

the hyperfine coupling constants measured in derivatives of $\text{COT}^{\cdot-}$ may be providing less information about the degree of bond alternation at the equilibrium geometries of these radical ions than about the ease with which geometries with more nearly equal bond lengths are accessed.

On the basis of INDO calculations, Hammons, Bernstein, and Myers¹³ have advanced explanations of the effects of substituents on the EPR spectra of $\text{COT}^{\cdot-}$ that are similar to those presented here. Other researchers^{12,31} have proposed an alternative model, which assumes bond alternation does not occur, so that the NBMOs in eq 1 are not mixed. Instead, this latter model postulates that there is a Boltzmann population of the lowest excited electronic state in which one electron is thermally excited from the lower energy of the two NBMOs to the upper.

Our CI calculations indicate that the basic assumption of the latter model is incorrect, since we find that bond alternation is energetically favorable, not only in $\text{COT}^{\cdot-}$, but also in its fluoro,

methyl, and cyano derivatives. Our calculations suggest that these substituents have a relatively small effect on the extent of bond length alternation at the equilibrium geometry. However, both F, a π donor, and CN, a π acceptor, are found to reduce substantially the barrier to bond equalization.

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Registry No. $\text{COT}^{\cdot-}$, 34510-85-5; F- $\text{COT}^{\cdot-}$, 70741-95-6; $\text{CH}_3\text{-COT}^{\cdot-}$, 34519-36-3; CN- $\text{COT}^{\cdot-}$, 70741-98-9.

Supplementary Material Available: ROHF/3-21G-optimized geometries and ROHF and CI energies for bond-alternated (C_s), angle-alternated (C_{2v}), and midpoint geometries of fluorocyclooctatetraene radical anion (2 pages). Ordering information is given on any current masthead page.

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Molecular Mechanics (MM3) Calculations on Aldehydes and Ketones

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Abstract: Aldehydes and ketones have been studied in some detail by using the MM3 molecular mechanics method. Approximately 50 structures have been calculated and compared with experimental data where available. Comparisons are also made of conformational equilibria, torsional potentials, moments of inertia, vibrational spectra, heats of formation, and other data. On the whole, the calculations yield information of experimental accuracy. The exception is in the case of vibrational spectra, where the rms error over four simple compounds amounts to 42 cm^{-1} . Heats of formation for 35 compounds are calculated to within 0.41 kcal/mol.

Introduction

Earlier papers have described the MM3 force field,³ which has previously been used for calculations on hydrocarbons,⁴ alcohols and ethers,⁵ amines,⁶ alkenes,⁷ and conjugated hydrocarbons.⁸ The present work is concerned with the extension of these calculations to the important class of carbonyl compounds.

A comprehensive study of carbonyl compounds with an early force field was reported some years ago.^{9,10} It was shown that

in general, a great many structural features for these compounds could be well reproduced. At the time that work was carried out, the rotational profile about the central bond in 2-butanone was not known, and it was assumed to be quite similar to the similar profile in propanal. It was subsequently shown by ab initio calculations reported by Wiberg and Martin¹¹ that the gauche conformation is not really a stable conformation, separated by a significant barrier from the anti, but rather the gauche conformation is just a shoulder on the side of the anti potential well. This was corrected in MM2(77).^{12,13}

Over the years it was shown¹⁴ that there are many errors, mostly small, built into the MM2 force field. Rather than try to continue to patch these, it was decided to start again from the beginning and generate a new force field, which is called MM3. In addition to fitting the information which was previously fit for carbonyl compounds with MM2, including the corrected 2-butanone ro-

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(3) The MM3 program is available from the Technical Utilization Corporation, Incorporated, 235 Glen Village Court, Powell, OH 43065, and from Molecular Design Limited, 2132 Farallon Drive, San Leandro, CA 94577. The current version is available to run on VAX computers. Modifications for other machines are being made, and interested parties should contact one of the distributors directly.

