JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office.

VOLUME 91, NUMBER 5 MARCH 11, 1969

Physical and Inorganic Chemistry

Ab Initio Calculation of the Barrier to Internal Rotation in Propylene Using a Gaussian Basis Self-Consistent Field Wave Function

Mark L. Unland, John R. Van Wazer, and John H. Letcher

Contribution from the Central Research Department, Monsanto Company, St. Louis, Missouri 63166. *Received September 13, 1968*

Abstract: An *ab initio* calculation of the barrier to internal rotation in propylene is accomplished by use of LCGO–MO–SCF wave functions. The basis set is composed of five 1s and two 2p Gaussian orbitals on the carbon atoms and three 1s Gaussian orbitals on the hydrogen atoms. The calculated barrier is 1.48 kcal/mole compared to the experimentally observed 1.98 kcal/mole. The calculated dipole moment of the stable (staggered) form is 0.357 D compared to the experimental 0.364 D. Population analysis and calculation of various properties such as potentials, charge densities, quadrupole moments, and diamagnetic susceptibility show that the effect of internal rotation is felt throughout the molecule. Analysis of overlap populations gives some evidence of an attractive contribution to the potential barrier to internal rotation in propylene.

The origin of the barrier to internal rotation within a molecule is of interest to theoretical, experimental, and biological chemists. The majority of the effort until the early 1960's has gone into experimental determination of barriers[1] in various molecules. Most of the theoretical work on the barrier problem was semiempirical until the *ab initio* calculation of the barrier in ethane by Pitzer and Lipscomb[2] in 1963. Since that time, there have been a number of papers on the theory of internal rotation in ethane and ethane-like molecules,[3-12] and it has only been quite recently that other types of molecules[13-17] were given theoretical consideration. In spite of the effort thus far, a simple generalized picture of the origin of the barrier has not emerged, and it now seems likely[13] that the detailed explanation of the barrier mechanism is as complex as the problem of describing the interactions within the electronic structure of the molecule. Because of this complexity, it would be helpful to study as many different facets of internal rotation as possible. Thus, in this work, several electronic properties, as well as the usual energy-component analysis, are given as a function of molecular conformation. While it is not expected that a general picture can emerge from a single study, it is hoped that, when a well-chosen series of molecules has been examined in this manner, useful trends will become apparent.

Propylene and its monofluoro derivatives are a

---

(1) For a review, see E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).
(2) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).
(3) R. G. Parr, *ibid.*, **40**, 3726 (1964).
(4) K. Ruedenberg, *ibid.*, **41**, 588 (1964).
(5) B. Kirtman, *ibid.*, **41**, 3262 (1964).
(6) R. E. Wyatt and R. G. Parr, *ibid.*, **41**, 3262 (1964).
(7) M. Cignitti and T. L. Allen, *J. Phys. Chem.*, **68**, 1292 (1964).
(8) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).
(9) R. E. Wyatt and R. G. Parr, *ibid.*, **43**, 5217 (1965); **44**, 1529 (1966).
(10) O. J. Sovers and M. Karplus, *ibid.*, **44**, 3033 (1966).
(11) E. Clementi and D. R. Davis, *ibid.*, **45**, 2593 (1966).
(12) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1966).
(13) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967); **46**, 2276 (1967).
(14) L. Pederson and K. Morokuma, *ibid.*, **46**, 3914 (1967).
(15) W. E. Palke and R. M. Pitzer, *ibid.*, **46**, 3948 (1967).
(16) R. J. Buenker, *ibid.*, **48**, 1368 (1968).
(17) J. R. Hoyland, *J. Am. Chem. Soc.*, **90**, 2227 (1968).

complete series as far as experimental data on barriers are concerned.[18–23] One of the more interesting compounds in the series is *cis*-1-fluoropropylene[23] which has a barrier about half as large as those observed for other members of the set. Beaudet and Wilson[23] reason that the anomalous barrier height could be caused by a nonbonded H–F interaction and review evidence indicating that a barrier mechanism which is totally replusive is not entirely correct. Because the experimental results indicate that a theoretical study of the propylene series may reveal interesting features of the barrier problem, it seems logical to choose propylene as the subject of the next *ab initio* determination of the barrier to internal rotation.

Calculation Details

The LCGO-MO-SCF orbitals used in this work were obtained from the Gaussian molecular SCF program MOSES written by Drs. Murray Geller and Lester M. Sachs and modified by N. Winter and Dr. J. H. Letcher for use on a CDC 6400 computer. The properties were calculated with a Gaussian properties program written by Dr. D. Neumann for use on a CDC 6600 as an integral part of the POLYATOM system. Density maps were obtained from a routine written by Dr. W. E. Palke and modified by T. H. Dunning.

Table I. Gaussian Representation of the Atoms in the Propylene Molecule[a]

	Exponents	Orbital energies and eigenvectors	
Carbon	S-GTF	1s	2s
		−11.3336430	−0.6780123
	381.00000	0.0235553	−0.0050421
	59.18000	0.1520701	−0.0312864
	13.79000	0.4653930	−0.1291575
	3.83300	0.4952628	−0.1643766
	0.29460	0.0186091	1.0417090
	P-GTF	2p	
		−0.3786753	
	1.55600	0.3392532	
	0.27950	0.8038511	
	Total energy =	−37.5131180 au	
Hydrogen	S-GTF	1s	
		−0.2484995	
	4.23900	0.0748200	
	0.65770	0.4159000	
	0.41830	0.6365000	
	Total energy =	−0.496979 au	

[a] The orbital exponents have been optimized to minimize the calculated total energy.

