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# **Ab Initio Investigation of the Conformational Energies, Rotational Barriers, Molecular Structures, Vibrational Frequencies, and Dipole Moments of Aldehydes and Ketones**

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A detailed quantum mechanical study of aldehydes and ketones has been carried out at the HF/6-31G\* level. Computed relative conformational energies, rotational barriers, and geometries were calculated for a wide variety of molecules and compared with experiment. For the most part, both the computed relative conformational energies and the barriers are in reasonable agreement with experiment. In several cases there were differences observed between the quantum calculations and experiment which suggested a reinterpretation of the experimental data. For example, in the case of diisopropyl ketone, it was suggested that two conformers rather than the three assumed by experiment were present in equilibrium in the gas phase. For both cyclobutanecarboxaldehyde and methylcyclobutyl ketone the calculations predicted an additional (*axial, gauche*) low-energy minimum which has not been observed experimentally but should be possible to detect in the microwave spectrum. Relative to experiment, the computed C=O bond lengths are  $\sim 0.025$  Å smaller and the computed C=O stretches are  $\sim 280$  cm $^{-1}$  higher. For cycloalkanones the calculations qualitatively reproduce the experimentally observed variation in the C=O bond length and the dramatic decrease in the vibrational frequency with increasing ring size. The dipole moments computed for aldehydes and ketones are  $\sim 10\%$  higher than experiment with the exception of *equatorial,trans*-cyclobutanecarboxaldehyde, where it is 59% higher.

## **Introduction**

In previous publications<sup>1,2</sup> we reported a methodology for deriving a consistent molecular mechanics force field (CFF93) for hydrocarbons. This was accomplished in two stages. The first stage was the derivation of a quantum mechanical force field (QMFF) by fitting an analytic representation of the potential to *ab initio* data generated at the HF/6-31G\* basis level. The *ab initio* data utilized for this purpose were the relative energies, gradients, Hessian, and dipole moments for stationary points as well as distorted configurations. In the next stage the QMFF was refined to fit experiment by scaling the force constants and adjusting the reference bond lengths in order to overcome the systematic errors introduced by Hartree–Fock approximations. We now wish to extend this methodology from the hydrocarbons to aldehydes and ketones.

Since we rely on *ab initio* data at the modest HF/6-31G\* basis level for the derivation of the QMFF parameters, we have undertaken an extensive investigation of the deviations in the HF/6-31G\* basis level calculations from experiment for aldehydes and ketones. The experimental observables used for comparison are the conformational energy differences, rotational barriers, molecular structures, vibrational frequencies, and dipole moments.

Wiberg and Martin<sup>3</sup> have studied the effect of basis set (STO-3G, 3-21G, and 6-31G\*) and electron correlation (MP2 and MP3) on the calculated barriers to internal rotation about the C–C bond adjacent to the C=O group. Their study concluded that the methyl rotation barrier in acetaldehyde and acetone was unaffected by basis set. However, the barrier in propanal and butanone was found to be strongly dependent on the basis set,

the barrier calculated at the 6-31G\* basis level being closest to experiment. The effect of electron correlation on the barrier was found to be small in these four molecules. Therefore, the HF/6-31G\* basis set chosen for this *ab initio* study should provide reasonable estimates of the rotational barriers in aldehydes and ketones.

We expect systematic errors in the calculated bond lengths but closer agreement with experiment for the calculated valence angles. Once such trends are apparent, experimental or calculated geometries that do not conform to these trends can be examined more closely. In addition to the bond lengths, we wish to investigate the frequency of the stretching vibrations in order to establish trends in the bond strength.

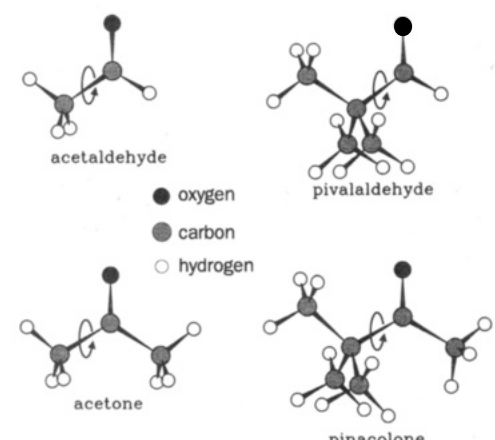
## **Method**

Most of the calculations were performed using the GAUSS-88, GAUSSIAN-90, and GAUSSIAN-92 *ab initio* codes on IBM RISC 6000 computers. The remaining calculations were conducted on the Convex and Multiflow computers using the GAUSSIAN code, and some of the frequency calculations were carried out on a Cray supercomputer using the program GRADSCF. The geometry of the transition states was optimized by the eigenvalue-following (mode-walking) method in the GAUSSIAN program. The location of barriers was verified by the calculated imaginary frequency. For situations where the experimental determination of the conformational energy difference was reported as a  $\Delta H$  or  $\Delta G$  value, zero point energy corrections and thermal energy corrections were applied to the calculated  $\Delta E$  in order to make valid comparisons to experiment.

## **Results and Discussion**

**Conformational Energies and Rotational Barriers** We are interested in examining the potential functions for internal

\* Abstract published in *Advance ACS Abstracts*, June 1, 1995.

TABLE 1: Effect of Methyl Substitution on the 3-Fold Rotational Barrier<sup>a</sup>


molecule	$\Delta E(\text{exp})$	$\Delta E(\text{HF/6-31G}^*)^b$
acetaldehyde	1.2 <sup>4</sup>	1.1 (-0.1) <sup>3</sup>
acetone	0.7 <sup>5</sup>	0.9 (0.2) <sup>3</sup>
pivalaldehyde	1.0 <sup>6</sup> –1.2 <sup>7</sup>	1.4 (0.3)
pinacolone	0.8 <sup>6</sup>	0.8 (0.0)

<sup>a</sup> Energy in kcal/mol. <sup>b</sup> Values in parentheses are deviations from experiment.

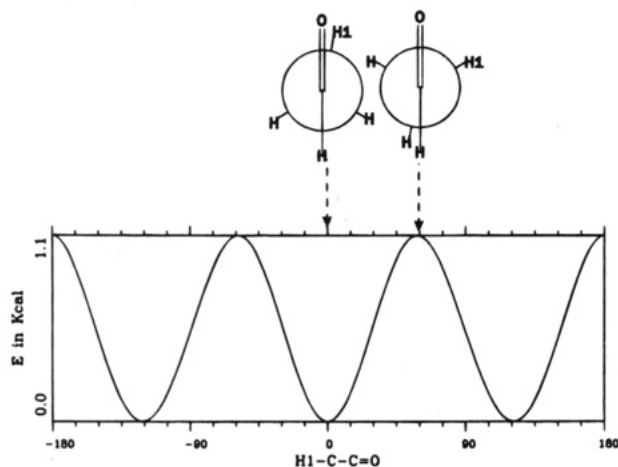


Figure 1. Energy as a function of the  $\text{H}_1\text{-C-C=O}$  dihedral angle ( $\Phi$ ) for acetaldehyde. Newman projections illustrate the eclipsed ( $\Phi = 0^\circ$ ) and staggered ( $\Phi = 60^\circ$ ) conformations.

rotation about the  $\alpha$  C–C bonds in aldehydes and ketones. In order to make the results clear we have described which bond and structure is under investigation in tables. In addition, graphs are shown for the energy changes which result as a function of the respective dihedral angle for internal rotation. These graphs also contain Newman projections of structures that correspond to energy minima and maxima. For example we initiate the study with acetaldehyde, whose structure is illustrated in Table 1; also depicted is the  $\alpha$  C–C bond about which the torsional motion is studied. Figure 1 contains the computed changes in potential energy as a function of the rotation about the  $\alpha$  C–C bond defined by the  $\text{H-C-C=O}$  dihedral angle. Newman projections are shown for the structures corresponding to the energy minimum and maximum on the torsional potential function.

