INTERNAL ROTATION IN SOME ORGANIC MOLECULES CONTAINING METHYL, AMINO, HYDROXYL, AND FORMYL GROUPS

By L. RADOM,* W. A. LATHAN,* W. J. HEHRE,*† and J. A. POPLE*

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Abstract

Ab initio molecular orbital theory is used to study internal rotation in 20 organic molecules of the types X–Y, X–CH₂–Y, X–NH–Y, X–O–Y, and X–CO–Y where X and Y are methyl, amino, hydroxy, or formyl groups. In some of these molecules, internal rotation about two bonds is possible. The theoretical results are generally in moderate agreement with available experimental data and, in addition, lead to a number of predictions for molecules for which experimental information is lacking.

INTRODUCTION

Molecular orbital theory has been extensively used in recent years to study the variation in the energy of small molecules with internal rotation about various bonds (see, for instance, ref. 1). In a previous paper, 2 we have presented a systematic survey of the energies of organic molecules (with up to three heavy atoms C, N, O, or F) using a standard model for conformations. In many of these molecules, there was the possibility of internal rotation about one or two bonds, but the choice of conformations examined was necessarily limited because of the large number of molecules involved. It is clearly desirable to extend such a survey by filling in more details of the rotational potential surfaces so that information is obtained about barriers separating rotamers as well as the energies at the potential minima. This has already been done 3 for some of the molecules containing a single rotor. In this paper, we shall present a fuller study of a set of organic molecules in which internal rotation about either one or two single bonds is possible.

The set of organic molecules studied involves rotation of the four groups methyl, amino, hydroxyl, and formyl. The systems considered are of the types X–Y, X–CH₂–Y, X–NH–Y, X–O–Y, and X–CO–Y where X, Y = CH₃, NH₂, OH, CHO. Nitrogen is only considered when bonded to a carbonyl group, in which case a near-planar arrangement of trigonal bonds is expected. No systems involving N–N,

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N–O, or O–O bonds are treated, nor are any with more than four non-hydrogenic atoms. The remaining molecules are considered in detail and are listed in Table 1. They are of interest as many of them represent groupings which occur widely in molecules of biochemical interest.

### Table 1

**TOTAL ENERGIES FOR UNROTATED CONFORMATIONS**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Molecule</th>
<th>Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃–CH₃</td>
<td>ethane</td>
<td>−79.11484</td>
</tr>
<tr>
<td>CH₃–OH</td>
<td>methanol</td>
<td>−114.87020</td>
</tr>
<tr>
<td>CH₃–CHO</td>
<td>acetaldehyde</td>
<td>−152.68475</td>
</tr>
<tr>
<td>NH₂–CHO</td>
<td>formamide</td>
<td>−168.67763</td>
</tr>
<tr>
<td>HO–CHO</td>
<td>formic acid</td>
<td>−188.47060</td>
</tr>
<tr>
<td>CHO–CHO</td>
<td>glyoxal</td>
<td>−226.24279</td>
</tr>
<tr>
<td>CH₃–CH₂–CH₃</td>
<td>propane</td>
<td>−118.09211</td>
</tr>
<tr>
<td>CH₃–CH₂–OH</td>
<td>ethanol</td>
<td>−153.85411</td>
</tr>
<tr>
<td>CH₃–CH₂–CHO</td>
<td>propionaldehyde</td>
<td>−191.66266</td>
</tr>
<tr>
<td>HO–CH₂–OH</td>
<td>methanediol</td>
<td>−189.60717</td>
</tr>
<tr>
<td>HO–CH₂–CHO</td>
<td>2-hydroxyacetaldehyde</td>
<td>−227.41128</td>
</tr>
<tr>
<td>CH₂–NH–CHO</td>
<td>N-methylformamide</td>
<td>−207.64589</td>
</tr>
<tr>
<td>CH₃–O–CH₂</td>
<td>dimethyl ether</td>
<td>−153.83570</td>
</tr>
<tr>
<td>CH₃–O–CHO</td>
<td>methyl formate</td>
<td>−227.43147</td>
</tr>
<tr>
<td>CH₃–CO–CH₂</td>
<td>acetone</td>
<td>−191.67626</td>
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<tr>
<td>CH₃–CO–NH₂</td>
<td>acetamide</td>
<td>−207.68824</td>
</tr>
<tr>
<td>CH₃–CO–OH</td>
<td>acetic acid</td>
<td>−227.46495</td>
</tr>
<tr>
<td>NH₂–CO–NH₂</td>
<td>urea</td>
<td>−223.65188</td>
</tr>
<tr>
<td>NH₂–CO–OH</td>
<td>carbamic acid</td>
<td>−243.43594</td>
</tr>
<tr>
<td>HO–CO–OH</td>
<td>carbonic acid</td>
<td>−263.23648</td>
</tr>
</tbody>
</table>