Table II. Coordinates (in Atomic Units) of the Atoms in the Staggered and Eclipsed Forms of Propylene

Atom	*x*	*y*	*z*
C1	−1.59699	0.0	2.34471
C2	0.0	0.0	0.0
C3	2.52469	0.0	0.0
H4	3.59328	0.0	−1.74071
H5	3.57173	0.0	1.77696
H6 (S)	−2.84340	−1.65825	2.38108
H7 (S)	−2.84340	1.65825	2.38108
H8 (S)	−0.43473	0.0	4.03302
H6 (E)	−1.17439	−1.65825	3.51785
H7 (E)	−1.17439	1.65825	3.51785
H8 (E)	−3.59365	0.0	1.88146
H9	−0.99951	0.0	−1.80021

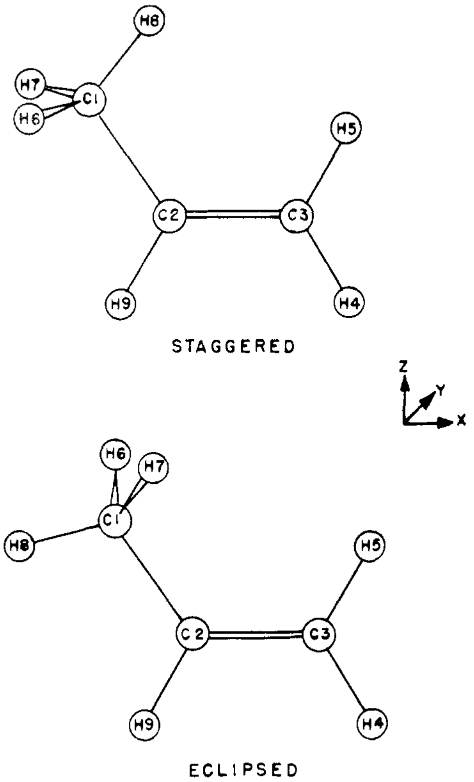

Figure 1. Schematic of the staggered and eclipsed forms of propylene. Carbon atom C2 is at the origin of the coordinate system.

The basis set was an uncontracted (52/3) set of Gaussian-type orbitals (GTO). The atom optimized orbital exponents, atomic coefficients, and total atomic energies are given in Table I.[24] The atomic coordinates given in Table II and illustrated in Figure 1 were obtained from the work of Lide and Christensen,[20] who did a complete structure determination by means of microwave spectroscopy. Only two conformations of propylene were studied, the stable staggered form[19] in which the methyl hydrogens are staggered with respect to the hydrogen atom on the C-2 carbon atom bonded to the methyl group and the eclipsed form in which a methyl hydrogen eclipses the hydrogen atom on carbon C-2 (see Figure 1).

The starting coefficients for the SCF cycling were determined from equivalent orbitals such as those used by Letcher and Dunning.[25] This method of choosing starting coefficients placed the energy within

---

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

(19) D. R. Herschbach and L. C. Krisher, *ibid.*, **28**, 728 (1958).

(20) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961).

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

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

(23) R. A. Beaudet and E. B. Wilson, Jr., *ibid.*, **37**, 1133 (1962).

(24) The exponents were made available to us by Dr. Murray Geller and are from calculations by D. Whitman at RIAS, Martin Co., Baltimore, Md.

(25) J. H. Letcher and T. H. Dunning, Jr., *J. Chem. Phys.*, **48**, 4538 (1968).

Table III. Summary of Energy Results for Staggered and Eclipsed Forms of Propylene (in Atomic Units)

	Staggered (S, stable)		Eclipsed (E)		Difference (E − S)	
	Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled
Kinetic energy, T	115.93911	116.39646	115.95016	116.39408	0.01105	−0.00238
Nuclear repulsion energy, V_{nn}	70.69848	70.83779	70.70268	70.87390	0.00420	0.00011
Nuclear attraction energy, V_{ne}	−411.43671	−412.24742	−411.47514	−412.26207	−0.03842	−0.01465
Electron repulsion energy, V_{ee}	108.40311	108.61671	108.42864	108.63601	0.02553	0.01930
Potential energy, V	−232.33512	−232.79292	−232.34382	−232.78816	−0.00870	0.00476
Total energy, E	−116.39601	−116.39646	−116.39366	−116.39408	0.00235	0.00238
Virial ratio, $V/(-2T)$	1.00197043	1.0	1.00191246	1.0	0.00005797	0.0
One-electron terms, $T + V_{nn} + V_{ne}$	−224.79912	−225.01317	−224.82230	−225.03009	−0.02318	−0.01692

0.5 au of the final result and saved the time required for the several additional interactions which would have been necessary if we had started with zero coefficients. No attempt was made to minimize the energy calculated from the initial coefficients by variation of calculation parameters such as bond polarities. Results of other studies show that when this minimization is done, the energy results from the equivalent[25] or bonding[17] orbitals are in good agreement with SCF results.

Energy Results

For both conformations of propylene, the total energy converged to more than eight significant figures and the coefficients had converged to the fifth or sixth decimal place. Thus, the energies are precise to all decimal places given and the calculated properties are good to four or five decimal places.