**Acetyl and *tert*-Butyl Derivatives.** For acetaldehyde it is experimentally<sup>4</sup> known that the minimum-energy conformation is the eclipsed geometry (methyl H eclipsing the C=O bond). The staggered geometry is found (Figure 1) at the top of the barrier 1.2 kcal/mol higher than the eclipsed geometry. Replacing the aldehydic H in acetaldehyde with a  $\text{CH}_3$  group leads

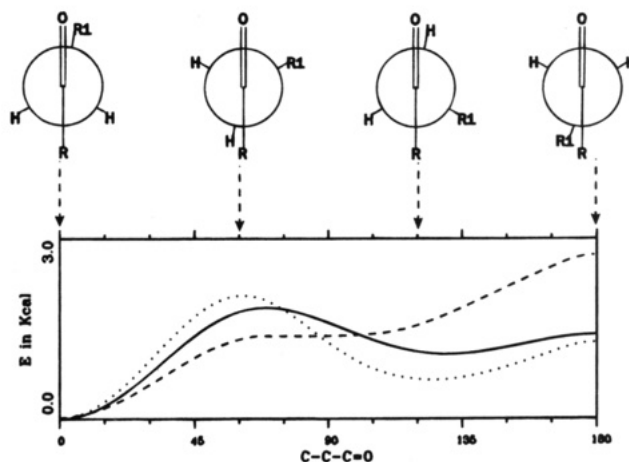


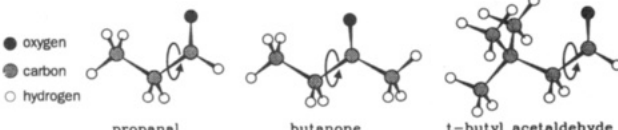
Figure 2. Energy as a function of the C–C–C=O dihedral angle ( $\Phi$ ) for propanal (solid curve,  $\text{R}_1 = \text{CH}_3$ ,  $\text{R} = \text{H}$ ), butanone (dashed curve,  $\text{R}_1 = \text{CH}_3$ ,  $\text{R} = \text{CH}_3$ ), and *tert*-butyl acetaldehyde (dotted curve,  $\text{R}_1 = \text{C}(\text{CH}_3)_3$ ,  $\text{R} = \text{H}$ ).

to acetone (Table 1), for which the staggered barrier was determined<sup>5</sup> to be 0.7 kcal/mol. Experimental measurements<sup>6,7</sup> have also established that replacement of a  $\text{CH}_3$  group in acetaldehyde or acetone with a bulky  $\text{C}(\text{CH}_3)_3$  group (pivalaldehyde and pinacolone) does not alter the height of the 3-fold barrier (Table 1). We decided to verify this independently with the help of *ab initio* (HF/6-31G<sup>\*</sup>) calculations.

For acetaldehyde and acetone, Wiberg and Martin<sup>3</sup> have shown that *ab initio* (HF/6-31G<sup>\*</sup>) predictions of an eclipsed minimum and of the height for the staggered barrier agree with experiment (Table 1). Our calculations (HF/6-31G<sup>\*</sup>) on pivalaldehyde and pinacolone also predict an eclipsed minimum. Furthermore, our calculations confirm that replacing the  $\text{CH}_3$  group in acetaldehyde and acetone with a bulky  $\text{C}(\text{CH}_3)_3$  group does not significantly change the height of the 3-fold barrier.

**Propanal, Butanone, and *tert*-Butyl Acetaldehyde.** This series of molecules provides an opportunity to investigate the effect of methyl substitution on the asymmetric torsional potential as a function of the C–C–C=O dihedral angle (denoted  $\Phi$ , see Figure 2). Experimental conformational studies<sup>8–10</sup> have identified the *cis* ( $\Phi = 0^\circ$ ) and *skew* ( $\Phi = 120^\circ$ ) conformers as minima in each of these three molecules. These experiments have determined the energy of the skew minimum relative to the *cis* minimum to be 1.0 ( $\Delta H$  at 0 K), 2.1 ( $\Delta G$  at 293 K), and 0.0 kcal/mol, respectively, for propanal,<sup>8</sup> butanone,<sup>9</sup> and *tert*-butyl acetaldehyde.<sup>10</sup>

Table 2 summarizes the calculated (HF/6-31G<sup>\*</sup>) conformational energies and compares them with experiment. The relative conformational energies of propanal are calculated within 0.2 kcal/mol of the energies obtained by fitting a torsional potential to microwave data.<sup>8</sup> For butanone, in addition to the  $\Phi = 0^\circ$  (*cis*) global minimum, we found two minima quite close to each other at  $\Phi = 83^\circ$  and  $\Phi = 120^\circ$  (*skew*), with relative energies of 1.5 and 1.7 kcal/mol, respectively. These calculations compare favorably with an electron diffraction study<sup>9</sup> where the conformational composition was determined by fitting theoretical curves for only two conformers (*cis* and *skew*) to the observed diffraction pattern. The present *ab initio* results for propanal and butanone are also within 0.3 kcal/mol of those of Wiberg and Martin,<sup>3</sup> who computed energies with the HF/6-31G<sup>\*</sup> basis set for geometries optimized at the 3-21G level. For *tert*-butyl acetaldehyde the relative energy calculated for the skew conformer disagrees by 0.6 kcal/mol with an experimental measurement<sup>10</sup> which was based on a temperature study of conformer bands in the microwave spectrum. The uncertainty in this experimental determination<sup>10</sup> was not reported.

**TABLE 2: Effect of Methyl Substitution on the Asymmetric Torsional Potential<sup>a</sup> about the C(O)—C (Bond)**


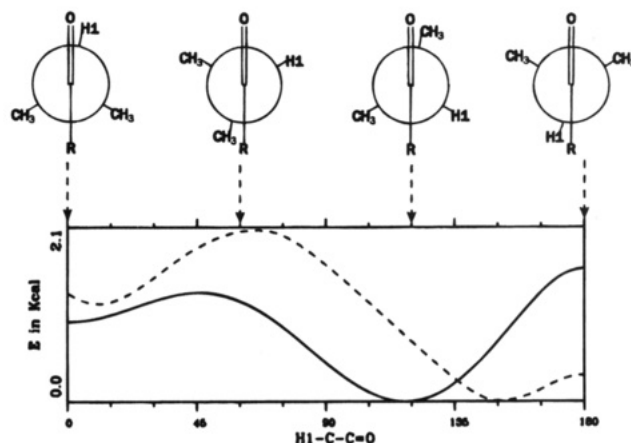
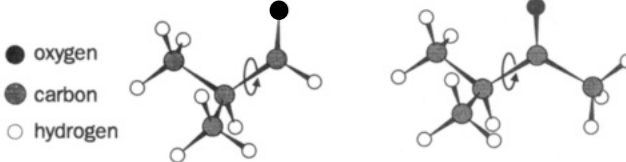
molecule	$\Phi(\text{C}-\text{C}-\text{C}=\text{O})$	$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6\text{-}31\text{G}^*)^b$
propanal	0.0	0.0	0.0
	60.0 <sup>c</sup>	2.1 <sup>8</sup>	2.1 (0.0)
	120.0		1.1
		$\Delta H(0 \text{ K}) = 0.9 \pm 0.1$	1.1 (0.2)
butanone	180.0 <sup>c</sup>	1.6	1.8 (0.2)
	0.0	0.0	0.0
	83.0		1.5
	120.0		1.7
		$\Delta G(293 \text{ K}) = 2.1 \pm 0.4^9$	1.9 (-0.2)
<i>tert</i> -butyl acetaldehyde	180.0 <sup>a</sup>		2.9
	0.0	0.0 <sup>10</sup>	0.0
	120.0	0.0	0.6 (0.6)
	180.0 <sup>c</sup>		1.6

<sup>a</sup> Energy in kcal/mol and dihedral angle in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment. <sup>c</sup> Barrier conformation.

Thus, our *ab initio* study finds the global minimum in propanal, butanone, and *tert*-butyl acetaldehyde to be the *eclipsed cis* form ( $\Phi = 0^\circ$ ). Upon replacing the aldehydic H in propanal by a  $\text{CH}_3$  group (i.e. butanone) the *skew* ( $\Phi = 120^\circ$ ) and *trans* ( $\Phi = 180^\circ$ ) conformations experience unfavorable  $\text{CH}_3 \cdots \text{CH}_3$  steric interactions. This interaction is largest in the *trans* ( $\Phi = 180^\circ$ ) conformation of butanone, whose relative energy of 2.9 kcal/mol is 1.1 kcal/mol higher than the relative energy for the *trans* form of propanal. It also explains the 0.6 kcal/mol increase in the relative energy of the *skew* conformation ( $\Phi = 120^\circ$ ) of butanone, thereby resulting in a relatively flat potential in the  $\Phi = 60\text{--}120^\circ$  region. This behavior was used by Allinger and co-workers<sup>11</sup> in MM2 (1987) to improve the torsional parameters in the MM2 (1977) force field in order to predict a shallow *skew* ( $\Phi = 120^\circ$ ) minimum for butanone. When the  $\text{CH}_3$  group in propanal is replaced by a bulky  $\text{C}(\text{CH}_3)_3$  group, the energy difference between the *cis* and *skew* minima is reduced from 1.1 to 0.6 kcal/mol. Here the *cis* conformation experiences additional destabilization due to steric strain between the *tert*-butyl group and the carbonyl oxygen.