### Method and Results

All calculations involve standard molecular orbital theory with the 4-31G extended Gaussian basis set. Bond angles* and bond lengths are chosen according to a standard model described previously. It should be noted that the C–N length is taken to be 1.32 Å for the amide-type bonds in these molecules. To specify the dihedral angles, we define an unrotated conformation for each molecule. This is taken to have a *trans* arrangement for single bonds in all cases. For the single rotor systems, the general conformation is simply defined by a single dihedral angle $\psi$ representing the rotation from the unrotated form. For the double rotor systems, the unrotated or (0,0) conformations are indicated in Figure 1. The general conformation of the double rotor X–A–Y is then defined by two dihedral angles $\phi$ and $\psi$ with the sense of the rotations $\phi$ and $\psi$ corresponding to positive rotations about X–A and A–Y, respectively, from the (0,0) conformation.

* All angles in this paper are in degrees.


# Table 2

## INTERNAL ROTATION IN ORGANIC MOLECULES

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\phi$</th>
<th>$\Delta E(\phi,0)$</th>
<th>$\Delta E(\phi,60)$</th>
<th>$\Delta E(\phi,120)$</th>
<th>$\Delta E(\phi,180)$</th>
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<tr>
<td>CH$_3$-CH$_3$</td>
<td>0</td>
<td>3.26</td>
<td>0</td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-OH</td>
<td>0</td>
<td>1.12</td>
<td>0</td>
<td>1.12</td>
<td></td>
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<tr>
<td>CH$_3$-CHO</td>
<td>0</td>
<td>0.74</td>
<td>0</td>
<td>0.74</td>
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<tr>
<td>NH$_2$-CHO$^b$</td>
<td>0</td>
<td>17.92</td>
<td>17.92</td>
<td>0</td>
<td></td>
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<tr>
<td>HO-CHO$^c$</td>
<td>0</td>
<td>8.89</td>
<td>11.01</td>
<td>6.30</td>
<td></td>
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<tr>
<td>CHO-CHO</td>
<td>0</td>
<td>5.47</td>
<td>7.93</td>
<td>6.13</td>
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</tr>
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<td>3.70</td>
<td>0</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-OH</td>
<td>0</td>
<td>1.33</td>
<td>0.66</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-CHO</td>
<td>0</td>
<td>0.94</td>
<td>0.70</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>HO-CH$_2$-OH</td>
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<td>1.76</td>
<td>-6.46</td>
<td>-6.78</td>
<td></td>
</tr>
<tr>
<td>HO-CH$_2$-CHO</td>
<td>0</td>
<td>-3.95</td>
<td>-3.33</td>
<td></td>
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<tr>
<td>CH$_3$-NH-CHO</td>
<td>0</td>
<td>0</td>
<td>2.99</td>
<td>2.99</td>
<td></td>
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<tr>
<td>CH$_3$-O-CH$_3$</td>
<td>0</td>
<td>2.98</td>
<td>7.00</td>
<td>7.00</td>
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<tr>
<td>CH$_3$-O-CHO</td>
<td>0</td>
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<tr>
<td>CH$_3$-CO-CH$_3$</td>
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<td>0.75</td>
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<tr>
<td>CH$_3$-CO-NH$_2$</td>
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<td>0</td>
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<td>CH$_3$-CO-OH</td>
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<td>NH$_2$-CO-NH$_2$$^d$</td>
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</tr>
<tr>
<td>NH$_2$-CO-OH</td>
<td>0</td>
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<td>0.97</td>
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<tr>
<td>HO-CO-OH</td>
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<td>0</td>
<td>0.97</td>
<td>14.11</td>
<td></td>
</tr>
</tbody>
</table>

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$^a$ 1 hartree = 627.5 kcal/mol.

$^b$ $\Delta E(90) = 24.67$ kcal/mol.

$^c$ $\Delta E(90) = 12.11$ kcal/mol.