Table III presents a summary of the energy results. Both scaled and unscaled results are given. The scaling procedure assures that the wave function will satisfy the virial theorem but, as Löwdin[26] points out, satisfaction of the virial theorem is only a necessary and not a sufficient criterion for the accuracy of a wave function. Because the scaling factor $(-V/2T)$ is close to unity for the present wave functions, the effect of scaling on the calculated barrier is minor, but the effect on the various energy-component differences is much more drastic and in some cases causes a reversal of sign. Fink and Allen[13] have discussed the problem of energy-component analysis with respect to internal rotation. They point out that details of the barrier mechanism must be discussed in terms of energy components which are "stable under small geometrical perturbations, scaling to satisfy the virial theorem, and improvement in the variational wave functions." From a study of ethane, methyl alcohol, methylamine, and hydrogen peroxide, Fink and Allen[13] conclude that the phase and relative amplitudes of the one-electron term $(T + V_{ne} + V_{nn})$ and the two-electron term (V_{ee}) provide the desired invariant energy components. From Table III, it appears that similar conclusions are valid for propylene. Thus, in propylene as in ethane, methyl alcohol, methylamine, and hydrogen peroxide, the change in the two-electron term, V_{ee}, is of opposite phase to the change in the one-electron term, $T + V_{nn} + V_{ne}$, but in phase with the total energy change when passing from the lower to higher energy molecular conformation. The physical picture of the barrier mechanism as a balance between the interactions of all parts of the molecule is supported by the energy-component analysis of propylene.

Because of its sensitivity to small geometry changes, the nuclear-repulsion term, V_{nn}, is not a reliable index for predicting the barrier height. In fact, if one chooses an equilibrium geometry which is only slightly different from the true geometry, the nuclear-repulsion term can predict the wrong geometry as the most stable form. For example, Hoyland,[17] in his work on propylene, chose a molecular geometry which was in only fair agreement with the microwave structure.[18] This small structural discrepancy led to a calculated change in nuclear-repulsion energy, which showed that the eclipsed form was more stable than the staggered, and to the conclusion that empirical models[27] in which the nuclear-repulsion energy determines the lowest energy conformation are not applicable to propylene. From Table III, it is apparent that when an accurate structure[20] is used, the nuclear-repulsion-energy change correctly predicts the stable conformation. From Table III, we see that ΔV_{nn} and ΔV_{ee} are in phase with the total energy change and that $\Delta V_{ee} > \Delta V_{nn}$. Both of these conclusions are different from those of Hoyland,[17] who found that $\Delta V_{nn} \simeq \Delta V_{ee}$ and that both were out of phase with ΔE. It is interesting that in our calculation, the energy difference between the staggered and eclipsed forms as obtained from the starting coefficients give a ΔE(eclipsed − staggered) = −0.00155 au. That is, our starting wave functions, which are similar to Hoyland's[17] except that the energy was not minimized with respect to the bond-polarity coefficient, predict the wrong form to be more stable. We conclude from this that bonding orbitals such as Hoyland's[17] and/or equivalent orbitals such as used by Letcher and Dunning[25] may not be reliable for calculations of internal-rotation barriers unless care is taken to ensure the accuracy of the various calculation parameters. Further, it seems apparent that an accurate structure should always be used.

From Table III, the difference in the total energy of the two rotational isomers is 0.00235 au or 1.48 kcal/mole. The experimental value[18] is $\Delta E = 0.00315$ au or 1.978 ± 0.017 kcal/mole. From data in Tables I and III, the theoretical binding energy of the stable (staggered) form of propylene is −0.875 au which may be compared to an experimental binding energy[28] of −1.29 au.

The orbital energies of the staggered and eclipsed

---

(26) P. O. Löwdin, *J. Mol. Spectrosc.*, **3**, 46 (1959).

(27) M. Karplus and R. G. Parr, *J. Chem. Phys.*, **38**, 1547 (1963).

(28) Thermochemical data for the calculation of the experimental binding energy were taken from "The Handbook of Chemistry and Physics," 39th ed, Chemical Rubber Publishing Co., Cleveland, Ohio.

Table IV. Comparison of Orbital Energies for the Staggered and Eclipsed Forms of Propylene (in Atomic Units)

MO	Staggered form (S)	Eclipsed form (E)	Difference (E − S)
1	−11.28874	−11.28763	0.00111
2	−11.26386	−11.26233	0.00153
3	−11.25714	−11.25549	0.00165
4	−1.04304	−1.04209	0.00095
5	−0.90696	−0.90640	0.00056
6	−0.72300	−0.72162	0.00138
7	−0.59511	−0.59353	0.00158
8	−0.53118	−0.53266	−0.00148
9	−0.51756	−0.51653	0.00103
10	−0.46765	−0.46838	−0.00073
11	−0.43575	−0.43313	0.00262
12	−0.31570	−0.31406	0.00164
13 (1st virtual)	0.25330	0.24909	−0.00421
Total (occ MO's)	−39.34569	−39.33385	0.01184

forms are compared in Table IV. Because the orbitals are often highly delocalized, their nature is not always clear from inspection of the MO coefficients; however, the following qualitative descriptions may be given: (a) orbitals 1, 2, and 3 are primarily inner shells of atoms C2, C3, and C1, respectively; (b) orbital 9 is predominantly π in character and acts to bond atoms C2, C1, and the out-of-plane hydrogen atoms H6 and H7; and (c) orbital 12 is the π bond between atoms C2 and C3. The first ionization potential of propylene,[29] 0.3576 au, is in reasonable agreement with the negative of the energy of the π-bond orbital between C2 and C3, 0.3157 au.

Electronic Properties

This section will present calculations of various one-electron properties for the two conformations of propylene. The purpose here is twofold: (a) to look at the effect of internal rotation from other than an energy standpoint, and (b) to provide data for comparisons with future work.

