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CONFORMATIONAL ANALYSIS—LXXIX

AN IMPROVED FORCE FIELD FOR THE CALCULATION OF THE STRUCTURES AND ENERGIES OF CARBONYL COMPOUNDS*†

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Abstract—Our previously described force field method has been extended to allow the calculation of structures and energies of molecules containing aldehyde or ketone groups. The method has been applied to a large number of simple cyclic and acyclic compounds, and has been shown to give good structures and energies insofar as these can be checked against available experimental data. Strain energies of ketones have been calculated, and comparison of these values to strain energies in the hydrocarbon series is discussed.

INTRODUCTION

DURING THE LAST FEW YEARS a considerable interest has developed in the *a priori* calculation of molecular structures.[1] While methods which explicitly include the quantum mechanics of the electronic system have been used to a slight extent,[2] calculations on larger molecules have most profitably followed the "molecular mechanics" scheme for practical reasons. Most of these latter calculations have been directed at one or another of two widely diverse classes of compounds: hydrocarbons, or proteins. In an earlier paper,[3] we showed that such calculations could give useful and interesting results for a variety of ordinary organic structures containing one or two of several different functional groups. Those calculations were preliminary in nature, being based upon a force field that was somewhat marginal in its characteristics. We have subsequently modified the force field for hydrocarbons,[4] and in the present paper will discuss the extension of this force field to molecules which contain a carbonyl group.

The basic force field used in the present work, including the parameters and the method of energy minimization, are all the same as described previously,[4] except for a few specific points which will be mentioned here. First, it is necessary to introduce a variety of parameters which pertain specifically to the carbonyl group. These include stretching, bending, and torsional force constants, dipole and van der Waals parameters for the unsaturated oxygen and carbon atoms. The values used are all given in Table 1. The force constants were either taken from the literature, sometimes with modifications so as to make them compatible with our force field, or in some cases evaluated by fitting to specific pieces of data concerning small molecules. The molecules acetaldehyde, acetone, propionaldehyde, and 2-butanone were used to pick numerical values for most of the unknown constants. The procedure used was similar to that described earlier.

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* Paper LXXVIII, N. L. Allinger and M. T. Tribble, *Tetrahedron Letters*, 3259 (1971)

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TABLE 1. PARAMETERS FOR CALCULATION OF MOLECULAR GEOMETRIES

van der Waals parameters for Hill equation[5]

Atom	r^*	ε
C_{sp^2}	1·85	0·033
O	1·54	0·070

Bond stretching parameters

Bond	l_0 (Å)	k (mdyn/Å²)[6,7]
$C_{sp^2}-C_{sp^3}$	1·504	4·4
$C_{sp}=O$	1·222	10·8
$C_{sp^2}-H$	1·111	4·6

Angle bending parameters

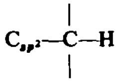
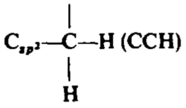
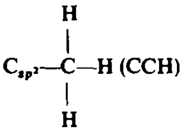
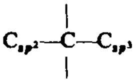
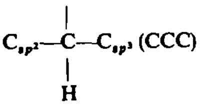
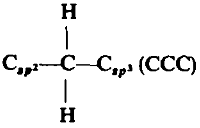
Angle		θ_0	k (mdyn/rad²)[8]
$C_{sp^3}-C_{sp^2}=O$	(in-plane)	122·2	0·57
	(out-of-plane)	0·0	0·80
$H-C_{sp^2}=O$	(in-plane)	122·0	0·25
	(out-of-plane)	0·0	0·80
$C_{sp^3}-C_{sp^2}-H$	(in-plane)	115·8	0·24
	(out-of-plane)	0·0	0·80
$C_{sp^3}-C_{sp^2}-C_{sp^3}$	(in-plane)	115·6	0·50
	(out-of-plane)	0·0	0·80
 $C_{sp^2}-\overset{\vert}{\underset{\vert}{C}}-H$		108·4	0·24
 $C_{sp^2}-\overset{\vert}{\underset{\underset{H}{\vert}}{C}}-H$ (CCH)		108·5	0·24
 $C_{sp^2}-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-H$ (CCH)		107·8	0·24
 $C_{sp^2}-\overset{\vert}{\underset{\vert}{C}}-C_{sp^3}$		109·5	0·40
 $C_{sp^2}-\overset{\vert}{\underset{\underset{H}{\vert}}{C}}-C_{sp^3}$ (CCC)		110·6	0·40
 $C_{sp^2}-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-C_{sp^3}$ (CCC)		110·2	0·40

TABLE 1—*continued*

Torsional effect

Angle	V_0 (kcal/mole)
$C_{sp^2}—C_{sp^3}—C_{sp^3}—H$	0·50*
$C_{sp^3}—C_{sp^3}—C_{sp^2}—C_{sp^3}$	−0·33
$C_{sp^3}—C_{sp^3}—C_{sp^2}—H$	−0·33
$C_{sp^3}—C_{sp^2}—C_{sp^3}—H$	0·08
$H—C_{sp^3}—C_{sp^2}—H$	0·50*
$C_{sp^3}—C_{sp^3}—C_{sp^2}=O$	−1·49
$H—C_{sp^3}—C_{sp^2}=O$	−0·61

Dipolar effect (where applicable)

	μ (Debeye)
C=O	2·70

Additional heat of formation parameters

	$C_{sp^2}—C_{sp^3}$	C=O	$C_{sp^2}—H$
normal	2·97*	−31·31	1·60
"strainless"	3·75*	−35·91	4·57

* These values were arbitrarily chosen to be the same as for hydrocarbons,[4] since the available parameters to be assigned are more than are necessary

As discussed earlier,[4] it is desirable that our bond lengths be consistent with those determined by diffraction experiments. Microwave spectra do not measure the same physical quantity, and "bond lengths" determined in that way are different, both by definition and in numerical value. We have therefore parameterized our model such that bond lengths between atoms other than hydrogen are on the average 0·006 Å longer than those obtained by microwave spectra, this being the optimum correction as near as we can judge.