$^d$ $\Delta E(90) = 18.87$ kcal/mol.
Total energies for the unrotated conformations of all molecules are listed in Table 1. Table 2 gives the relative energies
\[ \Delta E(\phi, \psi) = E(\phi, \psi) - E(0,0) \]
for a variety of conformations. Most of the molecules have been partly or fully examined with a 60° grid for \( \phi \) and \( \psi \), although larger steps are used in some cases.

![Unrotated or (0,0) conformations for molecules with two rotating groups.](image)

For the single rotors, the results with a 60° grid are usefully fitted to an analytical potential function of the form
\[ \Delta E(\phi) = \frac{1}{2} V_1 (1 - \cos \phi) + \frac{1}{4} V_2 (1 - \cos 2\phi) + \frac{1}{8} V_3 (1 - \cos 3\phi) \]  \hspace{1cm} (I)

Values of the constants \( V_1, V_2, V_3 \) are listed in Table 3.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( V_1 )</th>
<th>( V_2 )</th>
<th>( V_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3-\text{CH}_3 )</td>
<td>—</td>
<td>—</td>
<td>3.26</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{OH} )</td>
<td>—</td>
<td>—</td>
<td>1.12</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{CHO} )</td>
<td>—</td>
<td>—</td>
<td>0.74</td>
</tr>
<tr>
<td>( \text{NH}_2-\text{CHO} )</td>
<td>—</td>
<td>23.89</td>
<td>—</td>
</tr>
<tr>
<td>( \text{HO}-\text{CHO} )</td>
<td>5.75</td>
<td>8.93</td>
<td>0.55</td>
</tr>
<tr>
<td>( \text{CHO}-\text{CHO} )</td>
<td>5.73</td>
<td>4.85</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Discussion and Comparison with Experiment**

In this Section we shall discuss the rotational potential surface for each molecule in turn and compare it with results obtained by various experimental methods.
Some of these systems have already been studied by comparable ab initio molecular orbital techniques and these results will also be compared with the present work.

Ethane

The rotamer with staggered C-H bonds is found to be most stable with a barrier of 3.26 kcal/mol. This agrees with experiment (barrier 2.93 kcal/mol)\(^6\) and numerous other calculations.\(^7-15\)

Methanol

This is also found to have a staggered arrangement of single bonds but with a smaller rotational barrier of 1.12 kcal/mol. The experimental value\(^16\) is 1.07 kcal/mol and other theoretical studies have given similar results.\(^9,10\)

Acetaldehyde

The lowest energy conformation is predicted to be (1) with single bonds trans. The corresponding threefold rotational barrier is 0.74 kcal/mol. The same conformation is found experimentally\(^17\) (barrier values\(^17,18\) 1.16, 1.18 kcal/mol). Davidson and Allen\(^19\) have previously obtained comparable theoretical results using a Gaussian basis set of a similar type.

Formamide

This molecule is found to have lowest energy in the planar form with a barrier of 24.7 kcal/mol for rotation about the C-N bond. A microwave study\(^20\) has shown the nitrogen centre to be slightly non-planar (a possibility that is not permitted by our simplified geometrical model). The experimentally determined\(^21\) barrier to rotation about the C-N bond in formamide is 19 kcal/mol. Our calculated barrier is

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slightly higher than that (21.7 kcal/mol) of Christensen et al.\textsuperscript{22} who used a larger basis set (including d-type atomic functions). The assumption of a planar (or near-planar) disposition of bonds at nitrogen is probably a poorer approximation for the orthogonal conformation of formamide than for the planar form because delocalization of the nitrogen lone pair into the \( \pi \)-system of the CHO group is no longer possible. This factor may be responsible for the overestimation of the theoretical barriers.

**Formic Acid**

The lowest energy is found for the planar (OCOH) cis structure (2) with the OH bond eclipsing the carbonyl group. This conformation is in agreement with an experimental microwave study.\textsuperscript{23} According to the potential function (I) and the potential constants \( V_i \) in Table 3, a second local minimum in the potential curve occurs for the planar trans structure (3) with an energy higher by 6.3 kcal/mol. Experimentally, the absence of a microwave spectrum for the trans isomer has been invoked\textsuperscript{24} to suggest that the trans–cis energy difference is at least 4 kcal/mol, although a smaller value (2.0 kcal/mol) has been proposed on the basis of infrared work.\textsuperscript{25} The potential function (I) also predicts a rotational barrier in formic acid of 12.2 kcal/mol with the potential maximum occurring at \( \psi = 97^\circ \). This barrier is in reasonable agreement with experimental estimates\textsuperscript{25,26} (10.9 and 13.4 kcal/mol). Previous \textit{ab initio} molecular orbital calculations on formic acid\textsuperscript{27-29} have yielded trans–cis energy differences (8.1–9.5 kcal/mol) and rotational barriers (13.0–14.2 kcal/mol) comparable to those reported here.