An analysis of the gross, net, and overlap populations[30] in a molecule can often be of value in the interpretation of the bonding, and it seems likely that such an analysis may lend insight into the internal-rotation problem. Thus, Table V contains a population analysis for both conformations of propylene. From the gross atomic populations, it is apparent that there is a slight C^{-}–H^{+} polarity in the C–H bonds with the methyl C–H bonds being slightly less polar than those in the rest of the molecule. Also, in passing from the stable staggered form to the eclipsed form, the carbon atoms have gained charge while the hydrogen atoms with the exception of the in-plane methyl hydrogen have lost charge. In other words, in the stable form, the C–H bonds are somewhat less polar than in the unstable form. This trend was also observed in ethane.[2] Since one can take the overlap populations as measures of the bonding and antibonding strengths between atoms, one finds from Table V that in rotating the methyl group from the staggered to the eclipsed form, the C–C bonds are weakened while the C–H bonds are strengthened, again with the exception of the C–H bond involving the in-plane methyl hydrogen.

It is interesting to note that in the staggered form, the in-plane methyl hydrogen atom, H8, has an overlap population of +0.0012 with its nearest-neighbor hydrogen atom, H5, while in the eclipsed form, the corresponding overlap population between H8 and H9 has dropped to −0.0002. The internuclear distances for H8–H5 (staggered form) and H8–H9 (eclipsed form) are 4.5980 and 4.5038 au, respectively.

The overlap populations between the C3 carbon atom and the methyl hydrogen are also interesting as the total overlap population between the C3 carbon and all of the methyl hydrogens is 0.0016 in the staggered form but −0.0012 in the eclipsed form. The average of the distances between each methyl hydrogen and the nonmethyl hydrogen nearest to it is 4.7735 au for the staggered form and 5.0482 au for the eclipsed form. The average distance between the methyl hydrogen and C3 carbon atom is 5.7355 au for the staggered form and 5.7117 au for the eclipsed form.

In addition to being measures of bond strength, Mulliken[30] points out that overlap populations in the LCAO theory have practically a one-to-one correspondence with bonded attractions and nonbonded repulsions in valence-bond theory. A positive overlap population corresponds to a bonded attraction while a negative value corresponds to a nonbonded repulsion. With this, Table V, and the data quoted above in mind, the following simple pictures of the origin of the barrier in propylene seem plausible. (a) Ignoring overlap populations and assuming a totally repulsive barrier mechanism, the proton–proton interactions favor the eclipsed form while the proton–carbon interactions favor the staggered form. The stability of the staggered form is thus due to the dominance of the proton–carbon repulsion. (b) As a second alternative, one might argue that at certain internuclear distances, the proton–proton interaction is slightly attractive in nature but the proton–carbon interaction remains repulsive. Thus, both interactions would favor the staggered form. (c) Finally, on the basis of the observed overlap populations, one could argue that both proton–proton and proton–carbon interactions are slightly attractive at the particular internuclear distances observed in propylene. Overlap-population evidence alone is probably not sufficient to establish the nature of a given interaction, but there does seem to be some support for a barrier mechanism which is attractive at certain internuclear distances.

As a final point on the data in Table V, if one adds all the overlap populations for the staggered and eclipsed forms, one obtains the numbers 6.1251 and 6.1131, respectively. Thus, the more stable form is predicted by what could be called a molecular binding number. The stable form is also predicted by comparing the molecular binding numbers for the staggered and eclipsed forms of ethane.[2] Certainly two cases do not establish a trend but, because of the connection between overlap populations and covalent-bond energies and the expectation that the stable rotamer will be more strongly bound than the unstable form, it is not unreasonable to expect a correlation between differences in the molecular binding numbers and the barriers to internal rotation. If such a correlation can be established in a quantitative manner on a number of molecules, it might be possible to test future trial wave

---

(29) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966).

(30) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table V. Population Analysis for the Staggered and Eclipsed Forms of Propylene[a]

	C1	C2	C3	H4	H5	H6	H7	H8	H9
C1		0.7138	−0.0933	0.0004	−0.0001	0.7556	0.7556	0.7675	−0.0272
C2	0.6979		1.1832	−0.0370	−0.0451	−0.0331	−0.0331	−0.0381	0.7813
C3	−0.0955	1.1770		0.7706	0.7743	0.0001	0.0001	0.0014	−0.0389
H4	0.0004	−0.0360	0.7717		−0.0058	−0.0000	−0.0000	0.0000	−0.0002
H5	0.0003	−0.0461	0.7760	−0.0059		0.0000	0.0000	0.0012	0.0001
H6	0.7586	−0.0341	−0.0008	−0.0000	0.0001		−0.0119	−0.0082	−0.0000
H7	0.7586	−0.0341	−0.0008	−0.0000	0.0001	−0.0096		−0.0082	−0.0000
H8	0.7633	−0.0288	0.0004	−0.0000	0.0000	−0.0084	−0.0084		0.0001
H9	−0.0272	0.7835	−0.0387	−0.0003	0.0001	−0.0001	0.0001	−0.0002	
Net atomic (S)	5.1975	5.0290	5.1797	0.3970	0.4040	0.4266	0.4266	0.4131	0.4015
Gross atomic (S)	6.6336	6.2749	6.4785	0.7610	0.7663	0.7779	0.7779	0.7709	0.7590
Net atomic (E)	5.2117	5.0396	5.1870	0.3952	0.4032	0.4169	0.4169	0.4178	0.3985
Gross atomic (E)	6.6398	6.2793	6.4817	0.7601	0.7654	0.7698	0.7698	0.7768	0.7572

[a] Overlap populations for the staggered and eclipsed forms are respectively above and below the diagonal. Net and gross atomic populations for the two forms are denoted by "S" for staggered and "E" for eclipsed forms.

