

MOLECULAR ORBITAL STUDIES OF CONFORMATION

J. A. POPLÉ

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 12 January 1974)

Abstract—The application of single-configuration molecular orbital theory to the conformations of small organic molecules is reviewed. Emphasis is laid on systematic *ab initio* studies using simple gaussian-type basis sets for expansion of the molecular orbitals. Topics dealt with include the prediction of bond angles, single-rotor potential functions, effects of single and double (1,2) substitutions on such rotors and double-rotor potentials involving two internal rotation coordinates.

INTRODUCTION

During the last decade, single-configuration MO theory has developed sufficiently to permit a wide range of applications to the stereochemistry of small organic molecules. Early work (1963–68) involving zero-differential-overlap semiempirical schemes^{1–3} and simple *ab initio* calculations^{4–8} indicated that many qualitative features of bond valence angles and dihedral (internal rotation) angles are adequately described by single-determinant MO wave functions and energies. Progress during this period was reviewed by Allen⁹ in 1969. Since that time, the sensitivity of theoretical results to the accuracy of the MO's (choice of expansion basis set) has been widely explored. Also some comprehensive surveys have been made of stereochemical predictions for all organic molecules of a certain size or less using a particular basis.^{10–12} This article will deal with some of these more recent developments. Particular emphasis will be laid on results using the procedures developed at Carnegie-Mellon University, although many similar results using parallel methods have been obtained elsewhere.

Quantum mechanical procedures

We shall only be concerned with diamagnetic closed shell species in this article. For all such molecules, the usual form of single-configuration MO theory assigns electrons in pairs to MO's $\psi_1, \psi_2, \dots, \psi_n$ and then constructs an antisymmetric many-electron wave function as a single determinant

$$\Psi = A |\psi_1, \alpha)(\psi_1, \beta) \dots (\psi_n, \beta)| \quad (1)$$

where α and β are spin functions and A is a normalization constant. The perfect MO's are those which minimize the energy expectation value

$$\mathcal{E} = \int \dots \int \Psi^* \mathcal{H} \Psi \, d\tau \quad (2)$$

where \mathcal{H} is the full many-electron Hamiltonian including electron interaction.

In almost all practical applications of MO theory, the individual orbitals are approximated as linear combinations of a set of given functions (basis functions) ϕ_μ ,

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu} \quad (3)$$

This is sometimes referred to as the linear combination of atomic orbital (LCAO) approximation, but the basis functions ϕ_μ need not be precise representations of atomic orbitals. If the MO's (3) are fed into the wave function (1), the energy (2) can be minimized with respect to the linear coefficients $c_{\mu i}$ to give the lowest single configuration MO energy for the basis ϕ_μ . This leads to the well known algebraic equations of Roothaan¹³ (LCAO self-consistent field or LCAOSCF method).

If the basis functions ϕ_μ are centered at the atomic nuclei and are well-defined, then the LCAOSCF procedure with a given basis constitutes a 'theoretical chemical model' which can be applied to any molecule with any nuclear configuration, provided computation is feasible. Such models have been widely used in theoretical studies of molecular conformations.

Types of *ab initio* models can be classified according to the basis set ϕ_μ . The simplest type of basis is *minimal* and consists only of just enough functions ϕ_μ to permit a description of the ground states of the separated atoms. The minimal basis functions are usually chosen to correspond approximately to atomic orbitals. Thus, there will be one function(1s) for each hydrogen, five functions (1s, 2s, 2px, 2py, 2pz) for each carbon etc. A simple choice of a minimal basis consists of Slater-type orbitals (STO) with exponential radial parts.¹⁴ In practice, however, it is necessary to replace each STO by a least squares-fitted combination of gaussian

functions¹⁵ to permit explicit integration in (2). The minimal basis that we have mostly used contains three gaussians per STO and is referred to as STO-3G.¹⁶

At a simpler level the *ab initio* minimal basis studies are the semiempirical schemes based on zero-differential overlap approximations (CNDO, INDO etc.). These use a minimal Slater-type basis but invoke additional approximations to simplify the evaluation of the integral (2). In addition, some integrals are chosen empirically by appeal to experimental data. Although these methods give some features of stereochemistry correctly,³ they run into difficulties particularly with conjugated systems. They have been extensively used in conformational studies of quite large molecules, but the results must be treated as very tentative until backed up by *ab initio* methods. CNDO/INDO results will not be discussed in any detail in this article.

Proceeding to MO theories at a more sophisticated level than the minimal basis, the next level is one in which the valence region of the atoms is described more flexibly by introducing additional basis functions ϕ_n . If the 2s and 2p functions are replaced by separate inner and outer parts (2s', 2s'', 2p', 2p''), the additional flexibility permits selective contraction or expansion on a given atom in an anisotropic manner. This may be described as a split-valence basis. If the inner shells are also split into two parts, the basis is usually called 'double-zeta'. The split valence basis that we use mostly is designed for extensive application to organic compounds.¹⁷ It is denoted by 4-31G and contains a 4-gaussian inner shell function together with 3-gaussian inner parts and 1-gaussian outer parts for the valence functions. Most of the rotational potentials discussed here were obtained with the 4-31G basis. Other double-zeta bases are also in widespread use.¹⁸

At an even higher level are theories with a basis also including atomic functions of higher angular symmetry than those involved in the atomic ground state. These additional functions (frequently described as polarization functions) are d-functions on heavy atoms (carbon, nitrogen, etc.) and p-functions on carbon. Such bases were first used extensively for diatomics¹⁹ but are now commonly used for polyatomics. The simplest such basis that we use is 6-31G* in which a split-valence 6-31G basis is expanded by the addition of d-functions on non-H atoms.²⁰ If p-functions are added on hydrogen as well, the basis becomes 6-31G**. However, at this level, only the simplest conformational problems can be considered at present.