We have also divided the bending about the carbonyl group into in-plane and out-of-plane bending components. For the torsion about a $CH_3—CO$ bond, we have used a three-fold function with a negative torsional constant in order to make the hydrogen eclipse the oxygen in the ground state. In addition, an even larger negative torsional constant is used when carbon eclipses oxygen, as this gives us the correct preferred conformation for propionaldehyde, the conformation with the methyl eclipsing oxygen. In line with recent calculations by Allen,[9] this barrier is an attractive rather than a repulsive barrier. The interaction energy of the carbonyl dipole with other dipoles has been calculated using the C=O bond vector, rather than the vector for the lone pair orbitals, which is perhaps the more proper way of doing it.[10]

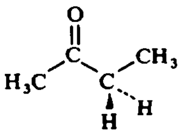
With these modifications, we have repeated much of our early work, and have checked that the 2-alkyl ketone effect and 3-alkyl ketone effect in cyclohexanone, and other such things, could be calculated with results comparable with or better than those previously obtained. For the most part, the differences obtained in the present work as compared with the earlier paper are small, and so these results will not be discussed further here. Our earlier work on carbonyl compounds[3] was limited to rather small molecules, since at that time the available computer (IBM 7074) and program required about 2 hours to do the structure of a molecule containing 30 total atoms. Because of improvements in our program as well as in computer capabilities (IBM 360/65 and CDC 6400 machines), such a structure now requires about 5 minutes of computer time, so we are now able to examine much larger and more complex systems (up to a total of 60 atoms).

In our earlier paper[3] we treated the bending around the carbonyl group in the same way as we had treated the bending at a tetrahedral carbon. This is a satisfactory approximation for calculations of structure under certain circumstances, but a more general method for treating such bending is to divide it into in-plane and out-of-plane components. This has been done in the present work, and the details are described in the Appendix. If this kind of procedure is not used, a serious error will come about in the structures of small ring ketones (for example), which can best be understood in the following way. The natural angles around the carbonyl group are approximately 120°. If the central C—C—C angle of a ketone is reduced to a much smaller value, as would happen in the case of cyclopentanone, the C—C—O angle is necessarily very much increased. If only the total angle is looked at, the calculation tries to reduce the C—C—O angle back to 120°, and it can only do this by bending the oxygen out of the plane of the three carbons. The actual molecule does not do this, of course; deformation in-plane occurs independently from the deformation out-of-plane, as is best understood by thinking of the σ system and the π system separately. In-plane deformation cannot be corrected by any out-of-plane motion, which will only distort the π system and serve to make things worse.

STRUCTURES

The structures of a few relatively simple molecules as given by the current calculation are reported in Table 2.

Our studies on the geometries and energies of small aliphatic carbonyl compounds have been straightforward and agree well with experiment. For example, the recent electron diffraction measurement for 2-butanone[15] and the calculations agree that the lowest energy conformer is as shown. We have also successfully reproduced the



conformational energy differences for the conformers of 2-pentanone reported in a recent study by Shimanouchi.[20]

Several structural studies of cyclic ketones have recently been reported. Cyclopentanone has been found to exist predominantly in the half-chair conformation in the gas phase[16] with no envelope conformation detected. Our calculations for the half-chair cyclopentanone are in excellent agreement with the experimental results,

TABLE 2. COMPARISON OF CALCULATED AND OBSERVED MOLECULAR GEOMETRIES[c]

Body length or angle	Calcd.[a]	Obsd.		
Acetaldehyde, *ecl.*		ED[11]	MW[12]	ED and MW[13]
$C{=}O$	1·223 Å	$1{\cdot}208_5 \pm 0{\cdot}003_5$	1·2155 ± 0·002	1·207 ± 0·004
$C_{sp^2}\text{—}C_{sp^3}$	1·513	$1{\cdot}514_2 \pm 0{\cdot}005_1$	1·501 ± 0·005	1·515 ± 0·005
$C_{sp^2}\text{—}H$	1·114	$1{\cdot}096_7 \pm 0{\cdot}053_5$	1·114 ± 0·15	1·114 ± 0·011
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}{=}O$	122·7°		123·9 ± 0·1	123·8 ± 0·2
$\sphericalangle H\text{—}C_{sp^2}{=}O$	119·6		118·6	118·1[b]
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}\text{—}H$	117·7		117·5 ± 0·8	117·5 (assmd)
Acetone, *ecl. ecl.*		ED[11]	MW[14]	MW[12]
$C{=}O$	1·224 Å	$1{\cdot}211_0 \pm 0{\cdot}004_1$	1·222 ± 0·003	1·215 (assmd)
$C_{sp^2}\text{—}C_{sp^3}$	1·512	$1{\cdot}516_7 \pm 0{\cdot}004_8$	1·507 ± 0·003	1·515 ± 0·005
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}{=}O$	121·9°		121·4[b]	121·9[b]
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}\text{—}C_{sp^3}$	116·3		117·2 ± 0·33	116·2 ± 1
2-Butanone, *trans*		ED[15a]	MW[15b]	
$C{=}O$	1·223 Å	$1{\cdot}218_6 \pm 0{\cdot}001_2$	1·222	
$C_{sp^2}\text{—}C_{sp^3}$ (1–2)	1·512	1·518	1·507	
$C_{sp^2}\text{—}C_{sp^3}$ (2–3)	1·515	1·518	1·507	
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}{=}O$ (1–2)	121·8°	$122{\cdot}5_5 \pm 0{\cdot}9_7$	121·4°	
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}{=}O$ (2–3)	121·5	$121{\cdot}3_3 \pm 0{\cdot}7_1$	$121{\cdot}4_0$	
$\sphericalangle C_{sp^3}\text{—}C_{sp^2}\text{—}C_{sp^3}$	116·7	116·2	117·2°	
Cyclopentanone, half-chair		MW[16a]	ED[16b]	
$C{=}O$	1·223 Å	1·215 ± 0·005	1·226	
$C_1\text{—}C_2$	1·509	1·504 ± 0·01	1·527 ± 0·001	
$C_2\text{—}C_3$	1·533	1·557 ± 0·007		
$C_3\text{—}C_4$	1·533			
$\sphericalangle C_5\text{—}C_1\text{—}C_2$	110·7°	110·5 ± 0·7	112·4 ± 0·3	
$\sphericalangle C_1\text{—}C_2\text{—}C_3$	103·2	104·5 ± 0·5	102·2 ± 0·3	
$\sphericalangle C_2\text{—}C_3\text{—}C_4$	103·8	103·0 ± 0·5		
τ	24·1	23·6 ± 0·4	22·1	
(angle between $C_5\text{—}C_1\text{—}C_2$ plane and the $C_3\text{—}C_4$ bond)				
Cyclohexanone, chair		MW[17]	ED[18]	MM[19]
$C_1\text{—}C_2$	1·511 Å	1·516	1·54 ± 0·01	1·510
$C_2\text{—}C_3$	1·529	1·535		1·532
$C{=}O$	1·224	1·222	1·24 ± 0·02	1·225
$\sphericalangle C_6\text{—}C_1\text{—}C_2$	114·9°	116·2°	117° ± 3°	115·9
$\sphericalangle C_1\text{—}C_2\text{—}C_3$	110·9	110·4°		111·8
$\sphericalangle C_2\text{—}C_3\text{—}C_4$	111·0	114·6°	109·5 ± 2·5	112·2
$\sphericalangle C_3\text{—}C_4\text{—}C_5$	110·6	110·7		112·1
$\sphericalangle C_1\text{—}C_2{=}O$	122·5		121·5° ± 1·5°	
$O\text{—}C\text{—}C\text{—}H_{eq}$	3·3			5·6
$O\text{—}C\text{—}C\text{—}H_{ax}$	112·9			104·4

