but will also allow examination of systems in which an *a priori* choice of molecular fragment for description of the system is not obvious (*e.g.*, development of a fragment that is not restricted to description of only "sp$^3$" environments but is continuously "rehybridizable" into any desired mixture of "sp$^3$" and "sp$^2$" hybridization).

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[58] No attempt was made in these initial studies to optimize the fragment description with respect to barrier to rotation predictions.

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# Calculations of Barriers to Internal Rotation in Propene and Monofluoropropenes

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**Abstract:** Barriers to internal rotation have been calculated by the Hartree–Fock method for propene, 2-fluoropropene, *cis*-1-fluoropropene, and *trans*-1-fluoropropene. The agreement of the calculated and experimental values is sufficiently close to suggest that Hartree–Fock calculations can be used quantitatively with reasonable error limits.

Propene and its fluorinated derivatives form an interesting sequence of molecules for the study of barriers to internal rotation. Only propene has undergone a complete microwave structure determination, but the barriers and some structural information have been found for all the monofluorinated propenes. We have calculated the barriers in propene, *cis*-1-fluoropropene, *trans*-1-fluoropropene, and 2-fluoropropene in order to determine whether the Hartree–Fock method is sufficiently reliable to be trusted in determinations of barriers in molecules that are either unknown or whose microwave spectrum has yet to be analyzed.

## Basis Sets and Geometries

The basis sets used are those suggested by Dunning[1] in which for each carbon and fluorine atom nine s- and five p-type Gaussian functions are contracted into four s- and three p-type basis functions. For each hydrogen, four s-type Gaussians are contracted into two basis functions. The methyl hydrogen basis functions were scaled to best fit a hydrogen orbital with exponent 1.159 (the optimized orbital exponent in ethane[2]); the remaining hydrogen basis functions were scaled to best fit the optimized ethylene hydrogen exponent (= 1.227).[2] The results of this paper further show that these basis sets are adequate for calculating barriers to internal rotation of methyl groups even though more extended basis sets were required to satisfactorily describe the hydrogen peroxide internal rotation potential.[3]

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[1] T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

[2] R. M. Stevens, private communication.

[3] N. W. Winter and T. H. Dunning, *Chem. Phys. Lett.*, **11**, 194 (1971).

The geometry used for propene is the complete substitutional structure as determined by Lide and Christensen.[4] The modifications of this structure by Beaudet and Wilson[5] were used for *cis*- and *trans*-1-fluoropropene. The structure of 2-fluoropropene was used as determined by Pierce and O'Reilly.[6]

**Table I.** Comparison of Calculated and Experimental Barriers to Internal Rotation

| Molecule | Calcd energy of staggered conformer, Hartrees | Calcd barrier, kcal/mol | Exptl barrier, kcal/mol |
|---|---|---|---|
| Propene | −117.0422 | 1.87 | 1.98[a] |
| *cis*-1-Fluoropropene | −215.8953 | 1.14 | 1.06[b] |
| *trans*-1-Fluoropropene | −215.8929 | 2.08 | 2.20[c] |
| 2-Fluoropropene | −215.8993 | 2.01 | 2.43[d] |

[a] Reference 4. [b] Reference 5. [c] Reference 17. [d] Reference 6.

## Results

Three of the calculated internal rotation barriers listed in Table I are within 10% of the experimental values and the fourth is within 20% of experiment. We predict the staggered conformation (one methyl hydrogen eclipsing the double bond) to be the stable one in each case. Previous results reported by Scarzafava and Allen[7] using a set of Gaussian orbitals contracted nearly to minimum basis set size [3s,1p/1s] do display the proper trend for propene (1.25 kcal/mol), *cis*-1-fluoropropene (1.07 kcal/mol), and *trans*-1-fluoropropene (1.34 kcal/mol); however, the calculated magnitudes and differences between these barriers are not in good agreement with experimental results. It seems likely that an extended p basis is required in order to adequately describe the different $\sigma$ and $\pi$ bonds of the carbon atoms. Also, the fluorine atom is much better described with an extended basis; a reasonable barrier for ethyl fluoride cannot be obtained with a minimum basis set.[8]