Valence angles in simple organic compounds

We begin with a brief survey of the application of MO theory to the calculation of bond or valence angles for polyvalent atoms, starting with the

one-heavy-atom molecules CH₄, NH₃ and H₂O. For methane, it appears that all MO techniques that have been applied give the tetrahedral bond angles correctly. The fullest SCF study of methane²¹ gives not only the correct equilibrium geometry but also values for the angular distortion force constants accurate to better than 10%. For ammonia and water, good bond angles are not obtained immediately, but it is now well established that the theoretical values become accurate to 1°-2° as the Hartree-Fock limit is approached. The results for the bases described in Section 2²²⁻²⁴ and for the best MO studies^{25,26} are listed in Table 1. These are characteristic of the various types of basis set. For the STO-3G basis, the valence angles are somewhat too small. At the split-valence or double-zeta level, the bond angles at

Table 1. Valence angles in ammonia and water

Method	Ammonia	Water
STO-3G	104.2	100.0
4-31G	115.8	111.2
6-31G*	107.5	105.5
Best SCF	107.2	106.6
Expt ^a	106.7	104.5

^a For experimental references, see original theoretical papers.

nitrogen or oxygen become considerably too large. Rauk, *et al.* showed²⁵ that at the sp limit (i.e. a basis with a large number of s and p but no d functions), ammonia was predicted to be planar (D_{3h}). They also showed that the addition of d-functions to the basis lowered the valence angle to a value in reasonable agreement with experiment. The series of results STO-3G → 4-31G → 6-31G* parallels their findings. Associated with these changes in bond angles are changes in the theoretical barrier to inversion in ammonia. With their fullest basis set, Rauk *et al.*²⁵ found a barrier of 5.1 kcal/mole in reasonable agreement with the experimental value of 5.8 kcal/mole.²⁷ For the water molecule, the results (Table 1) show similar trends. Again the bond angle is too large at the split-valence level but is brought down to a value in good agreement with experiment if d-type polarization functions are added.²⁶ These data indicate that the d-functions cause a greater energy lowering in the more pyramidal or more bent structure. This consistent with an expected tendency for d-functions to mix in more effectively with s- and p-functions as the geometry deviates further from the more symmetrical arrangements (planar trigonal for NH₃ or linear for H₂O).

Next we ask whether MO theory is able to give an adequate account of changes in bond angles at C, N or O if one or more hydrogens are replaced by substituents. Some illustrative results are given in Table 2. These show that, at least for hydrocarbons,

Table 2. Changes ($\Delta\alpha$) in valence angles at C, N, and O (degrees)^a

Molecule	Angle α	STO-3G	4-31G	6-31G*	Expt ^b
Ethane (H ₃ C-)CH ₃	HCH	-1.4 ^c	-1.9 ^d		-1.8
Ethylene (H ₂ C=)CH ₂	HCH	+6.0 ^c	+6.4 ^d		+7.0
Propane (H ₃ C-) ₂ CH ₂	CCC	+2.8 ^c			+2.8
	HCH	-2.4 ^c			-3.5
Cyclopropane (H ₂ C-)CH ₂	HCH		+4.2 ^c		+5.5
Fluoromethane (F-)CH ₃	HCH	-1.3 ^c			+0.3
Formaldehyde (O=)CH ₂	HCH	+4.9 ^c	+6.8 ^d		+6.9
Methanol (H ₃ C-)OH	COH	+3.8 ^c			+1.4
Peroxide (HO-)OH	OOH	+1.1 ^c		-6.0	-9.7
Nitrogen Trifluoride NF ₃	FNF	-2.1 ^c			-4.4

^a Angle change relative to valence angles in CH₄, NH₃, and OH₂.

^b For experimental references, see original theoretical papers.

^c Ref 22 ^d Ref 17 'Ref 28 'Ref 29

bond angle changes are given quite well even at the minimal basis level. Thus the HCH opening (relative to methane) in ethylene and cyclopropane is well given,²⁸ as is the CCC opening (presumably sterically caused) in propane. However for some of the other molecules the results are less satisfactory at the minimal level. For hydrogen peroxide, for example, the low OOH bond angle is not reproduced²⁹ unless a large basis is used (a result related to the difficulty in obtaining the dihedral angle to be discussed later and first noted by Veillard³⁰).

Single rotors involving two heavy atoms

In this section we consider the conformation of molecules with one single bond connecting two heavy (non-hydrogen) atoms and an appropriate number of hydrogens. For the atoms C, N and O there are six such molecules (ethane, methylamine, methanol, hydrazine, hydroxylamine and hydrogen peroxide), all of which have been studied extensively by MO theory.^{3-12,31-35} It is now clear that MO theory with a single electron configuration gives an adequate description of the stereochemistry of all these molecules.

The conformation of a molecule (H_mABH_n) which has a degree of freedom corresponding to an internal rotation about a bond AB can be partly described by a single dihedral angle ϕ . This may be specified by a series of four sequentially bonded atoms H'ABH" and fixing the angle between the planes H'AB and ABH". Alternatively other well-defined planes containing the line AB may be used. The potential describing the rotational motion may then be specified most simply by holding ϕ fixed and treating the groups -AH_m and -BH_n as rigid with some specified bond lengths and angles (rigid rotation model). This leads to a potential function $V_{\text{rigid}}(\phi)$. A more satisfactory procedure is to allow all of these other lengths and angles to relax to their optimum values as the angle ϕ changes (flexible rotation model). This should give a more accurate potential $V_{\text{flexible}}(\phi)$, but will involve far more compu-

tation. Intermediate possibilities (flexibility with symmetry constraints) can also be considered.

It is useful to write the rotational potentials $V(\phi)$ (either rigid or flexible) as Fourier series in ϕ . For most simple rotors, a cosine series up to 3ϕ is adequate (Eq 4)

$$V(\phi) = \frac{1}{2}V_1(1 - \cos \phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi). \quad (4)$$

We shall find that different qualitative electronic effects contribute to different terms in this series, so that the decomposition aids interpretation.