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tational profile, some additional points were considered. These include the vibrational spectra for compounds of this class. It was not possible to calculate very good spectra with MM2, because the force field was just too simplified. Vibrational spectra can now be calculated with MM3, although with only moderate accuracy. For hydrocarbons, the rms error in the vibrational frequencies over eight compounds was 35 cm^{-1} . This error is small enough that the structures and energies could be very well calculated, although it is not very good by the standards of vibrational spectroscopy. A similar accuracy was possible with the carbonyl compounds (42 cm^{-1} over four compounds). This accuracy can doubtlessly be improved by adding a few more cross terms into the force field. This addition has not yet been made, but we believe that the improvement will be negligible in all properties except the vibrational frequencies.

Results and Discussion

The procedure used for developing the carbonyl force field used the MM2 force field as a starting point. Because of various changes in the potential functions and in the hydrocarbon parameters, the structures as calculated initially using the MM3 force field but using MM2 parameters were only fair. Systematic adjustments were therefore made to the various parameters so as to improve the structures. The vibrational frequencies were then calculated for formaldehyde, acetaldehyde, propanal, and acetone. The various force parameters were then adjusted so as to improve the calculated frequencies. The structural parameters were then reoptimized. Additional compounds were then added to the data set, and the overall structures were gradually improved, while the four compounds were continually checked for their vibrational spectra. At a later stage, the heats of formation were also calculated, and then all of the parameters were optimized together from that point on. The optimization methods were mostly trial and error. Least-squares methods were used in the heat of formation calculations, but earlier experience¹⁸ showed us that attempts to use least-squares' methods for the structural parameters (as introduced by Lifson and Warshel¹⁹) really did not work very well, unless things were adjusted by hand additionally, and they consumed enormous amounts of computer time. They were consequently not used in the present work.²⁰

We also examined the vibrational spectra of cyclopentanone but did not weight this in the calculations, because the experimental spectrum is quite fragmentary. Later, we assumed that we could extend these calculations to cyclobutanone, in the same way that the alkane calculations had been extended to cyclobutane. The vibrational spectra of cyclobutane derivatives were not examined in the earlier work. When we looked at the spectra of cyclobutanone, we found some of the frequencies were seriously in error and concluded that it would be best to readjust some of the cyclobutane numbers, in addition to optimizing the cyclobutanone values. A discussion of the work on four-membered rings will be postponed to a later manuscript.

The parameters required to define the force field for carbonyl compounds (to which must be added to those for hydrocarbons⁴

(15) The MM2 force field for hydrocarbons was originally described in ref 16. Extensions to functionalized molecules have been described in subsequent papers, which are summarized in ref 17. The original program (MM2(77)) is available from the Quantum Chemistry Program Exchange, Creative Arts Building 181, 840 State Highway 46 Bypass, Bloomington, IN 47405, Program 395. The latest version of MM2, referred to as MM2(87), is available to academic users from QCPE and to commercial users from MDL.

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(20) Least-squares methods work directly with homogeneous data sets, where all the elements consist of quantities measured in the same units, and only their relative weightings need to be decided. In the present instance one wants to optimize many different kinds of physical quantities, and one needs to decide the relative weights of the different physical quantities. While we did this (ref 18) we found that it is expedient to just adjust the parameters being optimized, rather than to very indirectly adjust the weighting scheme. The application of trial and error methods becomes increasingly difficult as the size of the data sets increase, however, and we may be close to the practical limit for the use of these methods at this point.