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[a] Calculated bond lengths should be approximately 0·006 Å longer than experimental MW values (see text)

[b] Calculated by us assuming planar carbonyl group

[c] MW = microwave (experimental); ED = electron diffraction (experimental); MM = molecular mechanics (calculation)

and we find an energy difference between the half-chair and envelope forms of this compound to be 3·22 kcal/mole. (Pitzer and Donath calculated earlier a value of 2·4 kcal/mol for this quantity.[21]) This number is to be contrasted to the very low energy difference between the two forms of cyclopentane itself (~ 0 kcal/mol[21]). The experimental angle of twist (τ = the angle between the C_5—C_1—C_2 plane and the C_3—C_4 bond) in cyclopentanone is reported[16] as 22·1 and 23·6°; we calculate 24·1°. The high energy of the cyclopentanone envelope conformer above that of the half-chair is the result of increased van der Waals (~ 1·2 kcal) and torsional (1·3 kcal) energies associate with the eclipsing of the C_2—C_3—C_4—C_5 butane unit in the former. In cyclopentane envelope, the same degree of eclipsing is present, but very little is gained upon pseudorotation to the half-chair conformer, since there is a high degree of eclipsing in this conformer as well. Interestingly, these two different (C_2 and C_s) conformations seem to be all there are for the ketone. Other envelope and half-chair conformations which had the carbonyl off the C_2 axis or C_s plane did not correspond to minima, but slid downhill energetically and ended up as one of the symmetrical conformations.

Half-chair
0·00

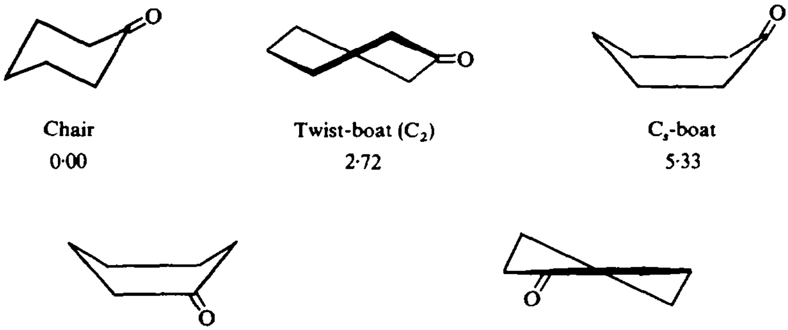
Envelope
3·22

Cyclopentanone

The microwave spectrum of cyclohexanone has recently been reported[17] but many geometrical assumptions had to be made before reaching structural conclusions. The authors did conclude, however, that cyclohexanone exists primarily in the chair form, and our calculated geometry agrees satisfactorily with one set of their tentative parameters.

Most of our earlier conclusions[22] concerning cyclohexanone rings have been confirmed and extended by the present work. Earlier,[22–24] we estimated from equilibrium data that the conformational energy of the boat form of cyclohexanone was 2·8–3·3 kcal/mole. In the present work we calculate a conformational energy of 2·72 kcal/mole for the twist boat (C_2) conformation, and 3·77 and 5·33 kcal/mole for the C_1 boat and C_s boat, respectively. The chair form therefore predominates for most substituted cyclohexanones, but the energies of the boat forms are relatively low, as is the barrier to inversion (calculated, 3·9; experimental,[25] 4·9 kcal/mole), and steric interactions can more easily affect the chair-boat equilibrium.[26] The reason for the low barrier to inversion in cyclohexanone compounds relative to cyclohexanone analogues is mainly a result of the much lower barrier to rotation about the C_{sp^2}–C_{sp^3} bond compared to that of the C_{sp^3}–C_{sp^3} moiety.

Bucourt[27] as well as Fournier and Waegell[19] have previously studied several conformations of cyclohexanone in some detail using molecular mechanical models with force fields which are superficially different from our own. Their calculated energy differences between the various conformers of this molecule are quite similar to our own values, but this fact is not too surprising considering the relatively strainless nature of cyclohexanone.