Early work on the rotational potentials for the single-bond single-rotor molecules was based on *ab initio* minimal (or near-minimal) bases or on the semi-empirical INDO scheme. This showed considerable promise. At the next level of basis set, Table 3 gives the results of a comprehensive study of the rigid rotor approximation with the 4-31G basis.¹¹ The general features parallel the known experimental facts quite well. However, further study indicates that, for some of the molecules, the theoretical results change if flexible rotation is taken into account. For ethane, the calculated SCF barrier seems to be almost unchanged either if the basis set is improved or if flexible rotation is permitted (Table 4). An equally satisfactory result has also been achieved with the scattered-wave $X\alpha$ method.⁴¹ Corresponding results for methanol (Table 5) are less complete. The rigid rotor barriers are in reasonable agreement with other calculations^{5,6,36,37} and with experiment but the STO-3G flexible result²⁹ indicates that this might change if a fuller study was made. For hydrogen peroxide, on the other hand, the prediction of a skew form no longer holds at the 4-31G level if the OOH bond angle is allowed to relax. Full geometrical optimization with this basis leads to a *trans* structure. However, if d-functions are added to the basis and if flexible rotation is allowed, the skew form is again obtained. This was first shown by Veillard.³³ The

Table 3. Rigid single rotor potentials (4-31G basis)

Molecule	Conformation ^a at $\phi = 0$	V_1	V_2	V_3	Description of potential
Ethane	HCCH eclipsed	0	0	-3.26	3-fold potential with minimum at staggered conformation and barrier of 3.3 kcal/mole.
Methylamine	HCNH eclipsed	0	0	-2.13	3-fold potential with minimum at staggered conformation and barrier of 2.1 kcal/mole.
Methanol	HCOH eclipsed	0	0	-1.12	3-fold potential with minimum at staggered conformation and barrier of 1.1 kcal/mole.
Hydrazine	:NN: <i>cis</i>	-7.42	-7.92	-1.26	Skew minimum at $\phi = 97^\circ$. <i>Cis</i> and <i>trans</i> barriers of 12.4 and 3.7 kcal/mole respectively.
Hydroxylamine	:NOH <i>cis</i>	+8.86	+6.62	-0.84	Lowest minimum at $\phi = 0$ with a second minimum (8 kcal/mole higher) at $\phi = 180^\circ$.
Hydrogen Peroxide	HOOH <i>cis</i>	-7.08	-3.51	-0.22	Skew minimum at $\phi = 120^\circ$. <i>Cis</i> and <i>trans</i> barriers of 7.9 and 0.6 kcal/mole respectively.

^aN: is used to denote the fourth tetrahedral direction in nitrogen. Bond lengths and angles chosen according to standard model (Ref 42).

Table 4. Rotation barriers in ethane (kcal/mole)

Basis	Rigid rotor	Flexible rotor	Expt.
STO-3G	3.3	2.9	
4-31G	3.3		
6-31G*	3.5		
Best ^a	3.4	3.2	2.9

^aE. Clementi and H. Popkie, *J. Chem. Phys.* **57**, 4870 (1972)

Table 5. Rotational barriers in methanol (kcal/mole)

Basis	Rigid rotor	Flexible rotor	Expt.
STO-3G		2.0 ^a	
4-31G	1.1		
6-31G*	1.0		1.1

^aRef 29

6-31G* results show similar features. With standard bond lengths but variable OOH angles, this basis gives a minimum at $\phi = 120^\circ$ together with *cis* and *trans* barriers of 8.8 and 0.5 kcal/mol respectively (Fig 1). The corresponding values of V_1 , V_2 and V_3 are -8.03, -3.70 and -0.31 kcal/mole.

There have been many discussions of the electronic nature of the C-C rotational barrier in ethane. Here we shall not review this extensive literature,^{38,39} but only note the important part played by vicinal H-H interaction. Table 6 shows the corresponding overlap populations⁴⁰ (6-31G* rigid rotor approximation). This clearly indicates some antibonding character between the hydrogens of eclipsed C-H bonds. There is some compensating bonding character if the dihedral angle is large, but the greater interatomic distance then leads to smaller populations. The origin of this antibonding can be partially understood from the nature of the degenerate e-type molecular orbitals (D_{3h} symmetry for eclipsed ethane) describing the C-H bonds (Fig

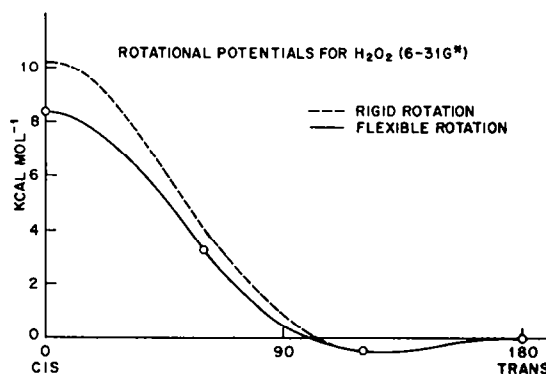
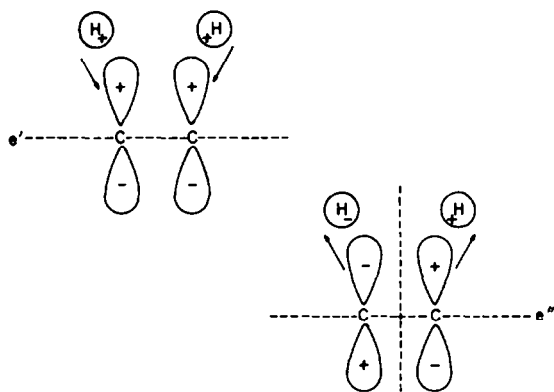
Fig 1. Rotational potentials for H_2O_2 (6-31G*).

Table 6. Vicinal H-H overlap populations in ethane (6-31G*)

Dihedral angle ϕ	Eclipsed	Staggered
0(<i>cis</i>)	-0.016	
60		-0.006
120	+0.006	
180(<i>trans</i>)		+0.008

2). The lower energy orbital (le') is C-C π -bonding and will be polarized with electrons towards carbon. The other orbital (le''), on the other hand, will be C-C π -antibonding and polarized towards hydrogen. The overall effect (since both MO's are occupied) is to lead to a net antibonding H-H population.

The ratio of the barriers in the series ethane, methylamine and methanol is close to 3:2:1 (Table 1) as found experimentally. Since the numbers of vicinal H-H interactions are in the same ratio, this suggests that the barriers in methylamine and methanol can be interpreted in the same way as in



π -Type Molecular Orbitals for Eclipsed Ethane (D_{3h})

Fig. 2. $1e'$ and $1e''$ molecular orbitals for eclipsed ethane.

ethane, there being no need to invoke additional interactions involving lone pairs.