Table I. Parameters (MM3) for Carbonyl Compounds

A. van der Waals' Parameters					
atom type ^a	ϵ	r	atom type ^a	ϵ	r
3	0.056	1.940	58	0.056	1.940
7	0.059	1.820	67	0.056	1.940
B. Bond Stretching Parameters					
bond	k_b , mdyn/Å	l_0 , Å	bond	k_b , mdyn/Å	l_0 , Å
3-7	10.10	1.208	7-58	10.15	1.202
1-3	4.80	1.509	3-5	4.37	1.118
1-3	4.80	1.514	5	4.20	1.486
56-58	4.56	1.543	4	11.42	1.196
C. Bending Parameters					
angle	k_θ , mdyn Å/rad ²	θ_0 , (deg)	angle	k_θ , mdyn Å/rad ²	θ_0 , (deg)
3-7	0.650		5-3-5	0.650	115.50
3-1	0.590		7-3-56	0.850	122.50
3-5	1.140		22-67-22	1.250	66.80
58-7	0.850		22-22-67	0.800	56.60
67-7	0.650		5-22-67	0.360	117.40
58-56	0.700		7-67-22	0.460	143.60
67-22	0.800		56-58-56	0.900	113.70
1-3-7	0.850	123.50	56-56-58	0.900	101.30
1-3-5	0.464	116.10	5-56-58	0.630	110.49
5-3-7	0.850	119.20	7-58-56	0.550	135.10
1-3-1	1.250	116.80	1-3-1	1.250	112.70
1-1-3	0.800	110.60	1-1-3	0.800	111.10
3-1-5	0.540	109.49			
D. Torsional Parameters					
dihedral angle	V_1	V_2	V_3		
1-1-3-5	0.655	0.266	0.474		
1-1-1-3	0.000	0.400	1.620	5	
1-1-1-3	0.000	0.400	0.010		
1-1-1-3-7	-0.457	1.106	-0.160		
3-1-1-3	0.000	0.000	0.100		
1-1-3-1	0.606	0.292	1.220	5	
1-1-3-1	0.406	0.292	0.014		
5-1-3-7	-0.154	0.044	-0.086		
5-1-3-1	0.000	0.000	0.150		
5-1-3-5	0.115	0.027	0.285		
3-1-1-5	0.000	0.000	0.180		
56-56-56-58	0.000	0.000	1.300	4	
56-56-58-56	0.000	0.000	0.500	4	
5-56-56-58	0.000	0.000	0.180		
5-56-58-56	0.000	0.000	0.130		
5-56-58-7	-0.154	0.044	0.100		
56-56-58-7	-0.457	1.106	0.160		
22-22-67-7	-0.300	1.200	0.150		
5-22-67-7	0.000	2.000	0.000		
5-22-22-67	0.000	0.000	0.300		
5-22-67-22	0.000	1.300	0.015		
E. Electronegativity Parameters					
bond	end of bond	atom type	correction (Å)		
1-1	1	3	-0.007		
56-56	56	58	-0.014		
22-22	22	67	0.033		
F. Torsion-Stretch Parameters					
atom type	K_{ts}				
1-3	0.100				
G. Bond Moments Parameters					
bond type	moment	bond type	moment		
1-3	1.01	56-58	0.75		
3-5	-0.60	7-58	-1.86		
3-7	1.86	22-67	0.53		
1-3	1.18	5	-1.86		

^a Atom type numbers are as previously in MM3, except for atoms contained in a four-membered ring. All of those discussed in this paper are also the same as those used in MM2 except 56, 58, and 67, which are used in MM3 for sp^3 , sp^2 , and carbonyl carbons in a four-membered ring, respectively.

Table II. Experimental and Calculated Spectra of Formaldehyde

exptl ²¹	MM3	diff	sym	assignment
2874	2879	5	B ₁	asym ^a C-H stretching
2780	2806	30	A ₁	sym C-H stretching
1744	1789	35	A ₁	C=O stretching
1504	1424	-80	A ₁	H-C-H bending
1280	1258	-22	B ₁	O-C-H in-plane-bending
1167	1112	-55	B ₁	O-C-H out-plane-bending

^aThe abbreviation asym is used throughout this manuscript for antisymmetric.

Table III. Experimental and Calculated Spectra of Acetaldehyde

exptl ²¹	MM3	diff	sym	assignment
3010	2973	-37	A''	asym CH ₃ stretching
3010	2973	-37	A'	asym CH ₃ stretching
2967	2877	-90	A'	sym CH ₃ stretching
2822	2821	-1	A'	CH stretching
1743	1757	14	A'	C=O stretching
1441	1425	-16	A''	asym CH ₃ def
1420	1421	1	A'	asym CH ₃ def
1400	1380	-20	A'	C-H in-plane-bending
1352	1331	-21	A'	sym CH ₃ def
1113	1016	-97	A'	C-C stretching
919	973	54	A''	CH ₃ rock, C-H out-plane-bending
867	897	30	A'	CH ₃ wagging
763	776	13	A''	C-H out-plane-bending
509	525	16	A'	O-C-C bending
150	155	4	A''	H-C-C-O torsion
rms		42		

