Methyl Rotation Barriers and Hyperconjugation[1]

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Abstract: *Ab initio* self-consistent-field calculations of barriers to methyl rotations are reported and analyzed for ethane, propane, propene, and acetaldehyde. All of the calculations were performed with equivalent atomic optimized Gaussian bases and at idealized molecular geometries to obtain results which are directly intercomparable. Total barriers show good agreement with experimental values, revealing virtual independence of basis and precise molecular geometries. Although barrier component analyses are geometry and basis dependent, resolution of the barrier energy into one-electron and pure repulsive components is demonstrated to be useful. Hyperconjugation is found in both propene and acetaldehyde, with small changes in the extent of hyperconjugation as methyl rotation occurs. The results support the conclusion that in alkanes the methyl rotation barrier is due to repulsive interactions, while in π-electron molecules attractive-type one-electron interactions predominate.

Barriers to internal rotation in molecules are among the most interesting problems in chemistry that are directly amenable to quantum mechanical treatment. Experimental methyl rotation barriers are generally reproduced well by *ab initio* self-consistent-field calculations.[2-13] However, such calculations have not been so successful in identifying the precise nature of these barriers. They have been variously attributed predominantly to nuclear repulsions,[14] to C–H bond orbital repulsions,[8] to one-electron attractions,[12] and to a balance of electrostatic contributions.[15] Two different groupings of barrier components have been proposed as most significant,[4,16] while Pedersen and Morokuma[5] have emphasized the ambiguities inherent in ascribing a barrier to any single factor. The many barrier calculations have not been readily intercomparable, since they were performed with different bases, varying geometries, and often minimal or conflicting analyses.

The present calculations of barriers to methyl rotation in ethane, propane, propene, and acetaldehyde are designed to facilitate intercomparison of results, and to maximize conceptual usefulness. For this purpose the calculations were performed with equivalent hybridized atomic bases and with standardized molecular geometries. It is found that experimental barriers are reproduced well, and that calculated total barriers are insensitive to bases[3,6] and to precise geometries.[11] Upon partitioning the barriers into repulsive and one-electron contributions, the ethane and propane barriers are due to repulsions, while the smaller propene and acetaldehyde barriers arise from one-electron components. Hyperconjugation also is identified in the propene and acetaldehyde molecules as an ingredient in the barriers.

Calculations

The *ab initio* self-consistent-field IBMOL program of Clementi and Davis[17] was modified to permit transformation to hybridized atomic bases, while retaining the capacity for contraction of bases and linear transformation to symmetry orbitals. The bases used were atomic optimized Gaussian bases[18] which have proved useful and near optimal for molecular SCF calculations.[7,10,19] The bases for carbon and oxygen were the 5s3p sets, while the hydrogen functions were the 2s set optimized in methane.

For each heavy atom the five s functions were contracted to a 1s and a 2s function centered at the nucleus, and each set of three p functions was contracted to a single $2p_x$, $2p_y$, or $2p_z$. For each hydrogen the two s functions were contracted to a single 1s. The resultant 2s and 2p functions on each heavy atom were then linearly transformed to the appropriate sp^3 or sp^2 hybrid orbitals.

To maintain full compatibility with the ideally hybridized bases, standard molecular geometries were used throughout. All bond angles were exactly tetrahedral or trigonal, and bond lengths were constant at the standard values[20] in Table I.

Table I. Standard Bond Lengths,[a] Å

C–C		1.540
C=C		1.340
C=O		1.230
C–H	Tetrahedral	1.100
C–H	Trigonal	1.070
C–H	Trigonal, aldehyde	1.115

[a] Reference 20.

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(1) This research was supported in part by the National Science Foundation, Grant No. GY-8509.

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(20) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

Calculations were performed for each molecule at the minimum- and maximum-energy orientations of the methyl groups, and in some cases for intermediate angles of rotation as well. The system of specification of rotation angle for each molecule is shown in Figure 1. In each case $\theta = 0°$ corresponds with H_1 at 12 o'clock when looking down the C–C axis with the methyl group nearest the viewer. In each calculation the total energy was decomposed into its one-electron component, $H_0 = T + V_{ne}$, two-electron repulsion energy, V_{ee}, and nuclear repulsion energy, V_{nn}, in order to learn if the methyl rotation barrier generally can be attributed to specific components.