For hydrogen peroxide, additional effects must be present to account for the shape of the potential. A negative value of V_1 (favoring HOOH *trans* over *cis*) is to be expected both because of hydrogen repulsions and because of the interaction of the OH dipole moment components perpendicular to the

OO axis. This latter effect is probably overemphasized by the 4-31G basis which generally leads to dipole moments which are too large. But clearly the skew minimum energy conformation arises from a considerable negative value of V_2 which favors the orthogonal form over either planar form. One possible source of such an effect is a repulsive interaction between π -type lone pairs in the planar structures. The molecule then has four π -electrons and both the bonding and antibonding MO's are full. Under these circumstances the antibonding dominates and a net repulsion results. This repulsion will be partly relieved in the orthogonal conformation.

Single rotors involving three heavy atoms

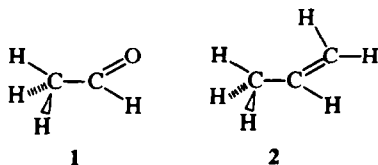
The next type of internal rotation to consider is one in which one or more of the hydrogens in the molecules considered in the previous section are substituted by atoms or groups which do not give rise to additional rotational degrees of freedom. The simplest such systems contain three heavy atoms and a number of these have been studied theoretically. The rotational potential is modified by a 'substituent effect' which can be quite large. However, the single bond rotational potential can still be expressed as a Fourier series (4) with modified value of the parameters V_1 , V_2 and V_3 . Table 7

Table 7. Rigid single rotor potentials of molecules with three heavy atoms(4-31G basis)

Molecule	Conformation at $\phi = 0$	$E(\phi = 0)$ (hartrees)	Potential constants (kcal/mole)			Description of potential
			V_1	V_2	V_3	
C-C Bonds						
Ethylfluoride	HCCF <i>cis</i>	-177.83576	0	0	-3.63	3-fold potential with minimum at staggered conformation and barrier of 3.6 kcal/mole.
Acetaldehyde	HCCO <i>cis</i>	-152.68475	0	0	+0.74	3-fold potential with minimum at HCCO <i>cis</i> Barrier 0.7 kcal/mole.
Propene	HCCC <i>cis</i>	-116.90203	0	0	+1.71	3-fold potential with minimum at HCCC <i>cis</i> -Barrier Barrier 1.7 kcal/mole.
C-O Bonds						
Fluoromethanol	FCOH <i>cis</i>	-213.60624	+5.25	-2.20	-0.96	Two equivalent minima with FCOH <i>gauche</i> ($\phi \approx 57^\circ$). <i>Cis</i> and <i>trans</i> barriers of 1.3 and 5.6 kcal/mole respectively.
Formic acid	OCOH <i>cis</i>	-188.47060	+5.75	+8.93	+0.55	Two inequivalent minima, OCOH <i>cis</i> being lowest and OCOH <i>trans</i> 6.3 kcal/mole higher. Barrier 12.2 kcal/mole above minimum.
Ethenol	CCOH <i>cis</i>	-152.66422	—	—	—	Incomplete study. CCOH <i>trans</i> is 0.2 kcal/mole higher and is probably a second minimum.
C-N Bonds						
Fluoromethylamine	FCN: <i>cis</i>	-193.79749	-4.86	+4.28	-2.01	Deep minimum with FCN: <i>trans</i> . Two additional minima at $\phi = \pm 39^\circ$, 6.6 kcal/mole higher in energy. Barrier of 7.7 kcal/mole.
Formamide	OCNH planar	-168.67763	0	+24.67	0	Two equivalent planar minima separated by a high barrier.

lists the results obtained with the 4-31G basis set (Rigid rotation with standard bond lengths and angles).^{11,43}

C-C bonds. If ethane is substituted at one end, the barrier remains threefold and can be adequately described by a single parameter V_3 . In ethyl fluoride, the staggered conformation remains most stable and the barrier is somewhat larger than in ethane. This is in agreement with experiment.⁴⁴ If two hydrogens are replaced by a single O atom to give acetaldehyde, the rotational barrier is greatly decreased but the stable conformation remains staggered (if C=O is treated as two bent bonds). This also agrees with experimental data, the barrier measured by microwave spectroscopy⁴⁵ being 1.16 kcal/mole. Similar conclusions have been reached in other molecular orbital studies.^{46,47} Propene can also be treated as a single rotor molecule if the CC double bond is regarded as rigid. Again a reduced barrier is found (but not reduced as greatly) and the staggered conformation II remains most stable in agreement with experiment (Barrier 2.0 kcal/mole⁴⁸). No clear interpretation of these changes in threefold barriers has been given. Some attempts have been made to analyze them by separation into repulsive and attractive components,⁴⁶ but work by Liberles *et al.*⁴⁷ has indicated that such a partition is somewhat dependent on basis set.



C-O bonds. If methanol is substituted on carbon, the C-O rotational potential is strongly modified and no longer has simple threefold character. Fluoromethanol is a clear example even though no experimental data is available. Wolfe *et al.*⁴⁹ first noted that *ab initio* MO theory gave a rotational C-O potential very different from methanol. The 4-31G potential with standard lengths and angles (Table 7) gives¹¹ the potential illustrated in Fig 3. The FCOH *trans* conformation ($\phi = 180^\circ$) is no longer a minimum (as it is in methanol) but rather a strong maximum. There are two equivalent minima corresponding to FCOH *gauche* with a smaller *cis* barrier between them. More recent work with the 6-31G* basis⁵⁰ gives similar results with the *trans-gauche* separation reduced to 4.6 kcal/mole.

Some insight into the origin of these effects may be obtained from the distribution of oxygen lone-pair electrons. In methanol itself, the $p\pi$ -type lone pair of electrons on oxygen undergoes some 'back-donation' into antibonding-type orbitals of appropriate symmetry on the Me group. This leads to a reduction of the gross ($p\pi$) population⁴⁰ from the value 2.00 appropriate to water (Fig 4) to 1.97. In

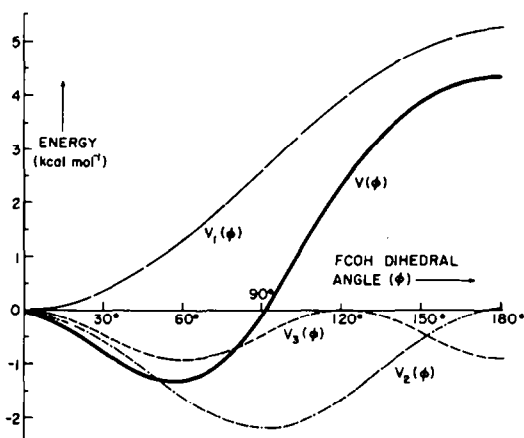


Fig 3. Fourier decomposition of rotational potential for fluoro-methanol (4-31G).