**Isobutyral and Methyl Isopropyl Ketone (MIK).** Experimental studies<sup>12,13</sup> place the lowest energy conformation for these two molecules as one where an isopropyl C—C bond and the C=O bond are nearly *eclipsed* ( $\Phi \sim 120^\circ$ , see Figure 3) and the high-energy minimum as the conformation either where the C—H bond *eclipses* the C=O bond (isobutyral,  $\Phi = 0^\circ$ ) or where the methyl groups are *eclipsed* (MIK,  $\Phi = 60^\circ$ ).

For isobutyral, the conformational energy difference calculated (HF/6-31G\*) by Wiberg and Murcko<sup>14</sup> and Durig and co-workers<sup>15</sup> agrees with experiment (Table 3). The calculated barriers at  $\Phi = 60^\circ$  and  $\Phi = 180^\circ$  are 0.3 and 0.6 kcal/mol, respectively, lower than experiment. Inclusion of electron correlation<sup>14</sup> was shown to have no significant effect on these barriers. *Ab initio* (HF/6-31G\*) calculations for MIK show that the global minimum shifts from  $\Phi = 140 \pm 4^\circ$  measured experimentally<sup>13</sup> to  $\Phi = 153^\circ$  and the form at  $\Phi = 0^\circ$  is actually a transition state 0.2 kcal/mol higher than the  $\Phi = 16^\circ$  minimum. The calculated energy difference ( $\Delta G$  at 295 K)

**Figure 3.** Energy as a function of the  $\text{H}_1\text{—C—C=O}$  dihedral angle ( $\Phi$ ) for isobutyral (solid curve,  $\text{R} = \text{H}$ ) and methylisopropyl ketone (dashed curve,  $\text{R} = \text{CH}_3$ ).**TABLE 3: Calculated Rotational Barriers<sup>a</sup> for Isobutyral and MIK Compared to Experiment**


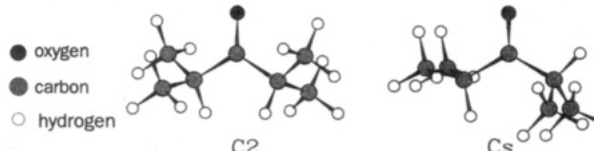
molecule	$\Phi(\text{H}-\text{C}-\text{C}=\text{O})$	$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6\text{-}31\text{G}^*)^b$
isobutyral	0.0	0.7 $\pm$ 0.1 <sup>12</sup>	0.7 (0.0) <sup>14,15</sup>
	60.0 <sup>c</sup>	1.8	1.5 (-0.3)
	120.0	0.0	0.0
	180.0 <sup>c</sup>	2.3	1.7 (-0.6)
methyl isopropyl ketone	0.0		1.5 <sup>c</sup>
		$\Delta G(295 \text{ K}) = 0.9 \pm 0.6^{13}$	
	16.3		1.3
			$\Delta G(295 \text{ K}) = 1.4$
	60.0 <sup>c</sup>		2.1
	153.0	0.0	0.0
	180.0		0.2

<sup>a</sup> Energy in kcal/mol and dihedral angle in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment. <sup>c</sup> Barrier conformation.

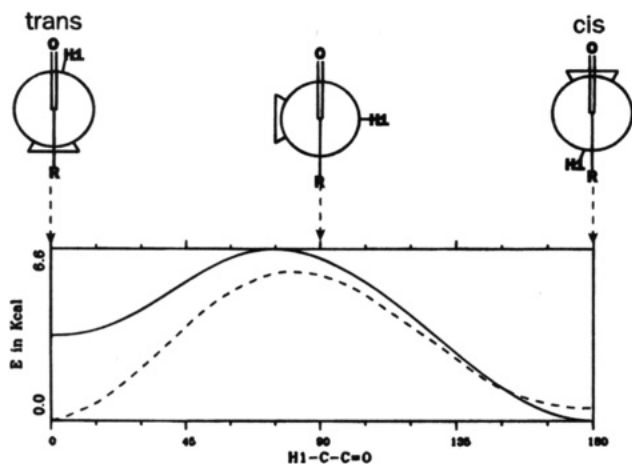
between the two minima of 1.4 kcal/mol is within the quoted uncertainty of the electron diffraction study<sup>13</sup> ( $0.9 \pm 0.6$  kcal/mol).

**Diisopropyl Ketone.** Electron diffraction results<sup>16</sup> indicate that diisopropyl ketone exists as an equal mixture of the  $\text{C}_1$ ,  $\text{C}_2$ , and  $\text{C}_s$  conformers at room temperature. The  $\text{C}_2$  conformer has the C=O group on the  $\text{C}_2$  axis of symmetry (Table 4) and the two isopropyl groups twisted above the below the plane formed by the  $\text{C}-\text{C}(=\text{O})-\text{C}$  atoms. The  $\text{C}_1$  conformer is similar to the  $\text{C}_2$  form with the exception that the two isopropyl groups twist on the same side of the  $\text{C}-\text{C}(=\text{O})-\text{C}$  plane. The  $\text{C}_s$  conformer has the two isopropyl groups maintaining the  $\text{C}-\text{C}(=\text{O})-\text{C}$  plane, but one of the isopropyl groups is *cis* to the carbonyl group and the other is *trans*. *Ab initio* (4-21G) calculations<sup>16</sup> predict relative energies of 0.0, 0.1, and 1.2 kcal/mol, respectively, for the  $\text{C}_1$ ,  $\text{C}_2$ , and  $\text{C}_s$  conformers. However, as reported<sup>16</sup> the optimization procedure for the  $\text{C}_1$  conformer was terminated when the largest residual Cartesian force was 0.0013 au.

At the HF/6-31G\* basis level a search for a minimum starting with a  $\text{C}_1$  geometry reverted to the  $\text{C}_2$  minimum with a largest Cartesian force of 0.000 017 au. The  $\text{C}_s$  minimum was

TABLE 4: Calculated Energy Difference<sup>a</sup> for Diisopropyl Ketone Compared with Experiment


conformer	exp <sup>16</sup>		6-31G*	
	$\Phi(\text{H}-\text{C}-\text{C}-\text{C})$	$\Delta E$	$\Phi(\text{H}-\text{C}-\text{C}-\text{C})$	$\Delta E$
C <sub>1</sub>	16, -62	0.0		
C <sub>2</sub>	59, 59	0.0	30, 30	0.0
C <sub>s</sub>	0, 180	0.0	0, 180	1.8

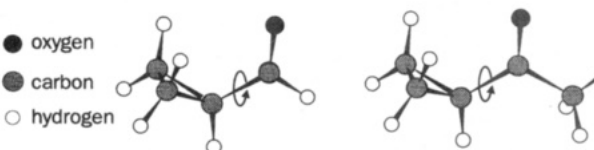
<sup>a</sup> Energy in kcal/mol and dihedral angle in degrees.Figure 4. Energy as a function of the H<sub>1</sub>-C-C=O dihedral angle ( $\Phi$ ) for cyclopropanecarboxaldehyde (dashed curve, R = H) and methyl cyclopropyl ketone (solid curve, R = CH<sub>3</sub>).

calculated 1.8 kcal/mol higher than the C<sub>2</sub> form. Disagreements between the present *ab initio* calculations and experiment over the relative stability of the conformers of diisopropyl ketone suggest the need for a more detailed experimental investigation, possibly utilizing these *ab initio* results to guide the analysis of the observed electron diffraction pattern or the microwave spectrum.