Ethane

The rotation barrier in ethane has probably received more attention than has any other. Pitzer and Lipscomb[2] in 1963 studied this molecule using a basis of Slater orbitals, and subsequently a number of other investigators have performed similar calculations with different bases and different geometries, and with varying interpretations. In nearly every case the agreement with the experimental[21] barrier value, 0.0048 hartree, has been good. The methyl rotation barrier in ethane is therefore a conventional test for barrier calculation methods, albeit one for which failure appears to be nearly impossible.

The results of the present methyl rotation barrier calculation are compared in Table II with those of Fink and Allen,[4] for which similar component analyses are available. The present calculation yields a total barrier once again in good agreement with the experimental values, and the component analyses agree well with those of Fink and Allen. In ethane, at least, the methyl rotation barrier appears to be due mostly to electron repulsions, with smaller contributions from nuclear repulsions. The one-electron energy is actually lowest in the eclipsed, high-energy conformation.

Table II. Comparisons of Ethane Energies and Components (hartrees)

	0°	60°	Δ
Fink and Allen[a]			
H_0	−188.2909	−188.3092	−0.0183
V_{ee}	67.21208	67.22699	0.01491
V_{nn}	41.93098	41.93485	0.00747
E_{total}	−79.14778	−79.14377	0.00401
This work			
H_0	−186.79086	−186.81370	−0.02284
V_{ee}	65.95160	65.97204	0.02044
V_{nn}	42.01964	42.02726	0.00762
E_{total}	−78.81963	−78.81440	0.00523
Experimental[b]			0.0048

[a] Reference 4. [b] Reference 21.

Propane

Since propane contains two methyl groups simultaneous rotations can and do occur. The microwave spectrum of transitions between the first excited torsional states has been reported and analyzed by Hirota, Matsumura, and Morino.[22] Hoyland[7] has also analyzed their data, finding the value 0.0052 hartree for the barrier to single methyl rotation.

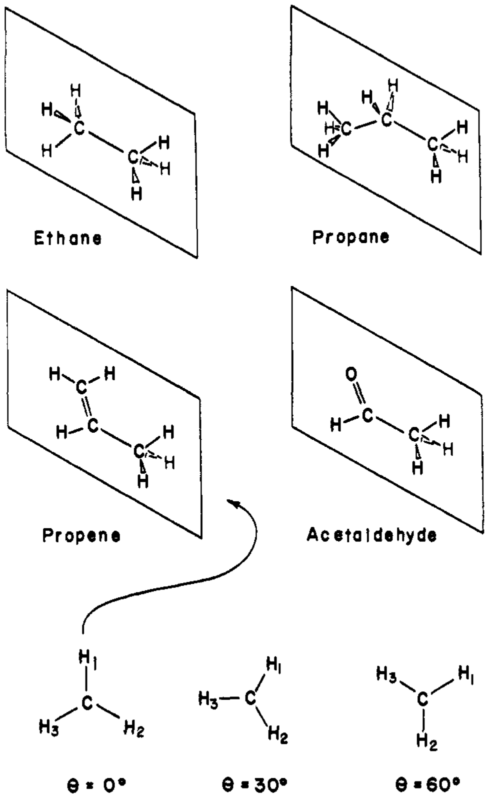

Figure 1. Molecular geometries and methyl rotation angles for ethane, propane, propene, and acetaldehyde.

Hoyland has also carried out *ab initio* calculations of the barrier, using two different bases. The smaller was a 5s2p/2s set, and the larger a 7s3p/3s Gaussian set. The calculated barriers were in both cases in good agreement with the experimental value, but no component analyses were published. Table III contains a comparison of the present results with those of Hoyland and also includes our component analyses. Once again the results agree reasonably well with experiment, despite the rigid molecular geometry.