The relative lack of agreement for 2-fluoropropene can possibly be explained by a number of arguments. Vibrational effects which can amount to hundreds of calories per mole[9] could be the cause. However, these effects are also present in the other fluoropropenes. A larger basis set including polarization functions might be necessary as it is in hydrogen peroxide. But it seems probable that the basis set used is equally adequate for all isomers. To us, it seems more likely that there may be a small error in the equilibrium geometry of 2-fluoropropene which, when altered, would yield considerably better agreement with the experimental barrier. The 2-fluoropropene geometry was determined by assuming that all geometrical parameters are identical with those in propene and then solving for the CF bond length and the CCF bond angle. The CF bond length obtained in this process was 1.324 Å (±0.02 Å), significantly shorter than that of fluoroethylene (1.344 Å) or *cis*- or *trans*-1-fluoropropene (1.342 Å). If a CF bond length of 1.342 Å were assumed for 2-fluoropropene and the CCF and CCC angles were determined, the CCC angle would have to be larger than that of propene (124.3°). The mentioned change in bond length and changes of 2 or 3° in bond angles are within the stated error of the microwave structural determination.[6] This alteration would surely raise the calculated barrier, probably by about 0.2 kcal/mol.

A previous explanation of the difference in the barriers of propene and *cis*- and *trans*-1-fluoropropene[10] is that a fluorine in the cis position results in greater steric repulsion in the equilibrium staggered conformation; thus, the minimum of the potential well is raised and the barrier is decreased. As pointed out by Beaudet and Wilson,[5] this is equivalent to saying that the heat of formation of *cis*-fluoropropene is more positive than that of the trans isomer. This is not the case. *cis*-Fluoropropene has been measured to be 0.75 kcal/mol more stable than *trans*-fluoropropene.[11] We hope that the same type of cancellation of errors which allows an accurate calculation of barriers also applies in calculating the relative energies of *cis*- and *trans*-1-fluoropropene. Our calculation predicts that the staggered cis isomer is 1.5 kcal/mol more stable than the staggered trans isomer. This is in the same direction but twice as large as the experimental difference in heats of formation.

We have also calculated dipole moments of these four molecules. As usual for wave functions such as these, the calculated values are consistently too large. See Table II. Our calculated propene dipole moment supports the assumption that the angle between the dipole and the CC single bond is 33° in that molecule and not 17°, which was considered to be another possibility.[12]

The dipole moment is predicted to change significantly in either magnitude or direction for each molecule as it rotates from staggered to eclipsed conformation. This effect might be large enough to allow observation of transitions between torsional levels.

## Conclusion

Barriers to internal rotation can be calculated accurately; however, they are sensitive to geometry and therefore fairly accurate experimental bond lengths and angles are required in the calculation. (The change in the ethane barrier with respect to the change in the CC bond length[9] is, for example, 11 kcal/Å.) Geometry optimization with the Hartree–Fock method is very expensive and in some cases even double $\zeta$ quality basis sets, such as we have used here, are not sufficient to ensure accurate results.[3,13] Nevertheless, we believe that if a good geometry (especially for those atoms closest to the top) can be inferred from data on similar molecules, a reliable barrier can be calculated. Extreme geometry accuracy is not always required. For example, if the older propene geometry of Lide and Mann[12] is used, the calculated barrier is 1.85 kcal/mol.

An interesting further test would be the calculation of the internal rotation potential of 3-fluoropropene

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(4) D. R. Lide and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

(5) R. A. Beaudet and E. B. Wilson, Jr., *J. Chem. Phys.*, **37**, 1133 (1962).

(6) L. Pierce and J. M. O'Reilly, *J. Mol. Spectrosc.*, **3**, 536 (1959).

(7) E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).

(8) W. E. Palke, *Chem. Phys. Lett.*, **15**, 244 (1972).

(9) C. S. Ewig, B. Kirtman, and W. E. Palke, unpublished work.

(10) V. W. Weiss, P. Beak, and W. H. Flygare, *J. Chem. Phys.*, **46**, 981 (1967).

(11) P. I. Abell and P. K. Adolf, *J. Chem. Thermodyn.*, **1**, 333 (1969).

(12) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

(13) R. M. Stevens, *J. Chem. Phys.*, **55**, 1725 (1971).