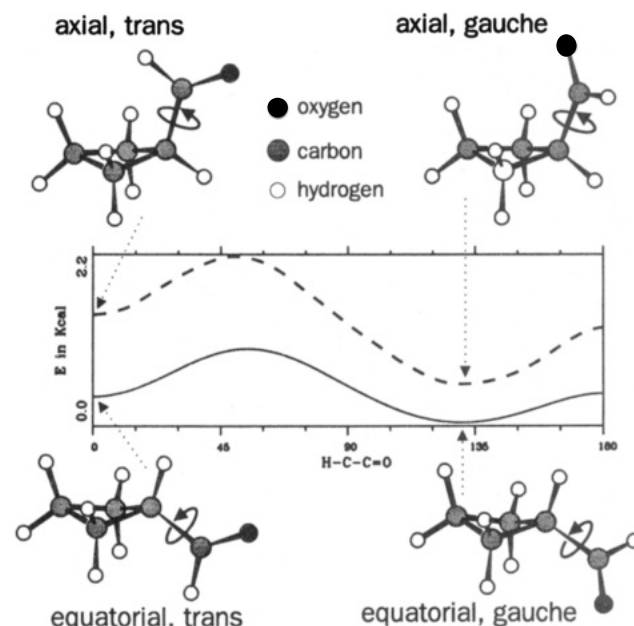
**Cyclopropanecarboxaldehyde and Methyl Cyclopropyl Ketone.** These two molecules exist as a mixture of *cis* and *trans* conformers separated by a large barrier (Figure 4). In the *cis* conformation the C=O group is *cis* to the bisector of the ring C-C<sub>α</sub>-C angle. For cyclopropanecarboxaldehyde<sup>17</sup> and methyl cyclopropyl ketone<sup>19</sup> experimental determinations of  $\Delta H$  at 298 K report the *cis* conformer to be 0.2 and 0.8 kcal/mol, respectively, more stable than the *trans* form.

At the HF/6-31G basis level *ab initio* calculations<sup>18</sup> for cyclopropylcarboxaldehyde predicted the *cis* conformation to be 0.5 kcal/mol more stable than the *trans* form. Inclusion of polarization functions on the carbon and oxygen atoms (i.e. the HF/6-31G\* basis set) results in the *cis* conformation lying 0.3 kcal/mol lower than the *trans* one (Table 5). Clearly, both experiment and *ab initio* results agree that the energy difference between the two minima is small. However, the calculated barrier (5.8 kcal/mol) is 1.5 kcal/mol higher than the experimental barrier (4.3 kcal/mol) which was obtained from a potential that was derived by fitting the torsional transitions observed in the far-infrared spectrum.

For methyl cyclopropyl ketone the *cis* conformer is calculated to be 3.1 kcal/mol ( $\Delta G$  at 298 K) more stable than the *trans* form. This is 2.3 kcal/mol higher than the results from an

TABLE 5: Conformational Energy Differences and Rotational Barriers<sup>a</sup> for Cyclopropanecarboxaldehyde and Methyl Cyclopropyl Ketone


molecule	conformer	$\Delta E(\text{HF}/6-31\text{G}^*)^b$	
		$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6-31\text{G}^*)^b$
cyclopropane-carboxaldehyde	<i>cis</i>	0.0 <sup>17</sup>	0.0
	barrier	4.3	5.8 (1.5)
	<i>trans</i>		0.3
		$\Delta H(298 \text{ K}) = 0.2$	0.2 (0.0)
methyl cyclopropyl ketone	<i>cis</i>	0.0	0.0
	barrier		6.6
	<i>trans</i>		3.0
		$\Delta G(298 \text{ K}) = 0.8 \pm 0.7^{19}$	3.1 (2.3)

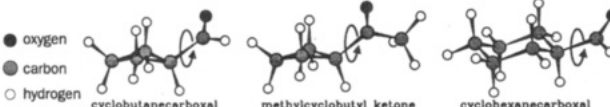
<sup>a</sup> Energy in kcal/mol and dihedral in angle degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.Figure 5. Energy as a function of the H-C-C=O dihedral angle ( $\Phi$ ) for the equatorial (solid curve) and axial (dashed curve) conformers of cyclobutanecarboxaldehyde.

electron diffraction experiment (0.8 kcal/mol) although the experimental uncertainty was substantial ( $\pm 0.7$  kcal/mol).

The large barriers calculated for cyclopropanecarboxaldehyde (5.8 kcal/mol) and methyl cyclopropyl ketone (6.6 kcal/mol) can be contrasted with the barriers for the corresponding open chain molecules formed by replacing the cyclopropyl group by an isopropyl group, i.e. isobutyral (1.5 kcal/mol) and methyl isopropyl ketone (2.1 kcal/mol). In force fields (i.e. QMFFs) which use the same set of parameters to describe the internal rotation of open chain and small ring compounds, inclusion of such barrier height information to the data used for fitting the parameters can help break the correlation between the torsional parameters.

**Cyclobutanecarboxaldehyde, Methyl Cyclobutyl Ketone, and Cyclohexanecarboxaldehyde.** The carbonyl group in these three molecules can be in an *equatorial* or an *axial* position with respect to the ring. Figure 5 illustrates the variation in energy as a function of the H-C-C=O dihedral angle for



**TABLE 6: Conformational Energy Differences<sup>a</sup> for Cyclobutanecarboxaldehyde, Methyl Cyclobutyl Ketone, and Cyclohexanecarboxaldehyde**


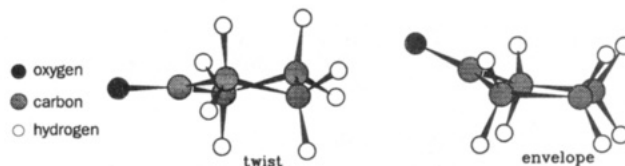
molecule	conformer	$\Delta E(\text{exp})$	$\Delta E(\text{HF/6-31G}^*)^b$
cyclobutane-carboxaldehyde	<i>eq, gauche</i>	0.0	0.0
	<i>eq, trans</i>		0.3
		$\Delta H(258 \text{ K}) = 0.2 \pm 0.1^{20}$	0.3 (0.1)
	<i>ax, gauche</i>		0.4
methyl cyclobutyl ketone	<i>ax, trans</i>		1.2
	<i>eq, gauche</i>	0.0	0.0
	<i>eq, trans</i>		2.1
		$\Delta H_{\text{liq}}(258 \text{ K}) = 1.4 \pm 0.2^{21}$	$\Delta H_{\text{gas}}(258 \text{ K}) = 2.2$
cyclohexane-carboxaldehyde	<i>ax, gauche</i>		0.6
	<i>ax, trans</i>		3.4
	<i>eq, gauche</i>	0.0	0.0
	<i>eq, trans</i>		0.7
		$\Delta G(253 \text{ K}) = 0.7 \pm 0.2^{22}$	0.5 (−0.2)
	<i>ax, gauche</i>		0.9
	<i>ax, trans</i> <sup>c</sup>		3.4

<sup>a</sup> Energy in kcal/mol. <sup>b</sup> Values in parentheses represent deviations from experiment. <sup>c</sup> Barrier conformation.

*equatorial* and *axial* cyclobutanecarboxaldehyde. For both the *equatorial* and the *axial* geometry, the expected minimum-energy conformations are *trans* and *gauche*. Experimental studies<sup>20–22</sup> on the conformational stability of these three molecules have found the *equatorial, gauche* form to be the lowest energy conformation. In each case the high-energy minimum was determined to be the *equatorial, trans* conformer. Notable in these experimental studies is the lack of any evidence for the *axial* conformers. Therefore, we have conducted an *ab initio* search for the *axial* as well as the *equatorial* minima of these three molecules in order to determine their relative stability. The *equatorial, trans* conformation of cyclobutanecarboxaldehyde was determined<sup>20</sup> to be  $0.2 \pm 0.1$  kcal/mol higher ( $\Delta H$  at 258 K) than the *equatorial, gauche* conformation by a temperature study of conformer bands in the microwave spectrum. *Ab initio* calculations correctly reproduce (Table 6) a small energy difference of 0.3 kcal/mol between the *equatorial, trans* form and the global *equatorial, gauche* minimum. However, the *axial* forms are only 0.4 kcal/mol (*gauche*) and 1.2 kcal/mol (*trans*) higher than the *equatorial, gauche* conformation. Therefore, with the help of the calculated rotational constants and dipole moment components, it should be possible to predict and locate the transitions of the *axial* conformers of cyclobutanecarboxaldehyde in the microwave spectrum.