Table III. Comparisons of Propane Energies and Components (hartrees)

	0°	60°	Δ
Hoyland[a]			
E_{total}	−117.58122	−117.57624	0.00498
Hoyland[b]			
E_{total}	−118.06452	−118.05952	0.00500
This work			
H_0	−318.40260	−318.47110	−0.06850
V_{ee}	118.33923	118.38230	0.04307
V_{nn}	82.38576	82.41689	0.03113
E_{total}	−117.67760	−117.67191	0.00569
Experimental[c]			0.0052

[a] Reference 7, 5s2p/2s basis. [b] Reference 7, 7s3p/3s basis. [c] References 7 and 22.

For propane the methyl rotation barrier consists of comparable contributions from electron repulsions and from nuclear repulsions, as compared with ethane in which the nuclear repulsions are distinctly smaller, even though the total barrier is similar. In propane

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(21) D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958).

(22) E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jap.*, **40**, 1124 (1967).

again, the one-electron energy is substantially lower in the eclipsed form.

Propene

The present calculations of the methyl rotation barrier in propene can be compared with that of Unland, Van Wazer, and Letcher (UVWL).[10] They used a similar 5s2p/3s basis containing the atomic-optimized 5s2p basis on carbons, but they also adopted the experimental geometry. Another, somewhat less adequate calculation with a Gaussian 5s3p/3s basis has been reported by Hoyland.[23] A comparison of the results of these calculations, together with available component analyses, is contained in Table IV.

Table IV. Comparisons of Propene Energies and Components (hartrees)

	0°	60°	Δ
Unland, Van Wazer, and Letcher[a]			
H_0	−295.49760	−295.52498	−0.02738
V_{ee}	108.40311	108.42864	0.02553
V_{nn}	70.69848	70.70268	0.00420
E_{total}	−116.39601	−116.39366	0.00235
Hoyland[b]			
H_0			0.0414
V_{ee}			−0.0200
V_{nn}			−0.0200
E_{total}	−116.2378	−116.2365	0.0013
This work			
H_0	−293.91126	−293.89561	0.01565
V_{ee}	106.60383	106.60953	0.00570
V_{nn}	70.80909	70.79044	−0.01865
E_{total}	−116.49834	−116.49564	0.00270
Experimental[c]			0.0032

[a] Reference 10. [b] Reference 23. [c] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

Both the UVWL results and the present ones are in adequate agreement with the experimental methyl rotation barrier, confirming again the insensitivity of barrier calculations to basis choice and precise molecular geometries. There the similarity ends, however, since the two calculations attribute the barrier to different factors. The UVWL calculation finds the barrier largely due to electron repulsions, with the one-electron component lowering the barrier. In contrast, the present calculations attribute the barrier predominantly to the one-electron component, with a large negative contribution from nuclear repulsions. Thus, between the two calculations, two of the three barrier components differ not only in magnitude, but even in sign.

The Hoyland calculation yields a poorer barrier, yet comparison of barrier components with those of UVWL is even more dramatic—the signs of all three components differ in these two calculations!

Acetaldehyde

Davidson and Allen[12] have published an extensive calculation of the methyl rotation barrier for acetaldehyde, using a large basis and the experimental geometry of Kilb, Lin, and Wilson.[24] The calculated total barrier agrees well with the experimental value[25] of 0.00185 hartree.

Table V. Comparison of Acetaldehyde Energies and Components (hartrees)

	0°	60°	Δ
Davidson and Allen[a]			
H_0	−345.31144	−345.29288	0.01856
V_{ee}	122.85056	122.84169	−0.00887
V_{nn}	69.60593	69.59796	−0.00797
E_{total}	−152.85495	−152.85323	0.00172
This work			
H_0	−342.20878	−342.18481	0.02397
V_{ee}	120.86766	120.85732	−0.01034
V_{nn}	69.11000	69.09851	−0.01149
E_{total}	−152.23111	−152.22898	0.00213
Experimental[b]			0.00185

[a] Reference 12. [b] Reference 25.

Table V contains a comparison of barrier calculation results. Although the present work yields a poorer total energy and rotation barrier, the calculations give barrier components of comparable magnitudes and like signs. Both calculations attribute the barrier to one-electron components, with electron repulsions and nuclear repulsions decreasing upon rotation.