Table IV. Experimental and Calculated Spectra of Propanal

exptl ²²	MM3	diff	sym	assignment
2991	2965	-26	A''	asym CH ₃ stretching
2991	2964	-27	A'	asym CH ₃ stretching
2951	2946	-5	A''	asym CH ₂ stretching
2940	2898	-42	A'	sym CH ₂ stretching
2905	2870	-35	A'	sym CH ₃ stretching
2808	2818	10	A'	C-H stretching
1753	1757	4	A'	C=O stretching
1467	1462	-5	A''	CH ₃ def
1467	1457	-10	A'	CH ₃ def, CH ₂ wagging
1421	1450	29	A'	CH ₃ def, CH ₂ wagging
1387	1411	24	A'	CH ₂ scissoring
1380	1388	8	A'	CH ₂ wagging
1334	1366	32	A'	C-H in-plane-bending, CH ₂ twist
1253	1198	-55	A''	CH ₂ wagging
1136	1028	-108	A'	CH ₂ twist
1097	1027	-70	A''	CH ₃ wagging, C-C (type 1-1) stretching
1010	1018	8	A'	CH ₃ rock
896	887	-9	A''	C-C (type 1-1) stretching, CH ₃ wagging
846	848	2	A'	CH ₂ , CH ₃ rock, C-H out-plane-bending
664	731	67	A'	C-C (type 1-3) stretching
648	605	-43	A'	O-C-C, C-C-C bending
272	283	11	A'	C-C-C bending
255	239	-16	A''	C-C (type 1-1) torsion
145	140	-5	A''	C-C (type 3-1) torsion
rms		37		

to obtain the full force field) are given in Table I. These parameters supercede the preliminary set which was included in MM3(90) and which were marked with ** to indicate that they were preliminary.

Vibrational Spectra. The experimental and calculated vibrational frequencies for five carbonyl compounds which were chosen to determine the force parameters are summarized in the following tables (Tables II-VI).

1. Formaldehyde. Infrared and Raman spectra were previously assigned²¹ for formaldehyde. This simplest carbonyl compound has C_{2v} symmetry and six vibration modes, three A₁ and three B₁. The rms error of our fit is 45 cm⁻¹.

2. Acetaldehyde. The gaseous infrared spectra and liquid Raman spectra were previously assigned²¹ for acetaldehyde. This

Table V. Experimental and Calculated Spectra of Acetone

exptl ²¹	MM3	diff	sym	assignment
3020	2976	-44	A ₁	asym CH ₃ stretching
3020	2975	-45	B ₂	asym CH ₃ stretching
2973	2974	1	A ₂	asym CH ₃ stretching
2973	2972	-1	B ₁	asym CH ₃ stretching
2926	2877	-48	B ₁	sym CH ₃ stretching
2926	2877	-48	A ₁	sym CH ₃ stretching
1738	1727	-11	A ₁	C=O stretching
1456	1432	-24	B ₂	asym CH ₃ def
1438	1425	-13	A ₂	asym CH ₃ def
1438	1418	-14	A ₁	sym CH ₃ def
1432	1416	-16	B ₁	asym CH ₃ def
1363	1407	44	B ₁	asym CH ₃ def
1360	1323	-37	A ₁	sym CH ₃ def
1218	1208	-10	B ₁	asym C-C stretching
1093	976	-117	B ₂	CH ₃ rock
1067	947	-120	A ₁	CH ₃ wagging
896	902	6	B ₁	CH ₃ wagging
	900		A ₂	CH ₃ rock
779	777	2	A ₁	sym C-C stretching
528	529	1	B ₁	C-C=O bending
483	479	-4	A ₁	C-C-C bending
384	395	11	B ₂	C=O out-plane-bending
105	126	21	B ₂	H-C-C=O torsion
105	102	-3	A ₂	H-C-C=O torsion
rms		43		