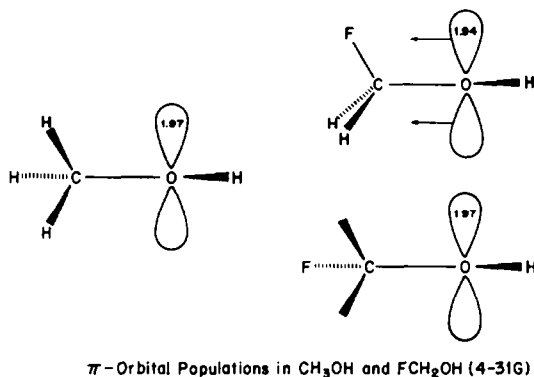


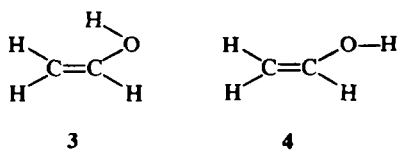
Fig 4. π -Orbital populations in CH_3OH and FCH_2OH (4-31G).

fluoromethanol, this electron displacement is expected to be comparable if the C-F bond is in the nodal plane of the oxygen $p\pi$ orbitals (FCOH *cis* or *trans*). This is indeed found (Fig 4). However, if the FCO and COH planes are perpendicular ($\phi = 90^\circ$; Fig 4), the σ -electrons in the C-F bond are drawn towards fluorine leaving the carbon end of the bond more vacant. This increases the magnitude of the back-donation leading to additional stabilization. In resonance terms, this corresponds to double-bond-no-bond structures $\text{F}^- \text{C}=\text{O}^+$ which are more effective at $\phi = 90^\circ$. This back-donation effect will lead to a negative contribution to the V_2 component in the rotational potential. To obtain the full potential this has to be combined with a V_1 term which is likely to favor FCOH *cis* because of the interaction of the dipole moment components of CF and OH perpendicular to the CO bond (positive V_1). The combination of these two effects leads to the complete potential function shown in Fig 3.

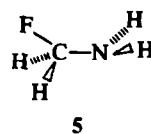
The next molecule considered is formic acid. This can also be considered as a derivative of

methanol by double substitution of two CH bonds by a single O atom. Again the modification of the threefold potential for internal rotation about the CO bond is very large. The 4-31G results indicate two minima in the two planar conformations (OCOH *cis* and *trans*). This preference for planarity is reflected in the large positive V_2 value (Table 7). It is associated with greatly enhanced back donation from the singly-bonded oxygen, the π -type orbitals in the carbonyl group being partially available as acceptors. This, of course, is a widely accepted explanation for the enhanced stability of the CO group O=C=O which is most effective in the planar conformation. It should be emphasized, however, that the qualitative nature of the explanation is the same in formic acid and fluoromethanol. Given that the planar conformations are preferred, the lower energy is found for OCOH *cis* primarily because of the positive V_1 term which reflects more favorable dipole interaction in the *cis* conformation. At the 6-31G* level, the difference between the *trans* and *cis* conformers is reduced to 5.0 kcal/mole.⁵⁰

Another molecule listed in Table 7 is the simplest enol, ethenol or vinyl alcohol. Rotation about the C-O bond in this molecule has not yet been investigated fully, but results to date indicate that the two planar conformers 3 and 4 are close in energy.



C-N bonds. Comparable studies on three-heavy-atom molecules with a C-N bond suggest that the operative effects are very similar. For fluoromethylamine, by far the greatest stability is found for the FCN: *trans* conformation 5. In this conformation, the nitrogen lone pair is favorably located for back donation into the C-F bond and, at



the same time, the dipole interactions are also most stabilizing. The 4-31G results suggest that two minima occur in FCN: *gauche* forms, but the energy is close to that of the FCN: *cis* conformation.

The remaining molecule in Table 7 is formamide where the back donation from nitrogen is very strong and leads to a great deal of double-bond character in the C-N bond. The 4-31G standard model results show this (assuming planar valences at nitrogen), although the calculated barrier is somewhat larger than the experimental value of 19 kcal/mole.⁵¹

Single rotor involving four heavy atoms

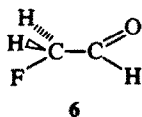
In this section we consider rigid rotors which may be considered as 1,2 disubstituted ethanes. Three such molecules which have been studied are 1,2-difluoroethane, 2-fluoroacetaldehyde and glyoxal for which 4-31G standard model results are given in Table 8. For these molecules, the precise threefold nature of the rotational potential is destroyed. In the case of 1,2-difluoroethane,⁵² the potential shows three distinct minima (FCCF *trans* at $\phi = 180^\circ$ and FCCF *gauche* at $\phi = \pm 72.7^\circ$) with the *trans* rotamer more stable by 1.0 kcal/mole. This would appear to be in disagreement with experimental data. The *gauche* form is known to be more stable in solution⁵³ and may well be so in the gas phase. The relative energies of the *gauche* and *trans* forms is strongly dependent on the V_1 term in the potential. It is possible that the 4-31G estimate of V_1 is too large because this basis is known to overestimate dipole moments. Corresponding results at the 6-31G* level would clearly be of interest.