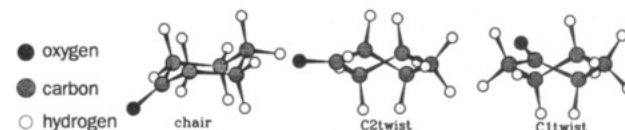
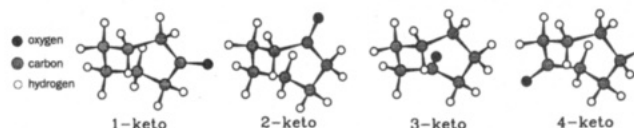
For cyclobutyl methyl ketone a temperature study of conformer bands in the Raman spectrum<sup>21</sup> of the liquid yielded an energy difference of  $1.4 \pm 0.2$  kcal/mol ( $\Delta H_{\text{liq}}$  at 258 K) between the *equatorial, trans* and the global *equatorial, gauche* minimum. *Ab initio* calculations also predict a global *equatorial, gauche* minimum. However, the *axial, gauche* form is calculated 1.5 kcal/mol lower in energy than the *equatorial, trans* minimum which was reportedly<sup>21</sup> detected in the vibrational spectrum. On the basis of these calculations it should be possible to observe the *axial, gauche* conformer in the gas phase.

For cyclohexanecarboxaldehyde, intensity measurements in the microwave spectrum<sup>22</sup> found the *equatorial, trans* form to be  $0.7 \pm 0.2$  kcal/mol higher ( $\Delta G$  at 253 K) than the global

**Figure 6.** Minimum-energy (*twist*) and barrier (*envelope*) conformations of cyclopentanone.**TABLE 7: Calculated Conformational Energy Differences and Rotational Barriers<sup>a</sup> for Cycloalkanones Compared with Experiment**

molecule	conformer	$\Delta E(\text{exp})$	$\Delta E(\text{HF/6-31G}^*)^b$
cyclopentanone	<i>twist</i>	0.0	0.0
	<i>envelope</i> <sup>c</sup>	2.4 <sup>23</sup> –3.7 <sup>24</sup>	2.9
cyclohexanone	<i>chair</i>	0.0	0.0
	<i>C<sub>1</sub>-twist</i>		4.5
	<i>C<sub>2</sub>-twist</i>		3.8
cycloheptanone, <i>twist-chair</i>	<i>1-keto</i>	0.0	0.1
	<i>2-keto</i>	0.2 <sup>26</sup>	0.0 (−0.3)
	<i>3-keto</i>	1.6	2.5 (1.0)
	<i>4-keto</i>	2.0	2.6 (0.7)
cyclodecanone	<i>1-keto</i>		3.5
	<i>2-keto</i>		5.3
	<i>3-keto</i>	0.0 <sup>27,28</sup>	0.0

<sup>a</sup> Energy in kcal/mol and dihedral angle in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment. <sup>c</sup> Barrier conformation.

**Figure 7.** Minimum-energy conformers found for cyclohexanone.**Figure 8.** Twist-chair conformers of cycloheptanone.

*equatorial, gauche* minimum. The calculated *ab initio* relative energy of  $\Delta G(253 \text{ K}) = 0.5$  kcal/mol is within the experimental uncertainty.

**Cycloalkanones.** The experimental value for the *envelope* barrier between the two equivalent *twist* minima (Figure 6) of cyclopentanone ranges from 2.4<sup>23</sup> to 3.7<sup>24</sup> kcal/mol. The *ab initio* value is 3.2 kcal/mol (Table 7), which is roughly in the middle of the experimental extremes. The barrier separating the global *chair* minimum from the remaining conformations of cyclohexanone is known to be  $\Delta G = 4.0 \pm 0.1$  kcal/mol<sup>25</sup> from NMR measurements. In the present *ab initio* work we find three minima: the *chair*, *C<sub>1</sub>-twist*, and *C<sub>2</sub>-twist* conformations (Figure 7) with relative energies of 0.0, 4.5, and 3.8 kcal/mol, respectively (Table 7). Although the relative stability of the minima is not known experimentally the MM3 force field<sup>29</sup> yields values of 0.0, 4.2, and 4.0 kcal/mol, respectively, for the *chair*, *C<sub>1</sub>-twist*, and *C<sub>2</sub>-twist* conformations.

Bocian and Strauss<sup>26</sup> fit a dynamical model for the ring pseudorotation of cycloheptanone to the low-frequency vibrational spectrum and found the *twist-chair* conformations to be the most stable. In the *twist-chair* framework, the carbonyl oxygen can be present as a substituent at the 1, 2, 3, or 4 position (Figure 8). The fitted potential<sup>26</sup> predicted a relative energy of 0.0, 0.2, 1.6, and 2.0 kcal/mol, respectively, for these conformations. As shown in Table 7, *ab initio* calculations correctly

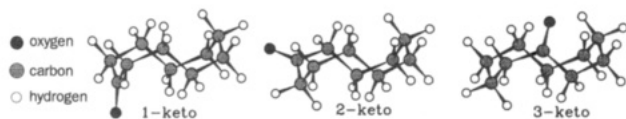


Figure 9. Minimum-energy conformers found for cyclodecanone.

TABLE 8: Calculated Conformational Energy Differences and Rotational Barriers<sup>a</sup> for Methyl-Substituted Cyclohexanones Compared with Experiment

molecule	conformer	$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6\text{-}31\text{G}^*)^b$
2-methylcyclohexanone	equatorial	0.0	0.0
	axial	2.1 <sup>30</sup>	2.1 (0.0)
3-methylcyclohexanone	equatorial	0.0	0.0
	axial		1.7
4-methylcyclohexanone	equatorial	0.0	0.0
	axial		2.3

<sup>a</sup> Energy in kcal/mol and dihedral angle in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.

TABLE 9: Calculated Conformational Energy Differences<sup>a</sup> for Cyclohexane-1,4-dione Compared with Experiment

molecule	conformer	$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6\text{-}31\text{G}^*)$
cyclohexane-1,4-dione	$D_2$ twist	0.0	0.0
	$C_{2h}$ chair		0.04
	$C_{2v}$ boat		6.3
		$\Delta H_{\text{liq}}(362\text{ K}) = 2.0 \pm 0.7^{31}$	$\Delta H_{\text{gas}}(362\text{ K}) = 0.3$

<sup>a</sup> Energy in kcal/mol.

predict the 1- and 2-keto conformers to be the low-energy forms and the 3- and 4-keto conformations to be higher in energy.

The crystal structure<sup>27</sup> and the NMR spectrum<sup>28</sup> of cyclodecanone provided evidence for only the 3-keto structure. Using the MM3<sup>29</sup> force field the 1-keto and the 2-keto conformers were calculated to be 2.5 and 4.4 kcal/mol, respectively, higher (Figure 9). The present *ab initio* study confirms that the 3-keto form is the lowest in energy and finds the 1-keto and 2-keto forms to be 3.5 and 5.3 kcal/mol, respectively, higher in energy (Table 7).

**Methyl-Substituted Cyclohexanones.** For methylcyclohexanones the *equatorial*, *chair* conformation is known to be the most stable form. The relative energy of the *axial*, *chair* conformation of 2-methylcyclohexanone has been experimentally determined<sup>30</sup> to be 2.1 kcal/mol. *Ab initio* results (Table 8) agree with experiment. For the 3- and 4-methyl-substituted cyclohexanones *ab initio* methods calculate relative energies of 1.7 and 2.3 kcal/mol, respectively.

**Cyclohexane-1,4-dione.** The relative stability of the *chair* ( $C_{2h}$ ) and *twist* ( $D_2$ ) conformations of cyclohexane-1,4-dione has been the subject of experimental<sup>31</sup> and *ab initio*<sup>29</sup> investigations by Allinger and co-workers. On the basis of a temperature study<sup>31</sup> of conformer bands in the Raman spectrum of the liquid, they report the *twist* form to be  $2.0 \pm 0.7$  kcal/mol more stable ( $\Delta H$  at 362 K) than the *chair* conformation. However, subsequent 3-21G level *ab initio* calculations<sup>29</sup> found the *chair* form to be 0.5 kcal/mol more stable than the *twist*. The present *ab initio* (HF/6-31G\*) study results in the *twist* form only 0.3 kcal/mol more stable ( $\Delta H$  at 362 K) than the *chair* (Table 9). This brings into question the interpretation of the rather subtle experimental results. In fact MM3<sup>29</sup> was parametrized to

TABLE 10: Calculated Conformational Energy Differences and Rotational Barriers<sup>a</sup> for Bicyclononanone Compared with Experiment

molecule	conformer	$\Delta E(\text{exp})$	$\Delta E(\text{HF}/6\text{-}31\text{G}^*)$
bicyclononanone	<i>chair, chair</i>	0.0	0.0
	<i>boat, chair</i>	$> 1.1^{32}$	1.8
	<i>twist, twist</i>		7.6

<sup>a</sup> Energy in kcal/mol.

reproduce the *ab initio* (3-21G) energy difference, presumably because of the intrinsic difficulty in interpreting this experimental data.