**Glyoxal**

The s-trans form (4) is found to have the lowest energy in agreement with electron diffraction results.\textsuperscript{30} According to the potential (I) (Table 3), a second minimum occurs in the s-cis form, the energy of this isomer being higher by 6.1 kcal/mol. Very similar results were obtained in a molecular orbital study with a comparable basis set by Pincelli, Cadioli, and David.\textsuperscript{31} They obtained 6.4 kcal/mol for the cis–trans separation. The cis structure has recently been detected experimentally with an energy 3.2 kcal/mol greater than the trans form.\textsuperscript{32}

**Propane**

This molecule is a double threefold rotor. At the 60° grid, there are three distinct conformations, double-staggered, staggered-eclipsed, and double-eclipsed. The

\textsuperscript{25} Miyazawa, T., and Pitzer, K. S., \textit{J. chem. Phys.}, 1959, 30, 1076.
\textsuperscript{27} Ros, P., \textit{J. chem. Phys.}, 1968, 49, 4902.
first of these (Fig. 1) is found to be the stable form in agreement with experiment.\textsuperscript{33} The barrier for a single methyl rotation is predicted to be 3.7 kcal/mol, somewhat larger than in ethane. Such an increase is also found experimentally.\textsuperscript{34,35} The energy required to rotate the second methyl group, given that the first is already in an eclipsed arrangement, is calculated to be 5.1 kcal/mol. However, this is likely to be an overestimate, since other studies (with the smaller STO-3G basis set) indicate some opening of the C–C–C angle due to steric repulsion in the double-eclipsed conformation.\textsuperscript{14} Similar conclusions have been reached in an \textit{ab initio} study by Hoyland.\textsuperscript{36}

**Ethanol**

This molecule is predicted to have its lowest energy in the \textit{trans} form (5). If the methyl group is held in a staggered arrangement, rotation about the C–O bond may be described by the potential function (I). The potential constants so obtained\textsuperscript{3} (V\textsubscript{1} = 0.93, V\textsubscript{2} = -0.05, V\textsubscript{3} = 1.14 kcal/mol) indicate that there is a second minimum corresponding to a gauche CCOH angle (\(\psi = 115^\circ\)) approximately 0.6 kcal/mol higher in energy than the \textit{trans} form (5). Rotation of the methyl group in (5) is found to have a barrier comparable to that in ethane. The microwave spectrum of the \textit{trans} isomer has been assigned\textsuperscript{37-39} and there is some evidence\textsuperscript{38} for the existence of another form with \(\psi = 125^\circ\). However, the \textit{gauche–trans} energy difference has not yet been determined experimentally.

![Chemical structures](image)

**Propionaldehyde**

The structure (6) with the methyl and carbonyl groups in a \textit{cis} relationship is found to be the most stable. Again, by fixing the methyl group in a staggered arrangement, the rotation about the other C–C bond may be described by the potential function (I). The potential constants in (I) are determined as V\textsubscript{1} = 0.70, V\textsubscript{2} = 0.23, V\textsubscript{3} = 0.59 kcal/mol. A second minimum is then predicted at an approximately gauche conformation (\(\psi = 117^\circ\)) with an energy 0.7 kcal/mol higher than the \textit{cis} form. A microwave study\textsuperscript{40} has shown the \textit{cis} form to be more stable than the gauche (\(\psi = 131^\circ\)) by 0.9 kcal/mol. The \textit{gauche–cis} energy difference determined

\textsuperscript{33} Lide, D. R., Jr, \textit{J. chem. Phys.}, 1960, 33, 1514.
\textsuperscript{36} Hoyland, J. R., \textit{J. chem. Phys.}, 1968, 49, 1908.
\textsuperscript{40} Butcher, S. S., and Wilson, E. B., Jr, \textit{J. chem. Phys.}, 1964, 40, 1671.
from an n.m.r. study in the liquid state was 1.0 kcal/mol. We have also determined the barrier to rotation of the methyl group and found it to be somewhat greater than that in ethane (Table 2). This value could be artificially high because of steric interaction in the methyl-eclipsed conformation, exaggerated by our rigid rotor approximation. An experimental value of 2.28 kcal/mol has been reported for this barrier.