**Table II.** Comparison of Calculated and Experimental Dipole Moments[a]

| | Eclipsed | | | Staggered | | | Experimental | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $z$ | Total | $x$ | $z$ | Total | $x$ | $z$ | Total |
| Propene | −0.196 | 0.385 | 0.432 | −0.269 | 0.344 | 0.437 | −0.20 | 0.31 | 0.364[b] |
| *cis*-1-Fluoropropene | −2.065 | −0.408 | 2.105 | −2.097 | −0.410 | 2.137 | −1.45 | −0.18 | 1.46[c] |
| *trans*-1-Fluoropropene | −0.041 | 2.581 | 2.581 | −0.107 | 2.528 | 2.530 | ∼−0.58 | ∼1.76 | >1.85[d] |
| 2-Fluoropropene | 1.493 | 1.598 | 2.187 | 1.487 | 1.515 | 2.123 | 1.35 | 0.85 | 1.60[e] |

[a] The C–C single bond is chosen as the $z$ axis and the 1 carbon is in the positive $x$, negative $z$, quarter plane. [b] Reference 1. [c] Reference 5. [d] Reference 15. Only one principal axis component of the dipole moment was determined. [e] Reference 6.

**Table III.** Energy Components

| Molecule | | Nuclear repulsion | Kinetic | Electron repulsion | Electron nuclear attraction |
|---|---|---|---|---|---|
| Propene | Eclipsed | 70.7177 | 117.0573 | 108.5493 | −413.3635 |
| | Staggered | 70.7304 | 117.0492 | 108.5434 | −413.3654 |
| | Difference | −0.0127 | 0.0081 | 0.0059 | 0.0019 |
| *cis*-1-Fluoropropene | Eclipsed | 115.6885 | 215.8824 | 193.0613 | −740.5256 |
| | Staggered | 115.7611 | 215.8794 | 193.1264 | −740.6622 |
| | Difference | −0.0726 | 0.0030 | −0.0651 | 0.1366 |
| *trans*-1-Fluoropropene | Eclipsed | 113.2358 | 215.8791 | 190.5892 | −735.5938 |
| | Staggered | 113.2491 | 215.8691 | 190.5732 | −735.5843 |
| | Difference | −0.0133 | 0.0100 | 0.0160 | −0.0095 |
| 2-Fluoropropene | Eclipsed | 117.9249 | 215.9269 | 195.1355 | −744.8834 |
| | Staggered | 117.9203 | 215.9154 | 195.0944 | −744.8294 |
| | Difference | 0.0046 | 0.0115 | 0.0411 | −0.0540 |

which is experimentally known in detail.[14] If Hartree–Fock calculations prove to be equally as accurate for this asymmetric case, then prediction of barriers in experimentally difficult molecules would be a useful technique with errors of about 10%.

We include for completeness, in Table III, the energy components and their differences for each molecule. Even though the virial ratio $-V/T$ for each of these calculations is in the range 2.0 ± 0.0002, scaling will change the contents of Table III somewhat. It seems to us that since the signs and magnitudes of these contributions to the barrier vary markedly from one molecule to another, a single interpretation of the origin of barriers cannot be deduced from them. Instead of invoking a different mechanism for barriers in such a series of similar molecules, we are hopeful that the explanation of the origin of barriers can be found elsewhere.[15]

A population analysis shows weak attractive overlap populations between the fluorine atom and the nearby methyl hydrogens in both *cis*-1-fluoropropene and 2-fluoropropene. This effect is approximately as strong as the similar interaction in ethyl fluoride. The population analysis also shows that the carbon bonded to the fluorine in the fluoropropenes is about 0.5 electron more positive than that carbon atom is propene itself. Furthermore, the carbons adjacent to it are predicted to become more negative by about 0.1 electron in the fluorinated molecule. This is similar to results found by Pople;[16] the fluorine donates $\pi$ population while withdrawing $\sigma$ electrons. Nevertheless, the carbon bonded to fluorine does not gain $\pi$ population relative to propene; this density is transferred to the other two carbons. The total $\pi$ overlap populations between fluorine and the ethylenic carbons are slightly negative in every case as are the $\pi$ overlap populations between the methyl carbon and the ethylenic carbons.

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(14) P. Meakin, D. O. Harris, and E. Hirota, *J. Chem. Phys.*, **51**, 3775 (1969).

(15) O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968).

(16) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(17) S. Siegel, *J. Chem. Phys.*, **27**, 989 (1957).