**Bicyclo[3.3.1]nonane-9-one.** Li and Li<sup>32</sup> have observed transitions of the *chair-chair* conformer in the microwave spectrum of bicyclononanone. On the basis of the sensitivity of their technique, the remaining stable forms were estimated to be at least 1.1 kcal/mol higher in energy.

In the present *ab initio* study the *chair-chair* conformation is calculated lowest in energy. The *boat-chair* and *twist-twist* minima (Table 10) are calculated to be 1.8 and 7.6 kcal/mol, respectively, higher. The *boat-boat* structure reverted to the *twist* form upon minimization.

**Trends in Molecular Structure and Vibrational Frequencies. C=O Bond.** The C=O stretching frequency is frequently used for the identification of carbonyl compounds, since it occurs in a relatively isolated region of the vibrational spectrum. Upon searching the literature for experimentally determined structures of open chain carbonyl compounds, we found that the C=O bond length varies in the range 1.206–1.209 Å in aldehydes and 1.210–1.219 Å in ketones (Table 11) with uncertainties of about 0.003 Å. The C=O stretching frequency observed in the vibrational spectrum ranged from 1743 to 1753  $\text{cm}^{-1}$  for aldehydes and from 1730 to 1734  $\text{cm}^{-1}$  for ketones. Therefore, we examined the C=O bond lengths and vibrational frequencies predicted by *ab initio* (HF/6-31G\*) calculations in order to establish if such trends were being followed.

The calculated (HF/6-31G\*) C=O length for the open chain aldehydes was 1.188 Å (except for 1.184 Å in formaldehyde), and those for the ketones were calculated to be  $\sim 0.005$  Å longer at 1.193 Å. The calculated C=O bond lengths were about 0.020 Å shorter than experiment. The C=O stretch frequencies were calculated to be about 280  $\text{cm}^{-1}$  higher than experiment and ranged from 2023 to 2032  $\text{cm}^{-1}$  in aldehydes and from 2002 to 2021  $\text{cm}^{-1}$  in ketones. Therefore, *ab initio* (HF/6-31G\*) calculations agree with the experimental trend that the C=O bond in aldehydes is slightly stronger than in ketones.

For aldehydes and ketones attached to small hydrocarbon rings (three and four membered) the calculated C=O bond lengths are about 0.030 Å shorter than experiment (Table 12) although the experimental lengths are not as well determined as for the open chain compounds. The calculated C=O stretching frequency for these molecules is  $\sim 280$   $\text{cm}^{-1}$  higher than experiment, similar to what was found for the open chain molecules.

For cycloalkanones the C=O bond length is experimentally known to increase (0.033 Å) with ring size from 1.191 Å in cyclopropanone to 1.224 Å in cyclodecanone (Table 13). *Ab initio* calculations predict a smaller (0.016 Å) increase in the C=O bond length. The experimental C=O stretch frequency

**TABLE 11: Comparison of Calculated C=O Bond Lengths and Stretching Frequencies<sup>a</sup> for Nonring Aldehydes and Ketones with Experiment**

molecule	bond length		vibrational frequency	
	exp	HF/6-31G <sup>*b</sup>	exp	HF/6-31G <sup>*b</sup>
formaldehyde	1.208 ± 0.003 <sup>33</sup>	1.184 (−0.024)	1746 <sup>34</sup>	2027 (281)
acetaldehyde	1.209 ± 0.003 <sup>35</sup>	1.188 (−0.021)	1743 <sup>36</sup>	2032 (289)
propanal	1.209 ± 0.004 <sup>37</sup>	1.188 (−0.021)	1753 <sup>37</sup>	2027 (274)
isobutyral, <i>skew</i>	1.209 ± 0.002 <sup>38</sup>	1.188 (−0.021)	1752 <sup>15</sup>	2024 (272)
isobutyral, <i>cis</i>	1.209 ± 0.002 <sup>38</sup>	1.188 (−0.021)		2027
pivalaldehyde	1.206 ± 0.006 <sup>39</sup>	1.188 (−0.018)		2023
acetone	1.210 ± 0.004 <sup>40</sup>	1.193 (−0.017)	1731 <sup>41</sup>	2021 (290)
butanone	1.219 ± 0.001 <sup>9</sup>	1.193 (−0.026)		2016
methyl isopropyl ketone, <i>skew</i>	1.217 ± 0.002 <sup>13</sup>	1.193 (−0.024)	1734 <sup>13</sup>	2011 (277)
diisopropyl ketone	1.215 ± 0.005 <sup>16</sup>	1.194 (−0.021)	1730 <sup>16</sup>	2002

<sup>a</sup> Bond lengths in Å and vibrational frequencies in cm<sup>−1</sup>. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 12: Calculated C=O Bond Lengths and Stretching Frequencies<sup>a</sup> for Aldehydes and Ketones Containing Three- and Four-Member Rings Compared with Experiment**

molecule	bond length		vibrational frequency	
	exp	HF/6-31G <sup>*b</sup>	exp	HF/6-31G <sup>*b</sup>
cyclopropanecarboxaldehyde, average	1.216 ± 0.002 <sup>42</sup>	1.190 (−0.026)		
<i>trans</i>		1.189	1722 <sup>17</sup>	2019 (297)
<i>cis</i>		1.191	1740	2004 (264)
cyclobutanecarboxaldehyde, <i>eq, gauche</i>	1.223 ± 0.017 <sup>20</sup>	1.189 (−0.034)	1739 <sup>20</sup>	2019 (280)
<i>eq, trans</i>	1.222 ± 0.019 <sup>20</sup>	1.188 (−0.034)	1739 <sup>20</sup>	2024 (285)
methyl cyclopropyl ketone, <i>cis</i>	1.220 ± 0.020 <sup>19</sup>	1.196 (−0.029)	1726 <sup>43</sup>	1996 (270)
methyl cyclobutyl ketone, <i>eq, gauche</i>		1.914	1731 <sup>21</sup>	2009 (278)

<sup>a</sup> Bond lengths in Å and vibrational frequencies in cm<sup>−1</sup>. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 13: Calculated C=O Bond Lengths and Stretching Frequencies<sup>a</sup> for Cycloalkanones Compared with Experiment**

molecule	bond length		vibrational frequency	
	exp	HF/6-31G <sup>*b</sup>	exp	HF/6-31G <sup>*b</sup>
cyclopropanone	1.191 ± 0.020 <sup>44</sup>	1.179 (−0.012)	1906 <sup>45</sup>	2153 (247)
cyclobutanone	1.202 ± 0.004 <sup>46</sup>	1.188 (−0.021)	1814 <sup>46</sup>	2087 (273)
cyclopentanone, <i>twist</i>	1.213 ± 0.004 <sup>47</sup>	1.189 (−0.024)	1748 <sup>48</sup>	2041 (293)
cyclohexanone, <i>chair</i>	1.229 ± 0.003 <sup>49</sup>	1.193 (−0.024)	1718 <sup>50</sup>	2018 (300)
cycloheptanone, <i>twist-chair</i>	1.219 ± 0.012 <sup>51</sup>		1718 <sup>26</sup>	
2- <i>keto</i>		1.194 (−0.025)		2002 (284)
3- <i>keto</i> cyclodecanone	1.224 <sup>29</sup>	1.195 (−0.029)		1994