Table VI. Total Forces (Atomic Units) on the Nuclei in the Staggered and Eclipsed Forms of Propylene as Calculated from the Gaussian 52/3 Basis SCF Wave Functions

	Total forces (staggered)				Total forces (eclipsed)			
Nucleus	F_x	F_y	F_z	F_{total}	F_x	F_y	F_z	F_{total}
C1	−0.0883	0.0	0.1765	0.1973	−0.0980	0.0	0.1727	0.1984
C2	−0.1783	0.0	−0.1228	0.2165	−0.1788	0.0	−0.1305	0.2214
C3	−0.2934	0.0	0.0192	0.2941	0.2917	0.0	0.0207	0.2924
H4	0.0377	0.0	−0.0647	0.0750	0.0374	0.0	−0.0644	0.0744
H5	0.0305	0.0	0.0553	0.0632	0.0299	0.0	0.0554	0.0629
H6	−0.0357	−0.0531	0.0014	0.0640	0.0139	−0.0511	0.0304	0.0611
H7	−0.0357	0.0531	0.0014	0.0640	0.0139	0.0511	0.0304	0.0611
H8	0.0431	0.0	0.0584	0.0726	−0.0731	0.0	−0.0157	0.0747
H9	−0.0319	0.0	−0.0604	0.0683	−0.0307	0.0	−0.0593	0.0668

Table VII. Comparison of the Potential at the Nuclei in the Eclipsed and Staggered Forms of Propylene (in Atomic Units)

Atom	*a*	$(1/R)_A^S$	$(1/R)_A^E$	$(1/R)_A^E - (1/R)_A^S$
C1	a	5.41463	5.41463	0.00000
	b	−20.04615	−20.04782	−0.00167
	c	−14.63152	−14.63319	−0.00167
C2	a	6.21712	6.21712	0.00000
	b	−20.81992	−20.82107	−0.00115
	c	−14.60280	−14.60395	−0.00115
C3	a	5.39663	5.39782	0.00119
	b	−20.02564	−20.02840	−0.00276
	c	−14.62901	−14.63058	−0.00157
H4	a	6.24838	6.24925	0.00087
	b	−7.38521	−7.38622	−0.00101
	c	−1.13683	−1.13697	−0.00014
H5	a	6.54163	6.53901	−0.00262
	b	−7.68036	−7.67890	0.00146
	c	−1.13873	−1.13989	−0.00116
H6	a	6.43519	6.59051	0.15532
	b	−7.58220	−7.73872	−0.15652
	c	−1.14701	−1.14821	−0.00120
H7	a	6.43519	6.59015	0.15532
	b	−7.58220	−7.73872	−0.15652
	c	−1.14701	−1.14821	−0.00120
H8	a	6.73150	6.42507	−0.30643
	b	−7.88250	−7.57495	+0.30755
	c	−1.15100	−1.14988	+0.00112
H9	a	6.83488	6.83372	−0.00116
	b	−7.97309	−7.97388	−0.00079
	c	−1.13821	−1.14016	−0.00195

[a] a, nuclear contribution; b, electronic contribution; c, total.

functions by a simple population analysis rather than a complete energy calculation.

Although the limiting Hartree–Fock wave functions must satisfy the Hellmann–Feynman theorem which states that the total force on each nucleus is zero, the limited-basis-set wave functions used here do not satisfy this criterion. Thus Table VI, which gives the direction and magnitude of the calculated forces on the nuclei for each form of propylene, shows the degree to which the Hellmann–Feynman theorem is obeyed.

The operator for the potential at a nucleus A is $\Phi(A) = \Sigma_{N \neq A} 1/r_{NA} + \Sigma_i 1/r_{iA}$. Since the total Hamiltonian contains $1/r$ terms, the calculated potentials at the atoms should be among the most accurate of the electronic properties. In Table VII, the calculated potentials at the atoms for the staggered and eclipsed forms of propylene are compared. There are three main points to be noted from Table VII: (a) rotation of the methyl group has caused a definite change in potential at the atoms throughout the molecule, *i.e.*, the rotation does not affect only nearest neighbor atoms; (b) the sign of the change in potential at the in-plane methyl hydrogen is different from the others; and (c) the change in the potential at the hydrogen atom *trans* to the methyl group is an order of magnitude lower than the rest. It is felt that point "c" is particularly important. If the primary interaction of the hydrogen atoms on carbon C3 with the methyl hydrogen occurs through the bonds, one would expect the potential changes at the *cis* and *trans* hydrogens, H5 and H4, to be about equal. Since this is not the case, the potential change at atom H5 which is *cis* to the methyl group must be regarded as abnormally

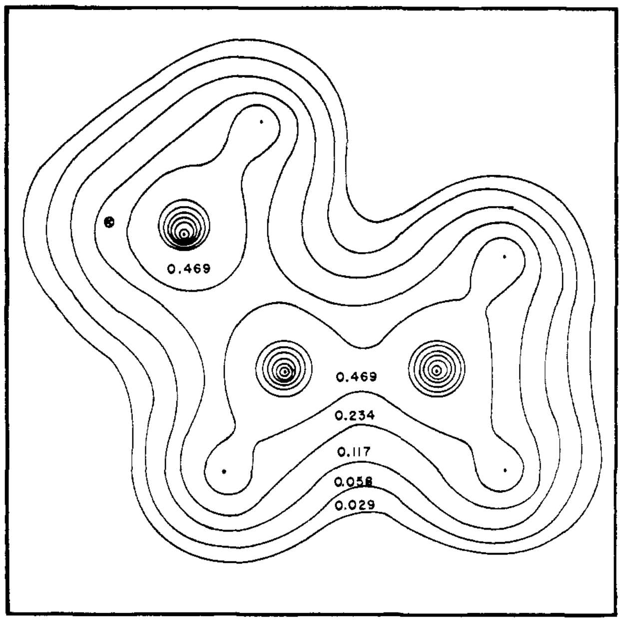

Figure 2. Total electron density map of the staggered form of propylene. The map is in the *xz* plane.

high and therefore indicative of an important nonbonded H(methyl)...H(*cis*) interaction. If it turns out that the abnormally low barrier in *cis*-1-fluoropropylene is reflected in the calculated changes in the potentials at the atoms when the methyl group is rotated, then it would seem that the role of the potential at the atom with respect to internal rotation should be given careful consideration.