The lower energy associated with a methyl group cis to carbonyl is a feature found both experimentally and throughout these calculations. Its origin is apparently not associated with hyperconjugation involving the carbonyl π-electrons since comparable studies on the n-propyl cation indicate that the orthogonal structure (7) is most stable. An alternative explanation is that methyl provides a polarizable group close to the high intrinsic dipole of carbonyl.

Methanediol

This molecule has been studied for all thirteen distinct structures arising from a 60° grid for φ and ψ. The results clearly indicate that rotations about the C-O bonds are very strongly coupled and that there is a much greater variation in energy than would be expected on the basis of the potential function for rotation about the C-O bond in methanol. The lowest energy corresponds to the (120,120) double-gauche structure (8). The structure of the molecule is not known experimentally, but it may be noted that dimethoxymethane has this arrangement of bonds. Other local minima are not apparent with this grid and are found to be very shallow when a finer grid is used. A very notable feature of the surface is the great instability of the double-trans (0,0) structure (Fig. 1) which is more than 11 kcal/mol above the minimum. This conformation is actually a local maximum rather than the minimum that would be expected on the basis of staggered conformations. The implications of these results in the theory of the anomeric effect in carbohydrate chemistry are discussed elsewhere.

2-Hydroxyacetaldehyde

This molecule was only examined with a 120° grid together with an additional calculation for the (0,180) conformation (9). This last structure (9) in fact has the lowest energy of the six distinct conformations of 2-hydroxyacetaldehyde investigated and is presumably stabilized by intramolecular hydrogen bonding. No experimental structural information on this molecule is available in the literature. Karabatsos and Fenoglio have deduced from n.m.r. measurements that for 2-methoxyacetaldehyde the conformation in which the methoxy group is cis to the carbonyl is favoured over the gauche conformation by 0.4 kcal/mol. It should be noted however that

stabilization of this cis conformation through hydrogen bonding as in (9) is not possible.

\[ \text{[Chemical structure diagram]} \]

\( \text{N-Methylformamide} \)

The lowest energy is found for the (0,0) conformation (10). This has the methyl and carbonyl groups in a cis relationship as in propionaldehyde. The other form (11) with trans methyl and carbonyl groups is predicted to have an energy 2.7 kcal/mol higher. This result is in good agreement with nuclear magnetic resonance and other experimental studies\(^{46-49}\) which show both forms to be present, the cis (10) being more stable. The cis C–N–C=O arrangement is also normally found in polypeptides.

The theoretical rotational barrier of the methyl group in the cis isomer is quite large (1.1 kcal/mol), the most stable conformation (10) being that with C–H eclipsing N–H. In the trans isomer, the most stable arrangement of the methyl group has C–H eclipsing N–C and the rotational barrier is 0.3 kcal/mol. There does not appear to be any experimental information concerning the rotation of the methyl group in N-methylformamide.

\( \text{Dimethyl Ether} \)

This molecule is found to have lowest energy in the (0,0) or completely staggered conformation (Fig. 1) in agreement with experiment.\(^{50,51}\) The barrier for a single methyl rotation is calculated (3.0 kcal/mol) to be considerably higher than in methanol (1.1 kcal/mol). This is also in agreement with experimental observations\(^{50,52}\) (2.7 kcal/mol for CH\(_3\)OCH\(_3\) and 1.1 kcal/mol for CH\(_3\)OH). The barrier for rotation of the second methyl group given that one is already eclipsed is predicted to be larger (4.0 kcal/mol) but this may be overestimated since no allowance is made for opening of the COC valence angle to avoid steric repulsion.

\( \text{Methyl Formate} \)

Only three points were obtained on this potential surface. The lowest energy is found for structure (12) which is analogous to that of formic acid. The methyl

group is cis to the carbonyl and there is a staggered arrangement about the C-O bond in agreement with the microwave structure.\textsuperscript{53} The barrier to rotation about the C-O bond is considerably higher than experimental estimates\textsuperscript{18, 53} (1.19 and 1.17 kcal/mol). This poor result is probably due to the overestimation of steric interactions between the carbonyl oxygen and a methyl hydrogen in (13) due to our use of fixed standard bond lengths and angles.