Only limited information is available for 2-

Table 8. Rigid single rotor potentials for molecules with four heavy atoms (4-31G)

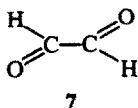
Molecule	Conformation at $\phi = 0$	$E(\phi = 0)$ (hartrees)	Potential constants (kcal/mole)			Description of potential
			V_1	V_2	V_3	
1,2-Difluoroethane	FCCF <i>cis</i>	-276.55009	-4.68	-2.72	-4.09	Perturbed 3-fold potential with FCCF <i>trans</i> more stable than FCCF <i>gauche</i> by 1.0 kcal/mole.
2-Fluoroacetaldehyde	FCCO <i>cis</i>	-251.39849	-4.09	—	—	Incomplete study. FCCO <i>trans</i> more stable than FCCO <i>cis</i> by 4.1 kcal/mole.
Glyoxal	OCCO <i>trans</i>	-22.24279	+5.73	+4.85	+0.40	Two minima for planar structures with OCCO <i>trans</i> 6.1 kcal/mole below OCCO <i>cis</i> . Barrier 8 kcal/mole above <i>trans</i> .

fluoroacetaldehyde for which only *cis* and *trans* forms have been examined. The FCCO *trans* form **6** appears to be most stable. However, the



dipole-dipole interaction between the C=O and C-F bonds (which favors the *trans* form) is again probably overestimated.

Internal rotation about the C-C bond in glyoxal has also been studied.^{43,54} Glyoxal is the simplest molecule showing the effects of conjugation between neighboring double bonds. This favors planar forms and contributes to the V_2 term in the potential. The 4-31G data (Table 8) shows the minima in both planar forms with the *trans* form **7** being the most stable. The other (*cis*) form is



predicted to be 6.1 kcal/mole higher in energy. Both forms are known experimentally, the *trans* being more stable by 3.2 kcal/mole.⁵⁵ Again it is likely that the stabilization of the *trans* form is overestimated because local dipole moments are too large with the 4-31G basis. This is probably a general deficiency of this basis (or any basis of the split-valence type) when applied to the interaction of vicinal polar bonds.

Double rotors

The next step in applying MO theory to stereochemical problems is to consider double-rotor systems. These are molecules in which two bonds have a degree of freedom of internal rotation. The simplest hypothesis for the complete potential for such a system would be to assume that the individual rotor potentials are uncoupled (additive) and can be transferred from simple single-rotor molecules. Such a hypothesis is frequently used in the de-

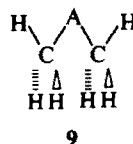
velopment of simple empirical potential functions for large molecules. The MO methods described here can clearly be used to make a full test of such a hypothesis and indicate how large coupling between such potentials might be. The large substituent effects on single-rotor potentials already noted in previous sections indicate that coupling in double rotors may be large.

In order to specify the conformation of a double-rotor molecule, two dihedral angles ϕ and ψ are needed. If X and Y are two groups attached to an atom A and if an appropriate (0,0) conformation is defined, then the general conformation (ϕ, ψ) can be represented by **8**.



A number of molecules of this sort have been investigated (in the rigid rotated approximation) with the 4-31G basis.^{10,43}

Double methyl rotors. If X and Y are both methyl groups, the individual rotational potentials remain threefold, but the barrier height for one dihedral angle is dependent on the value of the other. Three such molecules are propane, dimethylether and acetone (Table 9). For all of these molecules, the lowest energy is found for the double-staggered conformation **9** (treating C=O as two bent C-O bonds). All three molecules show similar features.



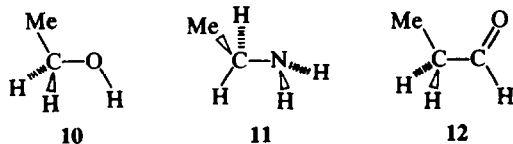
If one Me is held in the staggered conformation, the 3-fold barrier for the other group is higher than for the simpler single rotor. Thus the propane barrier is higher than ethane, dimethylether is higher than methanol but acetone is only slightly higher than acetaldehyde. If the other Me is held in the eclipsed conformation, the barriers become higher. These

Table 9. Rigid double rotor potentials for molecules with two methyl groups (4-31G)

Molecule	Conformation at (ϕ, ψ) = (0, 0)	$E(0, 0)$ (hartrees)	$E(\phi, \psi) - E(0, 0)$ (0, 60)	$E(\phi, \psi) - E(0, 0)$ (60, 60)	Description of potential
Propane	HCCCH <i>trans-trans</i>	-118.09211	3.70	8.77	3-fold barrier of 3.7 kcal/mole if other group staggered but 5.1 kcal/mole if other eclipsed.
Dimethylether	HCOCH <i>trans-trans</i>	-153.83570	2.98	7.00	3-fold barrier of 3.0 kcal/mole if other group staggered but 4.0 kcal/mole if other eclipsed.
Acetone	HCCCH <i>trans-trans</i>	-191.67626	0.75	2.22	3-fold barrier of 0.7 kcal/mole if other group staggered but 1.5 kcal/mole if other eclipsed.

results appear to be consistent with experimental data. They can probably be attributed to direct hydrogen interactions between the Me groups. It may be noted that a STO-3G flexible rotor study on propane predicts some opening of the C-C-C bond angle for the double-eclipsed conformation.³⁶

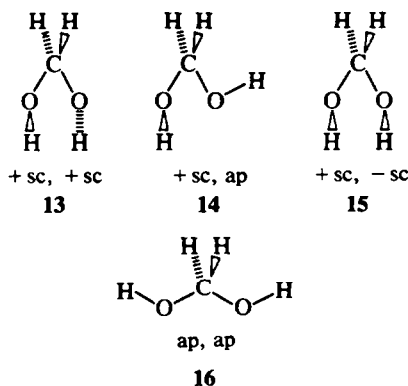
Ethyl-type double rotors. In compounds $\text{CH}_3\text{CH}_2\text{-Y}$, where Y is a rigid rotor, the C-C potential is threefold, but C-Y is lowered in symmetry. Examples are ethanol, ethylamine and propionaldehyde. Although full double rotor potentials have not been determined, some studies have been carried out for C-Y holding the methyl group in a staggered conformation.^{11,43} These are summarized in Table 10. They show that the substitution of H by Me has a fairly small effect of the C-Y rotational potential, the general threefold nature being retained. However, there are smaller energy differences between inequivalent conformations, all of which seem to be consistent with experimental observations.⁵⁷⁻⁶⁰ The most stable forms are 10-12 for



ethanol, ethylamine and propionaldehyde respectively. The origin of the extra stability of these rotamers is not clear at present. It is unlikely that it is a π -electron effect since the OH group is a π -acceptor yet both 10 and 12 have Me groups in the corresponding valence planes. All three are consistent with the hypothesis of a dominant H-Me repulsion between vicinal positions.