The operator for the charge density at a nucleus is defined as $\rho(A) = \Sigma\delta(r_{iA})$ and is probably the least accurate of the operators considered. Dunning, Winter, and McKoy[31] in their study of the one-electron properties of formaldehyde made a comparison of the expectation values of various operators for C, H, and O atoms and found that $\rho(A)$ was far more sensitive to the completeness of the basis set than the other operators considered. They conclude that the major deviation of atomic orbitals in an LCGO approximation from the true Hartree-Fock orbitals occurs very close to and very far from the nucleus. Therefore, one expects the charge densities at the nuclei given in Table VIII to emphasize the inaccuracies of the limited GTO basis set. However, differences in charge densities at given nuclei should be meaningful since identical assumptions were made in each calculation, and, indeed, the per cent changes given in Table VIII do show expected trends. For example, upon rotation of the methyl group, one would expect that methyl atoms are affected more than the atoms in the rest of the molecule, that atom H9 is affected more than the more distant atoms H4 and H5, and that H5, being furthest removed from the methyl group, will suffer the smallest density change. These expectations are borne out by the data in Table VIII. The one apparent anomaly is that the distant carbon, C3, shows more density change than the closer carbon atom, C2. This might be explained by a high ease of charge transfer through a double bond which could increase the interaction of C3 with the methyl group.

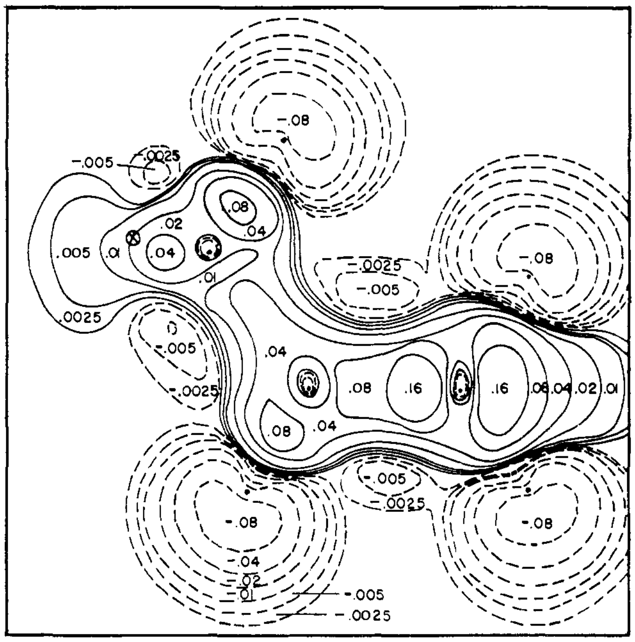

Figure 3. Density difference map of the *xz* plane of the staggered form of propylene. The difference map was obtained by subtracting the densities of the individual atoms at the equilibrium positions from the total molecular density map shown in Figure 2. The dashed lines show where the molecular charge density has decreased relative to that of the noninteracting atoms.

Table VIII. Charge Densities at the Nuclei in the Staggered Form of Propylene and the Per Cent Change upon Rotation of the Methyl Group

Center	Charge density	% change
C1	103.88619	−0.00118
C2	103.94946	−0.00062
C3	103.97190	−0.00093
H4	0.36921	−0.04063
H5	0.36469	0.07129
H6	0.36694	−0.21257
H7	0.36694	−0.21257
H8	0.37336	0.26784
H9	0.36882	0.10303

Table IX contains the expectation values for the dipole moment, quadrupole moment, and second-moment-of-charge operators. These operators are respectively

$$\mu_\alpha(A) = \sum_N r_{NA}^\alpha - \sum_i r_{iA}^\alpha \qquad \alpha = x, y, z \qquad (1)$$

$$\theta_{\alpha,\beta}(A) = \sum_N (3r_{NA}^\alpha r_{NA}^\beta - \delta_{\alpha,\beta} r_{NA}^2) - \sum_i (3r_{iA}^\alpha r_{iA}^\beta - \delta_{\alpha,\beta} r_{iA}^2) \qquad (2)$$

and

$$\langle r_\alpha r_\beta \rangle(A) = \sum_N r_{NA}^\alpha r_{NA}^\beta - \sum_i r_{iA}^\alpha r_{iA}^\beta \qquad (3)$$

In Table IX, $\mu_\alpha(A)$ is calculated with respect to the origin of the coordinate system, and $\theta_{\alpha\beta}(A)$ and $\langle r_\alpha r_\beta \rangle$ (A) are calculated with respect to the center of mass.

---

[31] T. H. Dunning, Jr., N. W. Winter, and V. McKoy, *J. Chem. Phys.*, **49**, 4128 (1968).