Rotation Barrier Components

Fink and Allen[4] originally introduced analysis of rotation barriers in terms of the components ΔV_{ee} and $\Delta(T + V_{nn} + V_{ne})$. More recently Allen[16] has proposed the partitioning of $\Delta(T + V_{nn} + V_{ee})$ and $\Delta V_{ne'}$ in order to permit identification of repulsive and attractive components. A still more useful form consists of the one-electron component $\Delta(T + V_{ne})$ and the pure repulsive component $\Delta(V_{nn} + V_{ee})$. This resolution facilitates physical interpretation and at the same time achieves improved structural invariance.

An analysis similar to that of Pedersen and Morokuma[5] shows that the variations of barrier energy terms upon virial-theorem scaling are closely approximated by

$$\delta\Delta T \simeq 2T\Delta\eta$$

$$\delta\Delta V_{ne} \simeq V_{ne}\Delta\eta$$

where $\Delta\eta$ is the change in the scale factor η between the methyl configurations of maximum and minimum energies. Examination of *ab initio* data[5] reveals that for these molecules V_{ne} is approximately $-3T$, and consequently

$$\delta\Delta(T + V_{ne}) \simeq (2T - 3T)\Delta\eta = -T\Delta\eta$$

$$\delta\Delta V_{ne} \simeq -3T\Delta\eta$$

Thus, the variation in the one-electron barrier component upon scaling is about one-third of that for the pure attractive term ΔV_{ne} alone. Nearly equal, but opposite variations occur for the complementary repulsive components.

$$\delta\Delta(V_{nn} + V_{ee}) \approx T\Delta\eta$$

$$\delta\Delta(T + V_{nn} + V_{ee}) \approx 3T\Delta\eta$$

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(23) J. R. Hoyland, *J. Amer. Chem. Soc.*, **90**, 2227 (1968).

(24) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, 26, 1695 (1957).

(25) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1953, p 240.

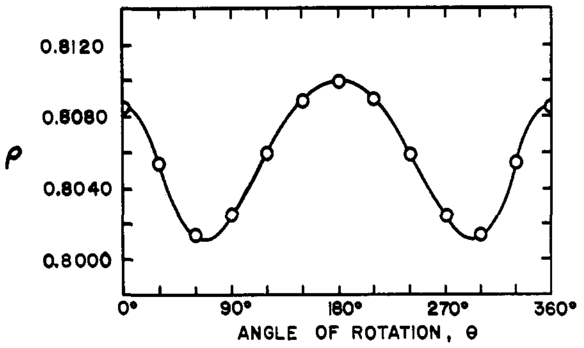

Figure 2. Single methyl proton electron density in propene as a function of methyl rotation angle.

Thus, resolution of rotation barriers into one-electron and pure-repulsive components is advantageous, as shown in Table VI. This resolution supports the conventional interpretation that the ethane and propane barrier is due to electron and nuclear repulsions, and thus is of the repulsive type. In contrast, in propene and in acetaldehyde this repulsive term decreases upon rotation, and the barrier arises from the increase in one-electron energy. This type of attractive barrier has been suggested by Hoyland[23] and hinted at by UVWL[10] for propene, and reported for acetaldehyde by Davidson and Allen.[12]

Table VI. Methyl Rotation Barrier Components for Ethane, Propane, Propene, and Acetaldehyde (hartrees)

	Ethane	Propane	Propene	Acetaldehyde
$\Delta(V_{ee} + V_{nn})$	0.0280	0.0742	−0.0129	−0.0218
$\Delta(T + V_{ne})$	−0.0228	−0.0685	0.0156	0.0240
Barrier	0.0052	0.0057	0.0027	0.0022
Experimental	0.0048[a]	0.0052[b]	0.0032[c]	0.0018[d]

[a] Referencs 21. [b] References 7 and 22. [c] Reference 24. [d] Reference 25.