Double polar rotors. If both C-X and C-Y in a double rotor system $\text{X-CH}_2\text{-Y}$ are bonds to polar groups, considerable coupling is found between them. This is to be expected from the results on substituent effects on single rotors. An important example of such a double rotor is methanediol, which can be regarded as a simple model compound for the anomeric center in carbohydrates. If we assume two independent C-O rotors, each with a threefold methanol potential, methanediol would

exist in the isomeric forms 13-16 and then would have equal energy. The first *ab initio* studies¹⁰ on these four conformations (using the 4-31G basis) showed that the relative energies were



0, 4.7, 5.4, and 11.2 kcal/mole respectively. This immediately indicates a very strong coupling between the rotors, these coupling terms being much larger than the single C-O barrier in methanol. Subsequently a fuller study of the two-dimensional (ϕ, ψ) potential surface has been carried out⁴³ (Fig 5). This

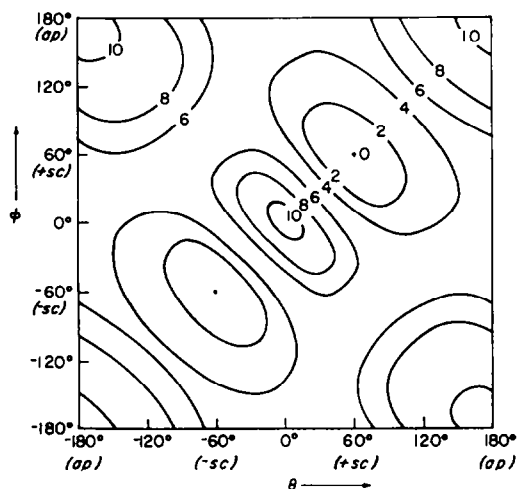


Fig 5. Double-rotor potential for methanediol (4-31G).

Table 10. Rigid rotor potentials for $\text{CH}_3\text{CH}_2\text{Y}$ molecules (4-31G)

Molecule	Conformation ^a at $\psi = 0$	E($\psi = 0$) (hartrees)	E(ψ)-E(0) (kcal/mole)			Description of potential
			60°	120°	180°	
Ethanol	CCOH <i>trans</i>	-153.85411	1.33	0.66	2.06	Most stable form has CCOH <i>trans</i> . Second minimum with CCOH <i>gauche</i> 0.7 kcal/mole higher.
Ethylamine	CCN: <i>trans</i>	-134.04823	2.23	-0.51	1.40	Most stable form has CCN: <i>gauche</i> . Second minimum with CCN: <i>trans</i> 0.5 kcal/mole higher
Propionaldehyde	CCCO <i>cis</i>	-191.66266	0.94	0.70	1.29	Most stable form has CCCO <i>cis</i> . Second form ($\psi = 120^\circ$) is 0.7 kcal/mole higher.

indicates that (+sc, +sc) is close to the overall minimum and also suggests that there are no other local minima on the surface. In particular, the all-*trans* (ap, ap) conformation is a very high maximum. Some work has since been done at the 6-31G* level which gives similar results although the height of the (ap, ap) point over (+sc, +sc) is reduced to 8.8 kcal/mole. No relevant experimental data is available on methanediol, but these results are consistent with the known structure of dimethoxymethane.^{61,62} The implications of these results in the interpretation of the anomeric effect has been discussed elsewhere.⁶³

Many of the qualitative features of the methanediol surfaces can be interpreted in terms of the same effects that we have already invoked in fluoromethanol. Fig 6 shows that the back donation from the oxygen p-type lone pairs is 0.05 electrons in the (+sc, +sc) conformation, significantly larger than in methanol. The π -bond orders are also shown and indicate some π -bonding in methanol. The π -bond orders are also shown and indicate some slight antibonding in methanol. Other factors must also be important. The stability of the (+sc, +sc) form XIII relative to the (+sc, -sc) form XVI must be partly due to unfavorable dipole-dipole interactions in XV.

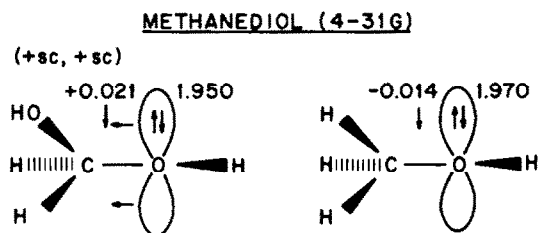


Fig 6. π -Orbital populations in CH_3OH and $\text{CH}_2(\text{OH})_2$ (4-31G).

CONCLUSIONS

The following general conclusions seem to follow from theoretical studies to date.

1. Bond angles seem to be given to considerable accuracy ($\sim 2^\circ$) at the Hartree-Fock limit. The minimal STO basis is moderately successful, but there are systematic deviations from experimental data at the split-valence or double-zeta level. Additional polarization functions have then to be added to achieve adequate results.

2. All the simple single-rotor potentials (two heavy atoms) are well described as the single-configuration limit is approached. However, in some cases such as H_2O_2 , adequate results are only obtained if polarization functions are used and flexible rotation is taken into account.

3. Single substituents can modify rotational potentials strongly. Large changes are predicted for polar substituents on polar rotors. These are as-

sociated both with dipolar interactions and back-donation of 'lone-pair' electrons.

4. It is not yet clear how well rotational potentials for 1,2-disubstituted rotors are given by single-configuration theory. Studies with a split-valence basis yield some apparent disagreement with experimental data. However, the role of polarization functions has not yet been fully assessed.

5. For double rotors, strong interaction terms are predicted if both rotors are polar as in methanediol. There is little experimental data on small molecules to check this, but the existence of such interactions has widespread implications for the stereochemistry of larger molecules.

Acknowledgement—This research was supported in part by the National Science Foundation under Grant GP-25617.