Table IX. Calculated Properties for the Staggered and Eclipsed Forms of Propylene

Property	Staggered form			Eclipsed form		
	Nuclear	Electronic	Total	Nuclear	Electronic	Total
μ_x[a]	5.6102	−5.7384	−0.1282	5.7893	−5.8914	−0.1021
μ_y	0.0	0.0	0.0	0.0	0.0	0.0
μ_z	21.0995	−21.0421	0.0574	21.2214	−21.1307	0.0907
$\bar{\mu}$			0.1405			0.1366
$\bar{\mu}$, D			0.357			0.347
Q_{xx}[b]	66.7816	− 65.2530	1.5286	65.7680	−64.4397	1.3283
Q_{yy}	−67.8990	65.0396	−2.8594	−67.7488	64.9246	−2.8242
Q_{zz}	1.1174	0.2135	1.3309	1.9807	−0.4849	1.4958
Q_{xz}	−20.4168	20.4422	0.0254	−20.3744	20.4046	0.0302
Asymmetry parameter[c]			−0.0714			−0.0630
$\langle r_x r_x \rangle$[d]	95.2866	−107.4632	−12.1764	94.5108	−106.8162	−12.3053
$\langle r_y r_y \rangle$	5.4996	−20.6014	−15.1018	5.4996	−20.5733	−15.0736
$\langle r_z r_z \rangle$	51.5105	−63.8188	−12.3082	51.9859	−64.1796	−12.1936
$\langle r_x r_z \rangle$	−40.8336	40.8844	0.0508	−40.7489	40.8091	0.0602
$\langle r^2 \rangle$	152.2968	−191.8833	−39.5865	151.9964	−191.5690	−39.5727

[a] Components of the dipole moment in atomic units. Experimental value = 0.364 ± 0.004 D. [b] Molecular quadrupole moment tensor calculated with respect to the center of mass. [c] Asymmetry parameter was determined from $\eta = (Q_{xx}^* - Q_{yy}^*)/Q_{zz}^*$ where Q^* is the quadrupole moment tensor in the principle axis system and $Q_{xx}^* \geq Q_{yy}^* \geq Q_{zz}^*$. [d] Second moments of the charge distribution calculated with respect to the center of mass. The diamagnetic susceptibilities are obtained from the electronic contributions to the second moments according to the following equations: $\chi_{av}^d = \chi_0 \langle r^2 \rangle$ and $\chi_{GG}^d = (3\chi_0/2)(\langle r^2 \rangle - \langle r_G r_G \rangle)$ ($G = x, y$, or z), where $\chi_0 = 0.791988$ emu/mole bohr^2.

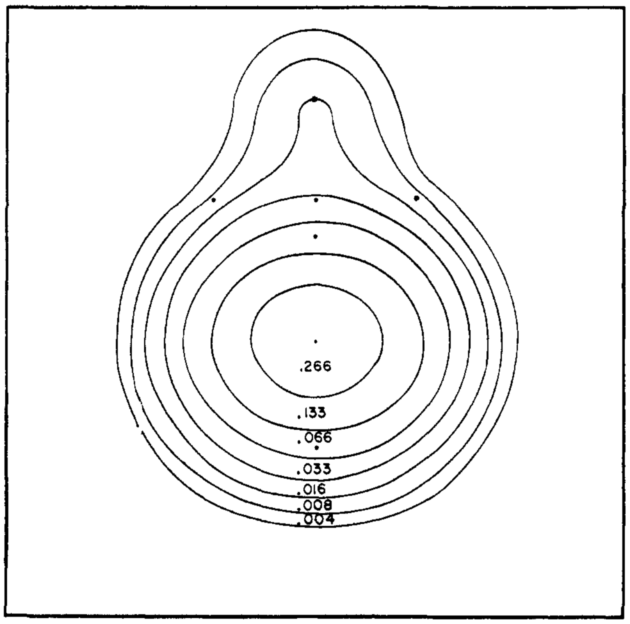

Figure 4. Total electron density map of the staggered form of propylene. The plane of the map is parallel to the yz plane and contains the midpoint of the C2=C3 bond. The points shown are the projections of the various atoms on the plane of the map.

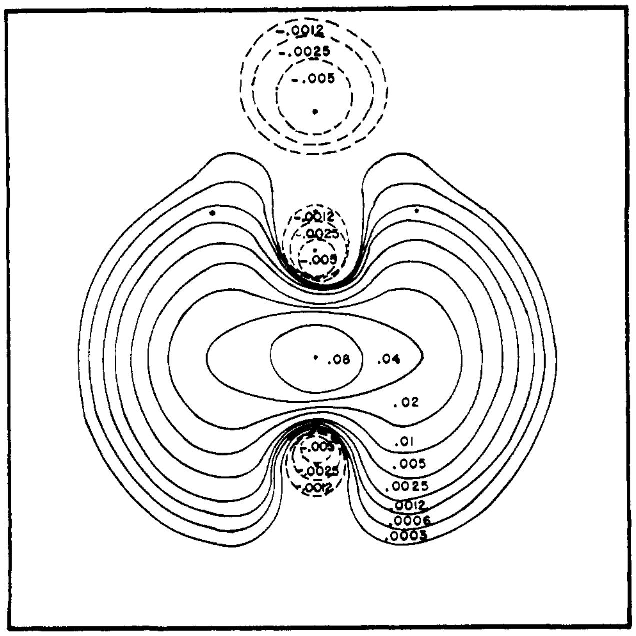

Figure 5. Density difference map in a plane parallel to the yz plane in propylene and containing the midpoint of the C2=C3 bond. The map was obtained by subtracting the densities of the individual atoms at the equilibrium positions from the total molecular density map shown in Figure 4. The dashed lines show where molecular charge density has decreased relative to that of the noninteracting atoms.