Hyperconjugation

Interaction of the electron densities of the methyl C–H bonds with the π-electron densities in propene and acetaldehyde constitutes hyperconjugation. The extent of these interactions changes with methyl rotation, as do the charges on individual atoms. In order to gain information about possible correlations of hyperconjugate effects and rotation barriers, Mulliken population analyses[26] were performed at various methyl rotation angles in propene and acetaldehyde. For propene, the electron densities at each atom for different rotation angles are listed in Table VII.

As rotation from the lowest energy conformation occurs, the most striking features are an increase of electron density at the methyl carbon, C_3, and a decrease in the density at the hydrogen, H_1, which rotates out of the carbon-atom plane. The density, ρ, at a methyl hydrogen varied throughout a full 180° of rotation, as shown in Figure 2. The electron density reaches two different maxima at the two different planar positions, and a minimum not at 90°, but rather at 60°. At this minimum density position the hydrogen projects from the carbon plane, yet is still relatively near the π-electron system.

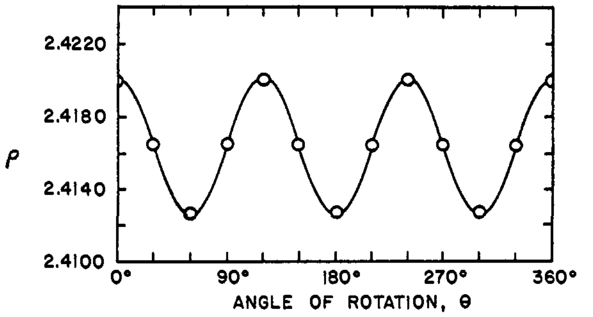

Figure 3. Total of three methyl proton electron densities in propene as a function of methyl rotation angle.

Table VII. Propene Atom Electron Densities at Different Methyl Rotation Angles

	0°	30°	60°
C_3 (methyl)	6.5590	6.5619	6.5646
H_1 (methyl)	0.8085	0.8053	0.8014
H_2 (methyl)	0.8058	0.8088	0.8099
H_3 (methyl)	0.8058	0.8024	0.8014
C_2 (methine)	6.1953	6.1956	6.1960
H_4 (methine)	0.8008	0.8011	0.8013
C_1 (methylene)	6.4077	6.4087	6.4094
H_5 (methylene)	0.8070	0.8069	0.8068
H_6 (methylene)	0.8100	0.8095	0.8091

The total density at the three methyl protons is a symmetric function with a period of 120°. As shown in Figure 3, this density reaches a minimum at 60°, when two of the protons, H_1 and H_3, are in position such that their electrons can interact with the π-electron system.

The extent to which the changes in electron distribution correlate with changes in hyperconjugation is measured by the π-electron densities at each of the three carbon atom groups in propene. Two occupied molecular orbitals, numbers 9 and 12, contain the π-electron density, and Table VIII shows the total distribution in these orbitals at the methyl configurations of minimum and maximum energy. Also included are the σ and total electron distributions in these groups.

Table VIII. Group Electron Distributions in Propene and in Acetaldehyde for Methyl Rotation Conformations of Minimum (θ = 0°) and Maximum (θ = 60°) Energy

	Propene		Acetaldehyde	
	0°	60°	0°	60°
$\rho(CH_3)$				
π	1.9900	1.9891	1.9815	1.9809
σ	6.9891	6.9882	6.9979	6.9975
Total	8.9791	8.9773	8.9794	8.9784
$\rho(CH)$				
π	0.9680	0.9699	0.8928	0.8921
σ	6.0281	6.0274	5.8589	5.8598
Total	6.9961	6.9973	6.7517	6.7519
$\rho(CH_2$ or O)				
π	1.0420	1.0411	1.1256	1.1270
σ	6.9827	6.9843	7.1435	7.1428
Total	8.0247	8.0254	8.2691	8.2698

At each configuration of propene there is a donation of electron density from the methyl group and from the

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(26) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

methine group to the methylene. The methyl group loses both σ and π density, while the methine registers an increase in σ density. The methylene increases in π density, but loses σ density to the CH group. As methyl rotation occurs to the high-energy conformation, the methyl group loses still more σ- and π-electron density, while in the remainder of the molecule both σ and π density excursions diminish.