Chair
0·00

Twist-boat (C_2)
2·72

C_s-boat
5·33

C_1-boat
3·77

6-1-2-3 planar
(Transition state)
3·86

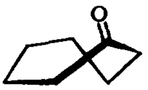
Cyclohexanone

The conformers of the medium ring ketones have been of interest to us for some time, but few structural studies have been carried out on this class of compounds.[28] Our choices of suitable conformers for each ring system were based on those which appeared to be the most promising from X-ray data on medium ring derivatives or from studies of molecular models.

The conformers of cycloheptanone can be placed into either the "chair" family or the "boat" family.[29] Since the twist boat-chair form of cycloheptane has previously been shown to be the lowest energy conformer of the hydrocarbon, this conformer was substituted at the 1, 2, 3, and 4 positions with the carbonyl moiety. In addition, the boat form was also substituted in the four non-equivalent positions although this form of the carbocyclic ring in the hydrocarbon is of higher energy than the twist boat-chair. The 2-substituted twist-chair conformer was found to be the lowest in energy, with the 1-substituted twist conformer only 0·25 kcal/mole higher. These results suggest that a conformational mixture of 1 and 2 exists at room temperature, a suggestion in agreement with earlier predictions.[29] The other twist boat-chair conformers contain ~ 1 kcal more torsional energy and ~ 0·5–1·0 kcal more van der Waals energy than cycloheptanone 2. The boat forms are consistently 2–4 kcal higher than this conformer.

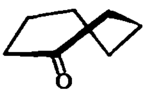
0·25

1



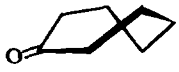
0·00

2



1·80

3



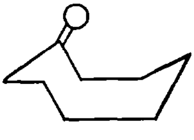
1·62

4

Previously we had predicted[30] that cyclooctanone would exist as a mixture of the boat-chair conformer **1** and the twist-crown conformer **6**. In our present calculations, we find that our earlier analysis was incomplete, and we calculate here that conformer **3** (not considered previously) has the lowest energy. Roberts[31] and Anet[32] have suggested that conformer **3** is the lowest in energy from some recent nmr studies.

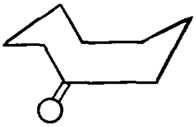
1

2·90



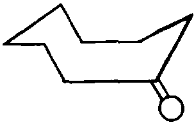
2

1·71



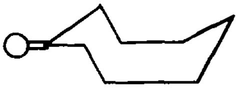
3

0·00



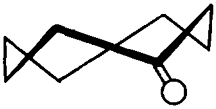
4

2·18



4

3·88

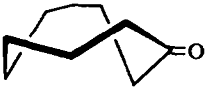


6

1·46

Cyclooctanone

There is very little discussion of the conformers of cyclononanone in the literature except for brief mention of the 4,4,7,7-tetramethyl derivative.[33] We have taken what was believed to be the lowest energy conformer of cyclononane discussed in an earlier paper,[4] as well as the symmetrical D_{3h} form which has subsequently been found to be of still lower energy,[54] and have substituted carbonyl groupings at five distinct centers on each hydrocarbon conformer. We find that cyclononanone **4** is substantially lower in energy than the other conformers. The energies of the 4,4,7,7-tetramethyl derivatives of the five conformations shown were similarly minimized, and the lowest energy conformers were found to be the ones with the conformations of cyclononanone **1** (0·00) and **2** (0·15). The other conformers of this molecule are much higher in energy than **1** and **2**. Steric interactions between Me groups are apparently the reason for preference for these conformers rather than those observed for the unsubstituted ketone. The conformation of the 4,4,7,7-tetramethyl derivative of cyclononanone **2** has been selected as the lowest energy conformer by NMR methods.[33]



ENERGIES	**1**	**2** (C_2)	**3**
Cyclononanone	1·59	5·59	3·94
4,4,7,7-Tetramethylcyclononanone	0·00	0·15	10·30

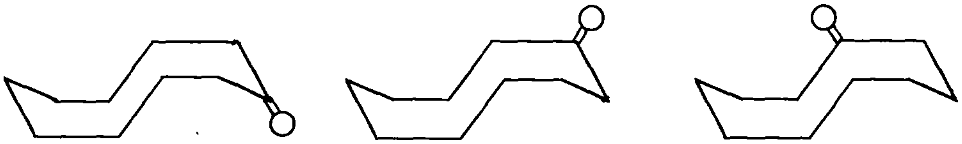
4 **5**

0·0 2·77

3·84 7·87

Cyclononanone

The preferred conformations of cyclodecanone have recently been discussed by Roberts,[31] and by Samuel and Weiss.[34] Roberts has suggested from ^{13}C NMR data that conformer **1** might be of lowest energy, and the latter authors have suggested that this form is of higher energy than **2** or **3** due to hydrogen-hydrogen van der Waals interactions in **1**. Our results indicate that **3** is the lowest energy conformer of the three by a substantial amount.

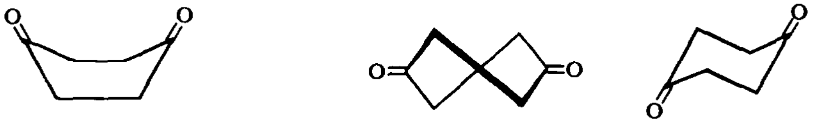


1 **2** **3**

5·45 2·38 0·00

Cyclodecanone

Several studies have been made on the conformation of cyclohexan-1,4-dione and similar compounds in solution.[22–37] and recently some conclusions contrary to our own have been voiced.[38] We have previously concluded from experimental dipole moment and spectroscopic data that this molecule is one of the few which exists preferentially in the boat form. It was further suggested that because of the relatively large dipole moment (1·3 D) measured in solution, a wide degree of pseudorotation was taking place at room temperature. Our present calculations indicate almost identical enthalpies for the chair and twist-boat (D_2) forms. The chair form would be expected to have less entropy, and therefore be less stable.