\includegraphics[width=0.5\textwidth]{figures/12_13.png}

\textit{Acetone}

The lowest energy form is found to be the (0,0) structure illustrated in Figure 1. This has single bonds trans (as in acetaldehyde). There does not appear to be any direct experimental evidence on the lowest energy conformation of the methyl groups. However, the theoretical barrier of 0.75 kcal/mol is in good agreement with experimental values\textsuperscript{35, 54, 55} of 0.78–0.83 kcal/mol. Rotation of the second methyl group requires a slightly larger energy.

\textit{Acetamide}

For this molecule, the amide group was held planar and only the barrier to methyl rotation was examined. The lowest energy form is found to be (14) with single bonds trans. However, the calculated barrier is very low (0.3 kcal/mol). There does not appear to be any experimental information on the conformation of the methyl group.

\includegraphics[width=0.5\textwidth]{figures/14_15.png}

\textit{Acetic Acid}

The two planar arrangements of the carboxyl group were considered and the O=C–O–H cis arrangement is found to be more stable as in formic acid. The cis-trans separation (7.7 kcal/mol) is rather larger than in formic acid. The methyl group is predicted to have lowest energy in the form with single bonds trans (15). The full structure of acetic acid has not been determined experimentally, but the small

\textsuperscript{55} Swalen, J. D., and Costain, C. C., \textit{J. chem. Phys.}, 1959, \textbf{31}, 1592.
theoretical barrier (0.3 kcal/mol) is in good agreement with values\textsuperscript{56,57} (0.48 kcal/mol) obtained by microwave spectroscopy.

\textit{Urea}

In addition to the planar structure of this molecule which is indicated from X-ray crystal studies (see, for example, ref.\textsuperscript{58}) we have carried out a calculation on the (0,60) and (0,90) conformations. The relative energy of the (0,90) form (18.9 kcal/mol) represents the barrier to rotation of an amino group in urea and is smaller than the corresponding rotational barrier in formamide (24.7 kcal/mol). This calculated barrier lowering is in agreement with experimental observations on related molecules\textsuperscript{60} and with previous approximate non-empirical molecular orbital calculations.\textsuperscript{60} It is easily rationalized\textsuperscript{60} in terms of reduced double bond character in the C–N bonds because of the competing effect of the two NH\textsubscript{2} groups.

\textit{Carbamic Acid}

The two structures (16) and (17) were considered; (16) with O=C–O–H \textit{cis} is found to be more stable, in line with other carboxylic acids. The energy difference between these two forms is found to be exceptionally large. The structure of the parent molecule has not been determined experimentally but a crystallographic study\textsuperscript{61} of the ethyl ester, ethyl carbamate, indicates a structure analogous to (16).

\textit{Carbonic Acid}

The three structures (18)–(20) were considered; (18) is found to be most stable, again corresponding to a conformation with all single bonds \textit{trans}. However, the asymmetric structure (19) is also predicted to be quite stable. This second form is

\textsuperscript{56} Tabor, W. J., \textit{J. chem. Phys.}, 1957, 27, 974.
\textsuperscript{58} Caron, A., and Donahue, J., \textit{Acta crystallogr.} (B), 1969, 25, 404.
possibly stabilized by a favourable dipole interaction between the two OH groups (which might be thought of as a very distorted hydrogen bond). The structure of this molecule has not been determined experimentally.

**Conclusions**

The principal conclusions reached in this paper may be summarized as follows:

(i) Molecular orbital theory at this level with a split valence shell basis set gives a generally satisfactory description of the rotational potential functions as far as these are known experimentally.

(ii) For most of the molecules considered, the conformation with lowest energy is predicted to be one with single bonds in a *trans* arrangement where possible. This agrees with the available experimental information.

(iii) The numerical agreement for rotational barriers is good except in a number of cases in which some long-range steric overlap is likely to be an important factor. Out of eleven molecules for which experimental barriers are known, seven have theoretical barriers within 0.4 kcal/mol of experimental values. In the remaining four molecules, the rigid rotor approximation, in which no relaxation of valence angles is permitted, is unsatisfactory and the errors are larger. The mean absolute deviation for all eleven molecules is 1.2 kcal/mol.

(iv) In molecules where an appropriate choice is available, lower energies are achieved if methyl groups are arranged *cis* to neighbouring carbonyl groups. This effect has been recognized in experimental structures and is well accounted for by the theory. It may be interpreted as a consequence of the dipole-induced dipole interaction between the highly polar carbonyl group and the polarizable methyl group.

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