In acetaldehyde the electron distributions and changes upon methyl rotation are similar to those in propene, although not identical. In acetaldehyde the methyl C–H bonds are more polarized than in propene, and the oxygen atom is more effective in electron withdrawal than is the methylene group of propene. A comparison of the σ, π and total group electron densities for acetaldehyde with those of propene is contained in Table VIII. Although the total electron donation by the methyl group of acetaldehyde is quite close to that of propene, in acetaldehyde this donation is nearly all of π-electron density. That is, hyperconjugation is, as expected, more prominent in acetaldehyde.

The experimental barrier to methyl rotation in acetaldehyde is 59% of the barrier in propene. It is interesting to note that as methyl rotation occurs in acetaldehyde, the loss in electron density at the methyl group is 62% as large as in propene.

Lowe[27] has proposed a simple MO explanation for the rotation barrier in ethane based essentially upon a hyperconjugate effect involving degenerate pseudo-π antibonding MO's which are lower in energy for the staggered ethane than for the eclipsed. England and Gordon[28] offer a barrier explanation in terms of one-electron interference energy differences, which they also relate to hyperconjugate effects and consider "largely equivalent" to the Lowe interpretation. While Epstein and Lipscomb[29] have commented upon the limitations of such interpretations when bond lengths charge during methyl rotation, nonetheless barrier explanations in terms of hyperconjugate effects are at least qualitatively useful in the case of ethane.

In the *ab initio* calculations for both propene and acetaldehyde, the higher energy π MO is antibonding across the methyl C–C bond, and is lowest in energy when the methyl group occupies its minimum energy configuration. Thus, just as in Lowe's observations for ethane, the pseudo-π antibonding MO of propene and of acetaldehyde stabilized the normal conformation and contributed a substantial portion of the methyl rotation barrier.

Additional perspective on the hyperconjugative effect is obtained by reference to the barrier component analyses of Table VI. Considering the ethane and propane data as representative of the "normal" case with little or no hyperconjugation, we see that the hyperconjugative effect in propene and in acetaldehyde is accompanied by a reduction in the total rotation barrier, and a reversal of the contributions of its two components. The "normal" methyl rotation occurs with an increase in the repulsive component, which is only partially compensated by the change in the attractive component. On the other hand, in the cases of propene and acetaldehyde, the one-electron energy component increases upon methyl rotation, while the repulsion component decreases. The hyperconjugative transfer of electron density from the methyl C–H bond regions into the π-electron system occurs with a net decrease in the magnitude of the (negative) one-electron energy. The more diffuse electron distribution is less attracted to the nuclei. Repulsive energies also decrease in magnitude with delocalization upon rotation, but this decrease is smaller than the loss of attractive energy.

Conclusions

Several conclusions can legitimately be drawn from the results of these *ab initio* calculations performed under carefully standardized conditions.

(1) While experimental methyl rotation barriers are reproduced well by *ab initio* calculations, barrier components are strongly basis and geometry dependent.[5,11,29,30] This suggests caution in drawing conclusions about the nature of barriers from intercomparisons of different types of calculations.

(2) It is useful and illuminating to resolve the calculated methyl rotation barrier into a one-electron component $\Delta(T + V_{ne})$ and a pure repulsive component $\Delta(V_{ee} + V_{nn})$.

(3) Component analyses support the interpretation that the methyl rotation barrier in ethane and in propane is of the repulsive type, while in propene and in acetaldehyde it is due to one-electron terms and consequently is described as of the attractive type.

(4) Hyperconjugation in the form of electron donation by the methyl group to the π-electron system of propene and acetaldehyde is discernible in *ab initio* calculations. The changes in extent of hyperconjugation with methyl rotation are small, but of the same relative magnitudes as the changes in total energy responsible for the barrier to rotation.

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(27) J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

(28) W. England and M. S. Gordon, *ibid.*, **93**, 4649 (1971).

(29) I. R. Epstein and W. N. Lipscomb, *ibid.*, **92**, 6094 (1970).

(30) A. Veillard, *Theoret. Chim. Acta*, **18**, 21 (1970).