The experimental value of the dipole moment in propylene[18] is 0.364 ± 0.003 D and makes an angle of either 17 ± 3 or 33 ± 3° with the C–C single bond. Two angles are given because the sign of the angle between the dipole moment and the **a** principle axis cannot be determined from the Stark effect. Using data from Tables II and IX, the angle is calculated to be 31° 37′, in good agreement with experiment. As can be seen from eq 2 and 3, $\theta_{\alpha\beta}(\mathrm{A})$ and $\langle r_\alpha r_\beta \rangle(\mathrm{A})$ are both measures of the r^2 dependence of the wave function. The $\langle r_\alpha r_\beta \rangle(\mathrm{A})$ operator is the more direct measure as $\langle r^2 \rangle = \mathrm{tr}\langle r_\alpha r_\beta \rangle$. From the $\langle r_\alpha r_\beta \rangle$ values in Table IX, we see that as the methyl group rotates from the staggered to the eclipsed conformation, the wave function expands in the x direction and contrasts in the y and z directions. The total effect, as indicated by $\langle r^2 \rangle$, is a contraction of the charge distribution as the methyl group rotates to the top of the barrier. This contraction is also reflected in the higher kinetic energy of the eclipsed conformation.[32]

Electron-density maps are useful in obtaining mental

---

(32) We refer here to the kinetic energy as calculated from the unscaled wave functions since unscaled functions were used to calculate the properties in Tables V–IX.

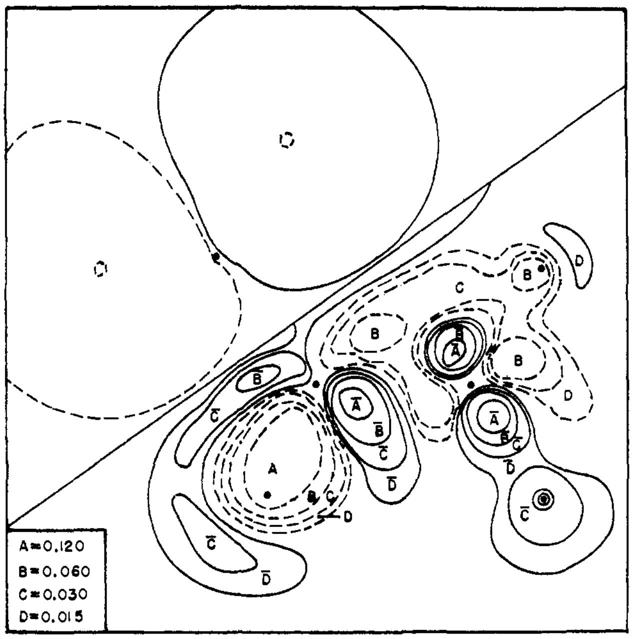

Figure 6. Electron-density difference map between the staggered and eclipsed forms of propylene. The dashed contours show where the molecular electronic density of the eclipsed form is greater than that of the staggered form and the solid contours indicate where the reverse is true.

pictures of the charge distributions in molecules.[33] Density-difference maps, obtained by placing the spherical, noninteracting, ground-state atoms at the equilibrium positions and subtracting the resulting atomic map from the molecular map, are also of interpretative value as they show how the charge density changes during the hypothetical formation of the molecule from appropriately positioned atoms. Figures 2–5 show total-density maps and density-difference maps for two views of the stable (staggered) form of propylene. In Figure 3, one can see the increase in charge density between formally bonded nuclei as well as the C^{-}–H^{+} polarity of the C–H bonds mentioned earlier. In Figure 5, the expected density increase in the area of the π bond is clearly seen.

Additional insight into the barrier mechanism is obtained through the density map of Figure 6, which is a difference map between the staggered and eclipsed forms of propylene. The dots show the positions of the nuclei which remain stationary during rotation of the methyl group. Because the methyl hydrogens shift positions, detail in the area above the diagonal line has been omitted. The dashed contours show where the density of the eclipsed form is greater than that of the staggered from, and the solid contours indicate regions where the reverse is true. Thus, Figure 6 allows one to observe that, as the methyl group rotates from the staggered to the eclipsed form, (a) the charge density between nuclei C2 and H9 increases, (b) the charge density in bond C3–H4 decreases, (c) the charge density in the regions of the C3–H5 and C2–C3 axes exhibits both increase and decrease with no clear net gain or loss, and (d) a small charge-density decrease occurs in the region out beyond the nonmethyl hydrogen nuclei, especially center H9. This latter effect means that the staggered form of the molecule is somewhat larger than the eclipsed form—an observation which is in accord with the kinetic energy and second-moment-of-charge data discussed earlier.

Summary

Examination of various properties and the population analysis for the two conformations of propylene shows that rotation of the methyl group has a definite effect on every atom in the molecule. This emphasizes the contention that the origin of the barrier is a complex interplay of many intramolecular interactions.

Overlap-population analysis seems to indicate that the potential barrier function should include an attractive term along with the usually dominant repulsion terms. Whether the indicated attractive contribution is general or unique to propylene cannot be determined until several different molecules have been studied theoretically. We have also proposed that changes in molecular binding numbers as determined from overlap populations should correlate with experimental barrier data, and have pointed out that small inaccuracies in atomic coordinates can cause appreciable errors in barrier calculations. Also, it appears that electron-density difference maps are a good means of describing the flow of electronic charge in the molecule due to configurational changes.

---

(33) R. F. W. Bader, I. Keaveny, and P. E. Cade, *J. Chem. Phys.*, 47, 3381 (1967), and references therein.