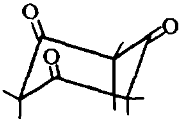


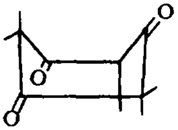
C_s-boat D_2-boat Chair

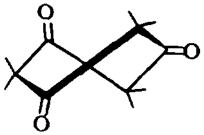
4·47 0·00 0·13

Klemperer[38] has recently suggested the chair conformation for cyclohexanedione in the gas phase. The weight of all previous evidence for the molecule in solution and in the crystal[39, 40] suggests that this conclusion is not correct. It is our feeling that the stable conformation in the gas phase, as in solution and in the crystal, is the twist-boat conformation, more or less distorted by a pseudorotational or wide vibrational motion toward the C_2 boat form. As long as the D_2 and C_2 structures are not separated by an appreciable barrier, one would anticipate that the molecular beam experiment (which gives a time average) would indicate a zero dipole moment, and yet dielectric constant measurements yield a very substantial moment. We believe that Klemperer's results, while consistent with the chair form as he suggested, are equally consistent with a pseudorotating twist-boat conformation as demanded by other data.

Dale[41] has recently reported the dipole moment of hexamethylcyclohexane-1,3,5-trione (1·03D), and concluded from studies of models that a conformational mixture of boat forms plus some small amount of chair form explained the experimental results.

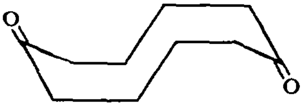

Chair
3·83

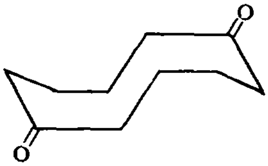

C_s boat
0·00

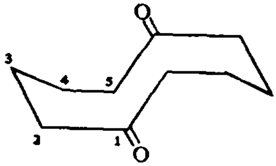

Twist-boat (C_2)
0·54

We calculate the C_s boat form to have the lowest energy ($\mu = 1·40$ D) and the twist-boat (C_2) is 0·54 kcal/mole higher in energy ($\mu = 1·24$ D). The very high dipole moment (3·94 D) and conformational energy (3·83 kcal/mole) of the chair form indicate that it is not a major component of the mixture at room temperature. The high energy of the chair form is largely a result of the steric crowding by the 1,3-methyl groups. The unsubstituted trione, on the other hand, has similar energies for all forms, including the chair, and the molecule probably exists as a mixture of all forms at room temperature (to the extent that it is non-enolic).

Dunitz[28] has recently reported the X-ray results for cyclodecane-1,6-dione, and has found that in the crystal the conformation is 3. Our calculations also show this conformer to be the one of lowest energy by a substantial amount. The distance between the C_1 and C_5 atoms we calculate to be 3·10 Å (3·13 Å, experimental) which is shorter than the analogous distance in cyclodecane.


1
3·81


2
10·30



3
0·00

Our calculated results for aliphatic aldehydes are essentially the same as reported earlier.[3] The most stable rotamer about the C_{sp^2}—C_{sp^3} bond in aldehydes is the one in which carbon eclipses the carbonyl oxygen. The addition of one or two bulky substituents on the α carbon can cause the preferential eclipsing of hydrogen instead however. This observation is manifested in the cycloalkane carboxaldehydes, a system which in many ways resembles the behavior of 2-methylpropanal.[42]

Stothers[43] and Karabatsos[44] have both studied the cyclohexane carboxaldehyde system by NMR methods and have concluded that the conformer with the carbonyl oxygen eclipsing the ring carbon is favored. Karabatsos calculates 0·4 kcal/mole difference between C-eclipsed and H-eclipsed rotamers in cyclohexane carboxaldehyde, and ~ 0 kcal/mole for this difference in cyclopentane carboxaldehyde. We calculate 0·76 and 1·06 kcal/mole, respectively, for these quantities (the envelope form of cyclopentane was used for the latter compound). While the energy difference between the conformers of cyclohexane carboxaldehyde is fair, our results for cyclopentane carboxaldehyde do not parallel those of Karabatsos, and the reason for the discrepancy is not apparent.

We wish to reproduce adequately the energies of compounds of this class, as well as their structures. With hydrocarbons this is a relatively easy problem, because there is an abundance of accurate experimental data for comparison purposes. The situation is not nearly as fortunate in the case of carbonyl compounds.

Only a few very accurate experimental papers have appeared on the subject. Two books[45, 46] and two papers[47, 48] have been selected by us as being consistent and accurate in reporting experimental results for aldehydes and ketones. The exact scheme that we use for the calculation of heats of formation and our method for estimating conformational contributions in each molecule is discussed in the Appendix.

In order to calculate heats of formation, it is necessary to assign bond energy contributions to the three kinds of bonds of a carbonyl group, C=O, C_{sp^2}—C_{sp^3}, and C_{sp^2}—H. These parameters were picked so as to fit the small and straight-chain molecules. For molecules which contain 4 or more carbons, the energies of the various conformational minima must be calculated separately, and the total energy of the Boltzman distribution determined for comparison with experiment.

The energy calculations are summarized in Table 3. Out of the 20 or so acyclic ketones reported here, only one set of glaring discrepancies exists and is worthy of note. For the 2-, 3-, and 4-octanones, our calculations are unreasonably far from the reported experimental values[49] (~ 3 to 6 kcal/mole errors). Since the experimental values are not consistent with the above mentioned standard references and since the ΔH_f° for even larger and more complex molecules than the octanones (such as 2,2,5,5-tetramethyl-3-hexanone and 6-undecanone) are well reproduced, we feel that this is an experimental problem.

On the whole, however, our calculated heats of formation for straight and branched chain ketones (Table 3) agree to within about 0·5 kcal/mol with the most recent experimental data. The aldehydes on the whole show reasonable agreement with experiments for heats of formation; however, ~ 1·0 kcal/mol should be the average error in these calculations.