<sup>a</sup> Bond lengths in Å and vibrational frequencies in cm<sup>−1</sup>. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 14: Comparison of Calculated C(O)–C Bond Lengths<sup>a</sup> for Nonring Aldehydes and Ketones with Experiment**

aldehydes			ketones		
molecule	exp	HF/6-31G <sup>*b</sup>	molecule	exp	HF/6-31G <sup>*b</sup>
acetaldehyde	1.514 ± 0.005 <sup>35</sup>	1.504 (−0.010)	acetone	1.517 ± 0.003 <sup>40</sup>	1.514 (−0.003)
propanal	1.515 ± 0.009 <sup>37</sup>	1.508 (−0.007)	butanone	1.518 <sup>9</sup>	1.519 (0.001)
isobutyral, <i>skew</i>	1.509 ± 0.003 <sup>38</sup>	1.513 (0.004)	MIK, <i>skew</i>	1.529 ± 0.001 <sup>13</sup>	1.525 (−0.004)
<i>cis</i>	1.507 ± 0.005 <sup>38</sup>	1.511 (0.004)	diisopropyl ketone	1.535 ± 0.002 <sup>16</sup>	1.534 (−0.001)
pivalaldehyde	1.516 ± 0.007 <sup>39</sup>	1.518 (0.002)	pinacolone		1.536

<sup>a</sup> Bond lengths in Å. <sup>b</sup> Values in parentheses represent deviations from experiment.

decreases (188 cm<sup>−1</sup>) from 1906 cm<sup>−1</sup> in cyclopropanone to 1718 cm<sup>−1</sup> in cycloheptanone. *Ab initio* calculations also predict a decrease although it is smaller (135 cm<sup>−1</sup>). As was seen for the open chain compounds the C=O bond lengths computed (HF/6-31G<sup>\*</sup>) for cycloalkanones are ~0.024 Å shorter than experiment and the C=O stretch is ~280 cm<sup>−1</sup> higher than experiment.

**C(O)–C Bond.** The calculated C(O)–C bond lengths are in the range 1.504–1.518 Å for aldehydes and 1.514–1.536 Å for ketones (Table 14). These bond lengths are within 0.01 Å of experimental results. Replacement of the acetyl hydrogens in acetaldehyde by methyl groups results in a small but noticeable elongation of the C(O)–C bond from 1.504 Å in acetaldehyde to 1.518 Å in the fully substituted pivalaldehyde. However, the uncertainty in experimental observations precludes us from confirming this trend. For ketones the uncertainty in

the experimental bond lengths is smaller and the calculated elongation in the C(O)–C bond upon increased methyl substitution of the acetone hydrogens matches experiment closely.

**C(O)–H Bond.** The C(O)–H bond lengths and C(O)–H stretching frequencies calculated (Table 15) for aldehydes are about 0.027 Å shorter and 360 cm<sup>−1</sup> higher, respectively, than experiment. The computed lengths increase by 0.006 Å from 1.092 Å in formaldehyde to 1.098 Å in pivalaldehyde. Experimentally such a trend is difficult to establish, since the reported uncertainty in the measurements is on the order of ~0.005 Å. With increasing hydrocarbon chain length the C(O)–H vibrational frequency decreases by 73 cm<sup>−1</sup> from the 3195 cm<sup>−1</sup> average in formaldehyde to 3124 cm<sup>−1</sup> in pivalaldehyde. The calculated decrease in the C(O)–H stretch of 64 cm<sup>−1</sup> from 3195 cm<sup>−1</sup> in formaldehyde to 3131 cm<sup>−1</sup> in *skew*-isobutyral matches closely the 56 cm<sup>−1</sup> decrease observed experimentally.



**TABLE 15: Comparison of Calculated C(O)—H Bond Lengths and Stretching Frequencies<sup>a</sup> for Nonring Aldehydes with Experiment**

molecule	bond length		vibrational frequency	
	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>
formaldehyde	1.116 ± 0.007 <sup>33</sup>	1.092 (−0.024)	2843 <sup>36</sup> 2782	3231 (388) 3159 (377)
acetaldehyde	1.128 ± 0.004 <sup>35</sup>	1.095 (−0.033)	2822 <sup>36</sup>	3150 (328)
propanal	1.131 ± 0.004 <sup>37</sup>	1.096 (−0.035)	2808 <sup>37</sup>	3142 (334)
isobutyral, <i>skew</i>	1.118 ± 0.002 <sup>38</sup>	1.097 (−0.021)	2757 <sup>15</sup>	3131 (374)
<i>cis</i>	1.116 ± 0.002 <sup>38</sup>	1.098 (−0.018)		3122
pivalaldehyde	1.130 ± 0.005 <sup>39</sup>	1.098 (−0.032)		3124

<sup>a</sup> Bond lengths in Å and vibrational frequencies in cm<sup>−1</sup>. <sup>b</sup> Values in parentheses represent deviations from experiment.

**C(O)—C—C Angle.** When the C—C bond eclipses the C=O bond, the calculated C(O)—C—C angle opens up by about 2–3° (Table 16) relative to the corresponding angle in the staggered form. With increased methyl substitution in aldehydes this angle decreases from 113.8° in *cis*-propanal to 112.0° in *skew*-isobutyral and 110.4° in pivalaldehyde. The C(O)—C—C angle corresponding to the staggered conformation also decreases from 111.8° in *skew*-propanal to 109.4–109.6° for isobutyral and 107.6° for pivalaldehyde. These calculated trends are in general agreement with experimental results. For the C<sub>2</sub> conformation of diisopropyl ketone there are two kinds of C(O)—C—C valence angles. For C(O)—C—C angle corresponding to  $\phi(\text{C—C—C=O}) = 31^\circ$  is 111.6°, and the angle corresponding to  $\phi(\text{C—C—C=O}) = -92^\circ$  is 108.4°.

**Angles at the Trigonal Carbonyl Center.** Methyl substitution of the acetyl hydrogens in acetaldehyde produces a 1.2°

increase in the C—C=O valence angle (Table 17) from 124.4° in acetaldehyde to 125.6° in pivalaldehyde. Experimental studies also indicate that this angle increases but by 2.7°. The calculated C—C=O angle for acetaldehyde is 1.1° larger than experiment although the uncertainty in the experimental determination was ±0.8°.

The calculated C—C(O)—C angle (Table 18) in open chain ketones increases 0.9° with increasing methyl substitution from 116.6° in acetone to 117.5° in the C<sub>2</sub> conformation of diisopropyl ketone. Such a trend is seen experimentally for acetone, butanone, and MIK. The C—C(O)—C angle reported<sup>16</sup> for diisopropyl ketone was poorly determined (±1.7°).

The calculated C—C(O)—C valence angles in three to ten-membered cycloalkanone rings agree to within 0.2° of experiment with the exception of cycloheptanone (Table 19). For cycloheptanone the calculated C—C(O)—C angle averaged over the low-energy *1-keto* and *2-keto twist-chair* conformations is 3.0° larger than the experimental determination of Dillen and Geise.<sup>51</sup> However, several assumptions were made in order to fit the limited electron diffraction data resulting in a poorly determined angle.

**Dipole Moment.** Literature values for the experimental dipole moments of aldehydes and ketones in the gas phase are listed in Table 20. These moments were obtained from Stark effect measurements in the gas phase. For aldehydes the moments range from 2.34 D in formaldehyde to 3.26 D in *trans*-cyclopropanecarboxaldehyde with the exception of that for the *equatorial, trans* conformation of cyclobutanecarboxaldehyde, which was reported<sup>20</sup> to be 2.06 ± 0.01 D. The calculated (HF/6-31G\*) dipole moments range from 2.67 D for formaldehyde

**TABLE 16: Comparison of Calculated C(O)—C—C Valence Angles<sup>a</sup> for Nonring Aldehydes and Ketones with Experiment**

molecule	C=O eclipsed		C=O staggered	
	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>
propanal, <i>cis</i>	113.8 ± 0.4 <sup>37</sup>	113.8 (0.0)		
<i>skew</i>			110.2 ± 0.4 <sup>37</sup>	111.8 (1.6)
isobutyral, <i>skew</i>	111.9 ± 0.3 <sup>38</sup>	112.0 (0.1)	109.3 ± 0.3	109.4 (0.1)
<i>cis</i>			109.3 ± 0.3	109.6 (0.3)
pivalaldehyde CCC <sub>3</sub>	110.5 ± 0.4 <sup>39</sup>	110.4 (−0.1)		
CCC <sub>4,5</sub>			107.4 ± 0.3	107.6 (0.2)
butanone, <i>cis</i>	113.5 ± 0.7 <sup>9</sup>	113.6 (0.1)		
methyl isopropyl ketone, <i>skew</i>	113.4 ± 1.0	112.0 (−1.4)	108.1 ± 1.0 <sup>13</sup>	109.4 (1.3)
diisopropyl ketone, C <sub>2</sub>		111.6		108.4