Table VI. Experimental and Calculated Spectra of Cyclopentanone

exptl ²³	MM3	diff	sym	assignment
2970	2965	-5	B	asym α,β -CH ₂ stretching
2978 (1)	2964		A	asym α -CH ₂ stretching
2950	2960	10	B	asym β,α -CH ₂ stretching
2974 (1)	2959		A	asym β,α -CH ₂ stretching
2893	2911	18	A	sym α -CH ₂ stretching
2893	2908	15	B	asym α,β -CH ₂ stretching
2882	2900	18	A	asym β,α -CH ₂ stretching
2882	2893	11	B	sym β -CH ₂ stretching
1770	1763	-7	A	C=O stretching
1458	1423	-35	A	β,α -CH ₂ scissoring
1458	1411	-47	B	β,α -CH ₂ scissoring
1415	1392	-23	A	α -CH ₂ scissoring
1415	1384	-31	B	α -CH ₂ scissoring
1318	1340	22	B	α,β -CH ₂ wagging, sym C-C (1-3) stretching
1318	1334	16	A	β -CH ₂ wagging
1280	1288	8	B	β -CH ₂ wagging
1280	1264	-16	A	α -CH ₂ wagging
1272 (1)	1189		B	asym C-C (1-3) stretching, α,β -CH wagging
1232 (1)	1152		A	β -CH ₂ twist
1232	1151	-81	B	α,β -CH ₂ twist
1200 (1)	1125		B	α -CH ₂ twist
1200 (1)	1096		A	β -CH ₂ twist
1151 (1)	1020		A	sym C-C (next to C=O) stretching
1021 (1)	974		A	ring motion
975	949	-26	B	asym C-C (next to C=O) stretching
830	896		B	α -CH ₂ rock
888 (1)	882		A	C-C stretching
832 (1)	799		A	α -CH ₂ rock
1142	792	38	B	β -CH ₂ rock
804	760	46	A	β,α -CH ₂ rock
(?)	573		B	C-C-C (1-1-1) bending
705 (1)	567		A	C-C-C (1-3-1, 1-1-3) bending
467	462	-5	B	C=O in-plane-bending
446 (1)	365		B	C=O out-plane-bending
238 (1)	254		A	ring motion
95	97	2	B	ring puckering

compound has C_s symmetry, and the 15 normal modes can be categorized as ten A' and five A''.

3. Propanal. The gas-phase infrared spectra and liquid-phase Raman spectra have been reported and assigned for propanal.²² This molecule has C_s symmetry, and the 24 fundamental vibrations

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Table VII. The Structure and Energies of Formaldehyde

	Structures			diff
	ED (r_g) ²⁴	millimeter ²⁵ wave	MM3	
C-O	1.209 (3)	1.2078 (30)	1.2075	-0.001
C-H	1.096 (53)	1.1161 (70)	1.1174	0.017
\angle OCH			121.08	
\angle HCH		116.52 (67)	117.84	
Moments of Inertia				
	exptl ²⁵	MM3	error (%)	
I _x	1.850	1.846	-0.22	
I _y	13.017	13.014	-0.02	
I _z	14.876	14.860	-0.05	
Dipole Moment				
	exptl (MW) ²⁶	MM3		
	2.339	2.479		

are distributed over 14 A' and 10 A". The rms error of the MM3 calculation is 37 cm⁻¹.

4. Acetone. This molecule was also studied by infrared in gas phase and Raman in the liquid phase.²¹ Acetone has C_{2v} symmetry. The largest MM3 errors are for the methyl rocking and wagging modes. The other modes are calculated nearer to the experimental values. The rms is 43 cm⁻¹.

5. Cyclopentanone. The infrared spectrum of cyclopentanone has been reported and partly assigned.²³ There are several possible configurations, planar (C_{2v}), envelope (C_s), and twist (C₂). It was found by MM3 calculation that the twist is the most stable form. The 36 normal modes are classified as 18 A and 18 B. This result disagrees with assignment made by the experimentalists, who preferred the planar conformation rather than the twist form. But, the MM3 structure fits well with the microwave and electron diffraction results. The moments of inertia show that the heavy atoms cannot be coplanar. The earlier descriptions of some of the modes are quiet different from our results. We utilized only the modes which relate to the five-membered ring skeleton for parameterization. Our spectroscopic assignments are shown in Table VI.