REFERENCES

- J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44**, 3289 (1966)
- J. A. Pople, D. L. Beveridge and P. A. Dobosh, *Ibid.* **47**, 2026 (1967)
- J. A. Pople and M. S. Gordon, *Ibid.* **49**, 4643 (1968)
- R. M. Pitzer, *Ibid.* **47**, 965 (1967)
- W. H. Fink and L. C. Allen, *Ibid.* **46**, 2261, 2276; **47**, 895 (1967)
- L. Pedersen and K. Morokuma, *Ibid.* **46**, 2941 (1967)
- E. Clementi and D. R. Davis, *Ibid.* **45**, 2593 (1966)
- W. Palke and R. M. Pitzer, *Ibid.* **46**, 3948 (1967)
- L. C. Allen, *Ann. Rev. Phys. Chem.* **20**, 315 (1969)
- L. Radom, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 289 (1971)
- L. Radom, W. J. Hehre and J. A. Pople, *Ibid.* **94**, 2371 (1972)
- L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *Ibid.* **95**, 693 (1973)
- C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951)
- J. C. Slater, *Phys. Rev.* **36**, 57 (1930)
- S. F. Boys, *Proc. Roy. Soc. A* **200**, 542 (1950)
- W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969)
- R. Ditchfield, W. J. Hehre and J. A. Pople, *Ibid.* **54**, 724 (1971)
- H. Basch, M. B. Robin and N. A. Kuebler, *Ibid.* **47**, 1201 (1967)
- P. E. Cade and W. M. Huo, *Ibid.* **47**, 614 (1967)
- P. C. Hariharan and J. A. Pople, *Th. Chim. Acta* **28**, 213 (1973)
- W. Meyer and P. Pulay, *J. Chem. Phys.* **59**, 2109 (1972)
- M. D. Newton, W. A. Lathan, W. J. Hehre and J. A. Pople, *Ibid.* **52**, 4064 (1970)
- W. A. Lathan, W. J. Hehre, L. A. Curtiss and J. A. Pople, *J. Am. Chem. Soc.* **93**, 6377 (1971)
- P. C. Hariharan and J. A. Pople, *Mol. Phys.* to be published.
- A. Rauk, L. C. Allen and E. Clementi, *J. Chem. Phys.* **52**, 4133 (1970)
- T. H. Dunning, R. M. Pitzer and S. Aung, *Ibid.* **57**, 5044 (1972)
- J. D. Swalen and J. A. Pople, *Ibid.* **30**, 1914 (1962)

- ²⁸L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 5339 (1971)
- ²⁹W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle and J. A. Pople, *Progress in Physical Organic Chemistry* to be published
- ³⁰A. Veillard, *Theor. Chim. Acta* **18**, 21 (1970)
- ³¹R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.* **39**, 1995 (1963)
- ³²R. M. Stevens, *Ibid.* **52**, 1397 (1970)
- ³³A. Veillard, *Theor. Chem. Acta* **5**, 413 (1966)
- ³⁴W. M. Fink, D. C. Pan and L. C. Allen, *J. Chem. Phys.* **47**, 895 (1967)
- ³⁵V. Kaldor and I. Shavitt, *Ibid.* **44**, 1823 (1966)
- ³⁶S. Rothenberg, *Ibid.* **51**, 3389 (1969)
- ³⁷L. M. Tel, S. Wolfe and I. G. Csizmadia, *Ibid.* **59**, 4047 (1973)
- ³⁸J. P. Lowe, *Prog. Phys. Org. Chem.* **6**, 1 (1968)
- ³⁹O. J. Sovers, C. W. Kern, R. M. Pitzer and M. Karplus, *J. Chem. Phys.* **49**, 2592 (1968)
- ⁴⁰R. S. Mulliken, *Ibid.* **23**, 1833, 1841, 2338, 2343 (1955)
- ⁴¹U. Wahlgren and K. H. Johnson, *Ibid.* **56**, 3715 (1972)
- ⁴²J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.* **89**, 4253 (1967)
- ⁴³L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *Aust. J. Chem.* **25**, 1601 (1972)
- ⁴⁴D. R. Herschbach, *J. Chem. Phys.* **25**, 358 (1956)
- ⁴⁵W. Kilb, C. C. Lin and E. B. Wilson, Jr., *Ibid.* **26**, 1695 (1957)
- ⁴⁶R. B. Davidson and L. C. Allen, *Ibid.* **54**, 2828 (1971)
- ⁴⁷A. Liberles, B. O'leary, J. E. Eilers and D. R. Whitman, *J. Am. Chem. Soc.* **94**, 6894 (1972)
- ⁴⁸E. Hirota, *J. Chem. Phys.* **45**, 1984 (1966)
- ⁴⁹S. Wolfe, A. Rauk, L. M. Tel and I. G. Csizmadia, *J. Chem. Soc. B* 136 (1971)
- ⁵⁰P. C. Hariharan and J. A. Pople, to be published
- ⁵¹T. Drakenberg and S. Forsen, *J. Phys. Chem.* **74**, 1 (1970)
- ⁵²L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **95**, 693 (1973)
- ⁵³R. J. Abraham and R. H. Kemp, *J. Chem. Soc. B* 1240 (1971)
- ⁵⁴V. Pincalli, B. Cadioli and D. J. David, *J. Mol. Struct.* **9**, 173 (1917)
- ⁵⁵G. N. Currie and D. A. Ramsay, *Canad. J. Phys.* **49**, 317 (1971)
- ⁵⁶L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4786 (1970)
- ⁵⁷C. O. Kadzhar, I. D. Isaev and L. M. Imanov, *Zh. Strukt. Khim.* **9**, 445 (1968)
- ⁵⁸Y. Sasada, M. Takana and T. Satoh, *J. Mol. Spec.* **38**, 33 (1971)
- ⁵⁹T. Masamichi, A. Y. Hiradawa and K. Tamagaka, *Nippon Kagaku Zasshi* **89**, 821 (1968)
- ⁶⁰S. S. Butcher and E. B. Wilson, J. R., *J. Chem. Phys.* **40**, 1671 (1964)
- ⁶¹K. Aoki, *J. Chem. Soc. Japan* **74**, 110 (1953)
- ⁶²E. E. Astrys, *Acta Chem. Scand.* **25**, 1494 (1971)
- ⁶³G. A. Jeffrey, J. A. Pople and L. Radom, *Carbohydrate Res.* **25**, 117 (1972)