<sup>a</sup> Valence angles in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 17: Calculated Valence Angles at the Carbonyl Carbon<sup>a</sup> of Nonring Aldehydes Compared with Experiment**

molecule	C—C=O		C—C—H		O=C—H	
	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>
formaldehyde					121.8 ± 0.7 <sup>33</sup>	122.2 (0.4)
acetaldehyde	123.3 ± 0.8 <sup>35</sup>	124.4 (1.1)		115.3		120.3
propanal, <i>cis</i>	124.5 ± 0.3 <sup>37</sup>	124.8 (0.3)	114.7	115.0	120.8	120.2
<i>skew</i>	125.1 ± 0.3	124.7 (−0.4)	114.1	115.1	120.8	120.2
isobutyral, <i>skew</i>	125.5 ± 0.3 <sup>38</sup>	125.2 (−0.3)	113.1 ± 0.3	114.7 (1.6)	121.4 ± 0.1	120.1 (−1.3)
<i>cis</i>	125.7 ± 0.3	124.9 (−0.8)	113.9 ± 0.3	114.9 (1.0)	120.4 ± 0.1	120.2 (−0.2)
pivalaldehyde	126.0 ± 0.5 <sup>39</sup>	125.6 (−0.4)	113.0 ± 0.3	114.4 (1.4)	121.0	120.0 (−1.0)

<sup>a</sup> Angles in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 18: Calculated Valence Angles at the Carbonyl Center<sup>a</sup> of Nonring Ketones Compared with Experiment**

molecule	C—C(O)—C		C—C=O		C—C=O	
	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>	exp	HF/6-31G* <sup>b</sup>
acetone	116.0 ± 0.3 <sup>40</sup>	116.6 (0.6)	122.0	121.7	122.0	121.7
butanone	116.1 <sup>9</sup>	116.5	122.6 ± 1.0	121.5 (−1.1)	121.3 ± 0.7	122.1 (0.8)
MIK, <i>skew</i>	118.0 ± 0.8 <sup>13</sup>	117.1 (−0.9)	121.2	121.3	120.8 ± 1.4	121.5 (0.7)
diisopropyl ketone, C <sub>1</sub>	116.6 ± 1.7 <sup>16</sup>		121.0		122.4	
C <sub>2</sub>		117.5		121.2		121.2

<sup>a</sup> Angles in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 19: Comparison of the Calculated C—C(O)—C Valence Angle<sup>a</sup> for Cycloalkanones with Experiment**

molecule	C—C(O)—C	
	exp	HF/6-31G* <sup>b</sup>
cyclopropanone	64.6 ± 0.8 <sup>44</sup>	64.4 (−0.2)
cyclobutanone	92.8 ± 0.3 <sup>46</sup>	92.7 (−0.1)
cyclopentanone, <i>twist</i>	108.6 ± 0.2 <sup>47</sup>	108.8 (0.2)
cyclohexanone, <i>chair</i>	115.3 ± 0.3 <sup>49</sup>	115.4 (0.1)
cycloheptanone, <i>twist-chair</i> average	117.3 ± 1.8 <sup>51</sup>	120.3 (3.0)
1-keto		120.7
2-keto		120.0
3-keto cyclodecanone	119.1 <sup>29</sup>	118.9 (−0.2)

<sup>a</sup> Valence angles in degrees. <sup>b</sup> Values in parentheses represent deviations from experiment.

**TABLE 20: Calculated Dipole Moment<sup>a</sup> for Aldehydes and Ketones Compared with Experiment**

molecule	exp	HF/6-31G* <sup>b</sup>
formaldehyde	2.34 <sup>52</sup>	2.67 (0.33)
acetaldehyde	2.75 ± 0.06 <sup>53</sup>	2.98 (0.23)
pivalaldehyde	2.72 ± 0.01 <sup>39</sup>	2.96 (0.24)
<i>cis</i> -propanal	2.52 ± 0.04 <sup>54</sup>	2.88 (0.36)
<i>gauche</i> -propanal	2.86 ± 0.01 <sup>55</sup>	3.07 (0.21)
<i>gauche</i> -isobutyral	2.69 ± 0.03 <sup>56</sup>	2.95 (0.26)
<i>cis</i>	2.86 ± 0.03	3.08 (0.22)
<i>trans</i> -cyclopropanecarboxaldehyde	3.26 ± 0.01 <sup>17</sup>	3.47 (0.21)
<i>cis</i>	2.74 ± 0.01	2.97 (0.23)
<i>eq, gauche</i> -cyclobutanecarboxaldehyde	2.66 ± 0.02 <sup>20</sup>	2.99 (0.33)
<i>eq, trans</i>	2.06 ± 0.01	3.27 (1.21)
acetone	2.90 <sup>57</sup>	3.12 (0.22)
butanone	2.78 ± 0.01 <sup>58</sup>	3.00 (0.22)
<i>cis</i> -cyclopropyl methyl ketone	2.62 ± 0.26 <sup>59</sup>	3.01 (0.39)
cyclopropanone	2.67 ± 0.10 <sup>44</sup>	3.15 (0.48)
cyclobutanone	2.89 ± 0.03 <sup>60</sup>	3.16 (0.27)
<i>twist</i> -cyclopentanone	3.25 ± 0.02 <sup>61</sup>	3.28 (0.03)
<i>chair</i> -cyclohexanone	2.87 ± 0.04 <sup>62</sup>	3.39 (0.52)

<sup>a</sup> Dipole moments in Debye. <sup>b</sup> Values in parentheses represent deviations from experiment.

to 3.47 D for *trans*-cyclopropanecarboxaldehyde and are 6–14% higher than experiment with the exception of that for *equatorial*, *trans*-cyclobutanecarboxaldehyde. The calculated dipole moment of 3.27 D for the *equatorial*, *trans* conformer of cyclobutanecarboxaldehyde is substantially (59%) higher than experiment<sup>20</sup> and may suggest a need for a more detailed experimental investigation. Furthermore, it is surprising that rotational transitions due to the *axial*, *gauche* conformer of cyclobutanecarboxaldehyde, which is calculated to be only 0.4 kcal/mol higher than the global *equatorial*, *gauche* minimum (Table 6), were not observed in the microwave spectrum. For ketones the dipole moments vary over a 0.63 D range from 2.62 D in *cis*-cyclopropyl methyl ketone to 3.25 D in *twist*-cyclopentanone. The calculated (HF/6-31G\*) dipole moments for ketones vary over a narrower range of 0.39 D from 3.00 D in butanone to 3.39 D in *chair*-cyclohexanone and are 1–18% higher than experiment.

In summary the dipole moments calculated (HF/6-31G\*) for aldehydes and ketones are ~10% higher than experiment. Thus, the calculated (HF/6-31G\*) moments adjusted by 10% can be used as a reasonable estimate of the "true" dipole moment. Another application of these calculations is the use of the calculated dipole moment components in the principal axis system ( $\mu_i$ ,  $i = a, b, c$ ) to predict the relative line strength ( $A_i$ ,  $i = a, b, c$ ) of rotational transitions in the microwave spectrum, since the line strength is directly proportional to the square of the dipole moment component ( $A_i \propto \mu_i^2$ ).

## Summary and Conclusions

The conformational energies, rotational barriers, molecular geometries, vibrational frequencies, and dipole moments computed by *ab initio* (HF/6-31G\*) calculations for aldehydes and ketones have been compared with experimental determinations. The relative conformational energies and rotational barriers were accurately predicted by *ab initio* methods. The calculated C(O)—C—C, C—C=O, and C—C(O)—C valence angles also agree with experiment. The computed (HF/6-31G\*) C=O bond length (~0.025 Å too short), C(O)—H bond length (~0.027 Å too short), C=O stretch frequency (~280 cm<sup>−1</sup> higher), C(O)—H stretching frequency (~360 cm<sup>−1</sup> higher), and dipole moments (~10% higher) deviate systematically from experiment. Situations where there is a large discrepancy between *ab initio* and experimental energies or structures were pointed out which may warrant reexamining the experimental data in greater detail, and perhaps these *ab initio* predictions can be used to guide the analysis of the experimental observations.

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