Structures and Energies of Carbonyl and Cyclic Compounds

Carbonyl Compounds. 1. Formaldehyde. The structure of this molecule has been studied by the electron diffraction method²⁴ and in the millimeter wave spectrum.²⁵ The MM3 calculation gives a good structure (Table VII), and moments of inertia are a little too small by 0.22, 0.02, and 0.05% for I_x, I_y, and I_z, respectively.

2. Acetaldehyde. This compound has been studied by microwave,²⁷ electron diffraction,²⁴ and the combined methods.²⁸ Acetaldehyde has one stable conformer with an eclipsed H-C-C-O torsional angle. The calculated barrier is 1.08 kcal/mol, compared with the experimental value, 1.162 ± 0.030 kcal/mol.²⁸ The MM3 structural parameters fit well with the observed values (Table VIII). The MM3 moments of inertia are a little too large, 1.71, 1.12, and 0.96% for I_x, I_y, and I_z, respectively.

3. Propanal. A microwave study²⁹ of propanal was reported by E. B. Wilson in 1964. In 1984, this structure was investigated by a joint analysis of ED, MW, IR,³⁰ and a valence force field from geometry relaxed ab initio calculation.³¹ The ground-state

Table VIII. The Structure and Energies of Acetaldehyde

	Structures				
	ED + MW (r_g) ²⁸	ED (r_g) ²⁴	MW (r_o) ²⁷	MM3	diff
C=O	1.207 (4)	1.208 (3)	1.2155 (20)	1.2088	0.002
C-C	1.515 (5)	1.514 (5)	1.501 (5)	1.5124	-0.003
C-H(3-5)	1.114 (11)		1.114 (150)	1.1191	0.005
C-H(1-5)				1.1159	
\angle CCO	123.80 (15)		123.92 (10)	124.23	0.43
\angle OCH			118.60	119.06	
\angle CCH(1-3-5)	117.48 (asum)		117.50 (80)	116.71	
ω OCCH					0.0
Moments of Inertia					
	exptl ²⁷	MM3	error (%)		
I _x	8.933	9.086	1.71		
I _y	49.741	50.302	1.12		
I _z	55.553	56.082	0.96		
Rotation Barrier					
	exptl (MW) ²⁸		MM3		
ecl	0.00		0.00		
gauche	1.162 (30)		1.08		
Dipole Moment					
	exptl (MW) ²⁶		MM3		
	2.69		2.737		

Table IX. The Structure and Energies of Propanal

	Structures		
	ED + MW (r_g , θ_o) ³⁰	MM3	diff
C=O	1.209 (4)	1.2088	0.000
C-C(3-1)	1.515 (9)	1.5169	0.002
C-C(1-1)	1.521 (9)	1.5277	0.007
C-H(3-5)		1.1194	
C-H(1-5)		1.1157	
\angle CCO	124.5 (3)	124.85	0.35
\angle OCH	120.80	118.81	-1.99
\angle CCH(1-3-5)	114.70	116.34	1.64
\angle CCC(1-1-3)	113.8 (4)	113.11	-0.69
ω OCC		0.0	
Moments of Inertia ^a			
	exptl ²⁹	MM3	error (%)
I _x	5.035	5.082	0.93
I _y	14.242	14.365	0.86
I _z	18.250	18.365	0.63
Rotational Energies			
	exptl (MW) ^b	ab initio ^{31,c}	MM3
ecl (0°)	0.00	0.00	0.00
gauche (60°)	2.10	2.19	2.17
skew (120°)	0.95	1.38	1.06
trans (180°)	1.55	1.97	1.87
Dipole Moment			
	exptl (MW)		MM3
	2.75		2.743

^aIn units of 10⁻³⁹ mg cm². ^bEstimated vis MW spectroscopy: Pichett, H. B.; Scroggin, D. G. *J. Chem. Phys.* **1974**, *61*, 3954. Butcher, S. S.; Wilson, E. B., Jr. *J. Chem. Phys.* **1964**, *40*, 1671. ^cUsing 6-31G*///6-31G*(MP3) basis set.

conformation of propanal is the one in which the methyl carbon eclipses the carbonyl oxygen. A less stable conformer (skew, with a 128° dihedral angle) is 1.16 kcal/mol above the eclipsed form, compared to the experimental value, 0.95 ± 0.10 kcal/mol. Table IX summarizes the calculated and observed values.