As pointed out by Schleyer,[50] there is a real convenience in having available "strain energies" for molecules when one is trying to make comparisons between energies of molecules which are not isomers. To this end, we have developed a set of strain energies for carbonyl compounds which correspond to those for hydrocarbons given earlier.[4] These are given in Table 3. Particularly interesting are the strain energy differences between the hydrocarbons and the corresponding ketones (Table 4).

TABLE 3. HEAT OF FORMATION AND STRAIN ENERGY DATA

	ΔH_f° Exp.	ΔH_f° Calc.	ΔH_f° Calc.-Exp.	Strain Energy
Straight and Branched Chain Ketones				
Acetone	−51·90 ± 0·12	−52·13	−0·23	0·00
2-Butanone	−57·02 ± 0·20	−57·27	−0·25	0·05
2-Pentanone	−61·92 ± 0·26	−62·23	−0·31	0·28
3-Pentanone	−61·65 ± 0·21	−62·22	−0·57	0·29
3-Methyl-2-butanone	−62·76 ± 0·21	−62·91	−0·15	1·36
2-Hexanone	−66·87 ± 0·28	−67·24	−0·37	0·46
3-Hexanone	−66·57 ± 0·22	−67·19	−0·68	0·51
2-Methyl-3-pentanone	−68·38 ± 0·27	−67·76	0·62	1·70
3,3-Dimethyl-2-butanone		−69·81		2·57
2-Heptanone		−72·26		0·63
3-Heptanone		−72·21		0·68
4-Heptanone		−72·16		0·73
2,2-Dimethyl-3-pentanone	−74·99 ± 0·33	−74·81	0·18	2·76
2,4-Dimethyl-3-pentanone	−74·40 ± 0·28	−73·67	0·73	2·74
4,4-Dimethyl-2-pentanone		−76·62		0·95
2-Octanone	−82·47 ± 0·49	−77·28	[a]	0·80
3-Octanone	−80·93 ± 0·80	−77·21	[a]	0·87
4-Octanone	−83·49 ± 0·61	−77·17	[a]	0·91
2,2,4-Trimethyl-3-pentanone	−80·84 ± 0·38	−79·21	1·63	5·31
5-Nonanone	−82·41 ± 0·32	−82·17	0·24	0·74
2,2,4,4-Trimethyl-3-pentanone	−82·64 ± 0·29	−83·02	−0·38	9·61
2,6-Dimethyl-4-heptanone	−85·44 ± 0·27	−84·88	0·56	1·91
2,2,5,5-Tetramethyl-3-hexanone	−94·15 ± 0·52	−94·26	−0·11	3·56
6-Undecanone	−92·55 ± 0·47	−92·21	0·34	1·44
Monocyclic Ketones				
Cyclobutanone		−18·80		29·03
Cyclopentanone	−46·03 ± 0·40	−46·52	−0·49	6·40
Cyclohexanone	−54·04 ± 0·52	−55·32	1·28	2·79
Cycloheptanone	−59·1 ± 0·4	−56·79	2·3	6·51
Cyclooctanone	−64·9 ± 1·3	−59·52	5·4	8·97
Cyclononanone		−61·18		11·70
Cyclodecanone		−67·18		11·69
4,4,7,7-Tetramethylcyclononanone		−87·47		16·33
2-Methylcyclohexanone		−62·26		2·80
3-Methylcyclohexanone		−62·41		2·65
4-Methylcyclohexanone		−63·56		1·50
2-Ethylcyclohexanone		−66·99		3·26
cis-2,4-Dimethylcyclohexanone		−69·39		2·62
trans-2,4-Dimethylcyclohexanone		−67·46		4·55
cis-3,5-Dimethylcyclohexanone		−68·45		3·56
trans-3,5-Dimethylcyclohexanone		−69·53		2·48
cis-2,6-Dimethylcyclohexanone		−69·22		2·79
trans-2,6-Dimethylcyclohexanone		−67·24		4·77
cis-3,4-Dimethylcyclohexanone		−67·62		4·39
trans-3,4-Dimethylcyclohexanone		−68·61		3·40
3,3,5-Trimethylcyclohexanone		−77·09		3·03
3,3,5,5-Tetramethylcyclohexanone		−81·98		6·25
2,2,5,5-Tetramethylcyclohexanone		−83·28		4·95
2-*i*-Propylcyclohexanone		−72·66		4·54

TABLE 3—*continued*

	ΔH_f° Exp.	ΔH_f° Calc.	ΔH_f° Calc.-Exp.	Strain Energy
2-*t*-Butylcyclohexanone		−79·19		6·12
3-*t*-Butylcyclohexanone		−79·30		6·01
4-*t*-Butylcyclohexanone		−79·09		6·22
cis-2-Methyl-4-*t*-butylcyclohexanone		−86·15		6·11
trans-2-Methyl-4-*t*-butylcyclohexanone		−84·21		8·05
cis-2,4-di-*t*-Butylcyclohexanone		−103·26		9·25
trans-2,4-di-*t*-Butylcyclohexanone		−101·10		11·41
Polycyclic Ketones				
Norbornan-2-one		−38·69		18·54
1,7,7-Trimethylnorbornan-2-one (camphor)		−59·89		20·51
Adamantan-2-one		−57·31		9·42
Bicyclo[2.2.2]octan-2-one		−51·00		11·42
cis-Bicyclo[3.3.0]octan-3-one		−45·57		16·85
trans-Bicyclo[3.3.0]octan-3-one		−43·04		19·38
Bicyclo[3.3.1]nonan-2-one		−56·53		11·08
Bicyclo[3.3.1]nonan-3-one		−60·75		6·86
Bicyclo[3.3.1]nonan-9-one		−54·25		13·36
cis-Hydrindan-1-one		−57·08		10·53
trans-Hydrindan-1-one		−57·90		9·71
cis-Hydrindan-2-one	−59·3 ± 0·3[b]	−58·36	0·9	9·25
trans-Hydrindan-2-one	−59·7 ± 0·4[b]	−59·03	0·7	8·58
cis-Hydrindan-3-one		−57·97		9·64
trans-Hydrindan-3-one		−57·87		9·74
cis-8-Methylhydrindan-1-one		−64·64		11·08
trans-8-Methylhydrindan-1-one		−62·29		13·43
cis-8-Methylhydrindan-2-one	−68·56 ± 0·81[c]	−66·26	2·30	9·46
trans-8-Methylhydrindan-2-one	−65·74 ± 0·55[c]	−64·16	1·58	11·56
cis-8-Methylhydrindan-3-one		−66·13		9·59
trans-8-Methylhydrindan-3-one		−63·40		12·32
cis-9-Methyl-1-decalone		−72·52		8·39
trans-9-Methyl-1-decalone		−72·45		8·46
cis-10-Methyl-1-decalone		−73·22		7·69
trans-10-Methyl-1-decalone		−73·91		7·00
cis-2-decalone		−66·90		5·90
trans-2-decalone		−69·10		3·70
cis-10-Methyl-2-decalone		−73·31		7·60
trans-10-Methyl-2-decalone		−73·44		7·47
Polyketones				
Cyclohexane-1,4-dione		−79·37		5·71
Cyclohexane-1,3,5-trione		−100·99		11·05
Hexamethylcyclohexane-1,3,5-trione		−137·10		20·13
Cyclodecane-1,6-dione		−97·62		8·22
Aldehydes				
Acetaldehyde	−39·73 ± 0·12	−39·45	0·28	0·00
Propionaldehyde	−45·45 ± 0·21	−44·37	1·08	0·27
Butanal	−48·94 ± 0·34	−49·31	−1·00	0·52
2-Methylpropanal	−52·25 ± 0·37	−50·48	1·77	1·11
Pentanal	−54·45	−54·32	0·13	0·70
Hexanal	−59·37	−59·33	0·04	0·88

TABLE 3—*continued*

	ΔH_f° Exp.	ΔH_f° Calc.	ΔH_f° Calc.-Exp.	Strain Energy
3,3-Dimethylbutanal		−63·89		1·00
Heptanal	−63·1 ± 1·0	−64·34	−1·24	1·06
2-Ethylhexanal	−71·60 ± 0·46	−69·01	2·59	3·34
Octanal	−69·23	−69·35	0·12	1·24
Nonanal	−74·16	−74·37	−0·21	1·41
Decanal	−70·09	−79·39	−0·30	1·58
Cyclopentanecarboxaldehyde		−43·55		8·83
Cyclohexanecarboxaldehyde		−55·32		2·25

[a] See text

[b] P. Sellers, *Acta Chem. Scand.* **24**, 2453 (1970)

[c] P. Sellers, private communication. We are indebted to Dr Sellers for this information in advance of publication

TABLE 4. STRAIN ENERGY DIFFERENCES (KETONE MINUS HYDROCARBON)

Ketones	Ketone Strain Energy	Hydrocarbon Strain Energy	Difference (Ketone—HC)
Monocyclic			
Cyclobutanone	29·03	27·17	1·86
Cyclopentanone	6·40	7·53	−1·13
Cyclohexanone	2·79	1·75	1·04
Cycloheptanone	6·51	8·04	−1·53
Cyclooctanone	8·97	11·52	−2·55
Cyclononanone	11·70	14·97	−3·27
Cyclodecanone	11·69	15·68	−3·99
Polycyclic			
Norbornan-2-one	18·54	17·90	0·64
Adamantan-2-one	9·42	6·81	2·61
Bicyclo[2.2.2]octan-2-one	11·42	11·69	−0·27
cis-Bicyclo[3.3.0]octan-3-one	16·85	13·19	3·65
trans-Bicyclo[3.3.0]octan-3-one	19·38	19·59	−0·21
Bicyclo[3.3.1]nonan-2-one	11·08	10·35	0·73
Bicyclo[3.3.1]nonan-3-one	6·86	10·35	−3·49
Bicyclo[3.3.1]nonan-9-one	13·26	10·35	3·01

These numbers can be used for the purpose of predicting the effect of steric energy on chemical reactions which convert a ketone into something structurally analogous to hydrocarbon: *i.e.*, a molecule in which the trigonal carbon is replaced by a tetrahedral one. Thus the rate at which a ketone is reduced by $NaBH_4$ to yield an alcohol,[51] or the equilibrium constant for cyanohydrin formation,[52] will be proportional to this difference in strain energy. Such calculations have been carried out previously. The results here are in good/fair agreement with experiment for the monocyclic ketones.

Note that with cyclobutanone and cyclohexanone the ketone is more strained than the hydrocarbon. With the other simple monocyclic ketones the reverse is true. In cyclobutanone, there is serious bending at the trigonal carbon which tends to raise the energy of the ketone relative to that of the hydrocarbon. For cyclohexanone, the reason for the calculated result is less obvious. In the case of cyclopentanone, the angle bending is unfavorable at the carbonyl carbon, but the torsion removed by replacing a CH_2 by a carbonyl carbon is more serious, and hence the ketone is more favorable than the hydrocarbon. With the medium rings, a combination of reduced van der Waals and torsional energies makes them all the more stable as the ketone than as the hydrocarbon. The numbers parallel moderately well the curve for the reduction of cycloalkanones with borohydride.[51]

The difference in strain energy in cyclohexanone compared to cyclohexane is worthy of comment. Note (Table 4) that cyclohexanone is 1·0 kcal/mole more strained than is cyclohexane. This apparent excess strain in cyclohexanone has been noted before.[53] Those authors interpreted the excess strain in cyclohexanone as due to the eclipsing of the carbonyl group by the α hydrogens. However, there is much indirect evidence against this, and that the eclipsed conformation is in fact the stable conformation, so the question remains, "Why does cyclohexanone turn out to be strained relative to cyclohexane?" An examination of the data shows that cyclohexanone is strained relative to an open chain analog, for example 3-pentanone, because in the open chain compound one can have an alkyl eclipsing the carbonyl, whereas in cyclohexanone, since the alkyl groups are tied back, a hydrogen eclipses the carbonyl. There are other smaller effects also, but the basic instability in cyclohexanone, relative to an open chain analog, comes from this eclipsing effect. This interpretation is quite different from any previously given, but seems to account for in a very straightforward way the excess strain in cyclohexanone.

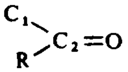
A set of previously experimentally unstudied bicyclic ketones has also been examined here. The replacement of a CH_2 group by a carbonyl group in bicyclo[2.2.2]octane-2-one relieves torsion, and hence the change in strain is negative. Also, *trans*-bicyclo[3.3.0]octane-3-one behaves similarly. On the other hand, introduction of a carbonyl group into norbornane causes an increase in strain, because the reduction in torsional energy is more than outweighed by the increase in the bending energy at the carbonyl carbon. For adamantanone, there is a rather large increase in energy in the ketone relative to the hydrocarbon. One might expect that the value should be about twice that in cyclohexanone relative to cyclohexane, and that is approximately true.

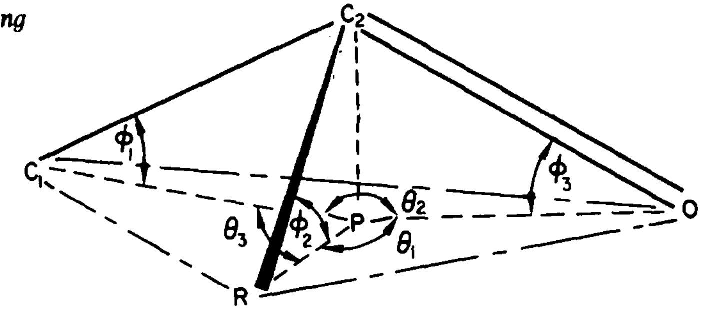
Note that cyclodecane → cyclodecanone involves a reduction in strain by 3·99 kcal/mole, since it removed 1 (of 2) serious internal H/H repulsions. Cyclodecanone → 1,6-cyclodecadione relieves the second repulsion, and the strain is reduced by another 3·47 kcal/mole. These large energy changes are in keeping with the chemistry of such compounds.

In summary, we believe that the calculated geometries obtained for carbonyl compounds are comparable in accuracy with those obtained for hydrocarbons earlier. Relative energies are also of comparable accuracy. The absolute values for heats of formation of carbonyl compounds are less accurate, simply because the available experimental data of high quality is insufficient to establish the necessary bond parameters with a high degree of reliability.

APPENDIX

Out-of-plane bending





For any group of four atoms (e.g. an sp^2-hybridized system) the bending may be divided into in-plane and out-of-plane components. In-plane components refer to the three angles, R—P—O, R—P—C$_1$, and C$_1$—P—O, where P is the projection of the central atom, C$_2$, into the plane of the other three atoms. These angles are designated θ_1, θ_2, and θ_3, respectively. The out-of-plane components refer to the three angles C$_2$—C$_1$—P, C$_2$—R—P, and C$_2$—O—P, referred to as ϕ_1, ϕ_2, and ϕ_3.

Our equations for bending in terms of each angle are as follows:

$$\underset{\text{(in-plane)}}{E_{\text{bend}}} = \sum_{i=1}^{3} k_i (\Delta\theta_i^2 + f\Delta\theta_i^3)$$

$$\underset{\text{(out-of-plane}}{E_{\text{benb}}} \quad \sum_{j=1}^{3} k_j (\Delta\phi_j^2 + f\Delta\phi_j^3)$$

where k_i is the in-plane bending constant, k_j is the out-of-plane bending constant, and f is the cubic bending constant defined in ref. 4. $\Delta\theta$ is the difference $(\theta_i - \theta_i^0)$ and $\Delta\phi$ is the difference $(\phi_i - \phi_i^0)$. (See Table 1 for values of θ^0 and ϕ^0.)

In the minimization scheme, when any atom a belonging to the four atom trigonal system described above is moved, the partial derivatives $\partial E/\partial X_a$, $\partial E/\partial Y_a$, $\partial E/\partial Z_a$ of all six angular bending energy equations are computed and are used in the determination of the new position of atom a.

Heat of formation calculation

In our previous paper[4] we described a method for calculating heats of formation and "strainless" heats of formation. To both of these calculations we must add the new quantities $\Delta H_{C=O}$, $\Delta H_{C_{sp^2}-C_{sp^3}}$, and $\Delta H_{C_{sp^2}-H}$ for the complete carbonyl system. These six quantities (3 for the normal calculation and 3 for the "strainless" ΔH_f^0 calculation) were evaluated by inspection in order to reproduce experimental heats of formation for acetone, 2-butanone, acetaldehyde, and propionaldehyde and to define these molecules as "strainless".

Since our heats of formation are for 25°C, it is necessary to correct for the fact that most molecules have a number of conformations present at this temperature. The energy is calculated or estimated for each conformation, a Boltzman distribution is assumed, and the resultant heat of formation is calculated from this distribution. For side chains extending no more than two carbons away from the carbonyl carbon, the energy of each possible conformation was calculated. For longer side chains, a standard increment of 0·34 kcal/mole was added for each carbon in the chain beyond the β carbon. This was found to be a mean and reasonably consistent value with the smaller chains. For example, the conformational contribution to the heat of formation of 2,6-dimethyl-4-heptanone was 1·03 kcal/mole, and was composed of the following increments: 0·35 (3-pentanone fragment) + 2 × 0·34 for the two additional extensions of the basic fragment.

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