4. Acetone. The molecular structure of acetone has been studied by microwave spectroscopy^{27,28} and the electron diffraction

(23) Howard-Lock, H. E.; King, G. W. *J. Mol. Spectrosc.* **1970**, *35*, 393.(24) Kato, C.; Konaka, S.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2148.(25) Takagi, K.; Oka, T. *J. Phys. Soc. Jpn.* **1963**, *18*, 1174.(26) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman and Company: El Cerrito, CA, 1963.(27) Swalen, J. D.; Costain, C. C. *J. Chem. Phys.* **1959**, *31*, 1562.(28) Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2159.(29) Butcher, S. S.; Wilson, E. B. *J. Chem. Phys.* **1964**, *40*, 1671.(30) Van Nuffel, P.; Van den Enden, L.; Van Alsenoy, C.; Geise, H. J. *J. Mol. Struct.* **1984**, *116*, 99.(31) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1988**, *9*, 488.

Table X. The Structure and Energies of Acetone

	Structures				diff
	ED ²⁴	MW ²⁸	MW ²⁷	MM3	
C=O	1.211 (4)	1.222 (3)	1.215 (asum)	1.2108	0.000
C-C(1-3)	1.516 (4)	1.507 (3)	1.515 (5)	1.5162	0.000
C-H(105)		1.085 (7)		1.1124 (in) 1.1175 (out)	
∠CCO		121.4	124.90	121.97	
∠CCH(3-1-5)				110.89	
∠CCC(1-3-1)		117.20 (33)	116.20 (1.00)	116.06	
ωOCCH				0.0	
Moments of Inertia					
	exptl ²⁸	MM3	error (%)		
I _x	49.732	50.165	0.87		
I _y	59.386	59.862	0.83		
I _z	102.956	103.416	0.45		
Rotational Barrier					
	exptl (MW) ²⁷		MM3		
ecl	0.00		0.00		
gauche	0.777 (20)		0.74		
Dipole Moment					
	exptl (MW) ²⁶		MM3		
	2.90		2.929		

Table XI. Structure and Energies of 2-Butanone

	Structures			
	ED ³³	MW ³²	MM3	diff
C=O	1.218 (1)	1.222	1.2109	-0.007
C ₁ -C ₂	1.518	1.507	1.5168	-0.001
C ₂ -C ₃	1.518	1.507	1.5212	0.003
C ₃ -C ₄			1.5280	
C-H(1-5)			1.1157	
C-C _{av}			1.522	
∠C ₁ C ₂ O	122.5 (9)	121.40	121.61	-0.89
∠C ₃ C ₂ O	121.3 (7)	121.40	122.50	1.20
∠CCC(1-3-1)		117.20	115.88	
∠CCC(1-1-3)	113.5 (7)		113.26	-0.24
ωOCCC			0.0	
ωCCCC			180.0	
Moments of Inertia				
	exptl ³²	MM3	error (%)	
I _x	52.9649	53.3604	0.75	
I _y	140.5428	141.5127	0.69	
I _z	184.0630	185.0553	0.54	
Rotational Barrier				
	exptl (MW) ^{33,34}	ab initio ^{31,a}	MM3	
ecl	0.00	0.00 (0°)	0.00 (0°)	
gauche		1.73 (80°)	1.47 (77°)	
skew	2.02	1.79 (100°)	1.39 (119°)	
anti		2.79 (180°)	2.38 (180°)	

^a Using 6-31G**/6-31G*(MP3) basis set.

method.²⁴ As with acetaldehyde, it is found that the methyl hydrogen eclipses the carbonyl oxygen in the ground state, and the energy maximum occurs around 60°. The MM3 calculated results agree well with the experimental values. The calculated and observed results are shown in Table X.

5. 2-Butanone. There are four conformations of interest for 2-butanone which are eclipsed, gauche, skew, and anti. Experimental methods like microwave spectroscopy,³² electron dif-

Table XII. Relative Energies of Different Conformations of Methylisopropyl Ketone

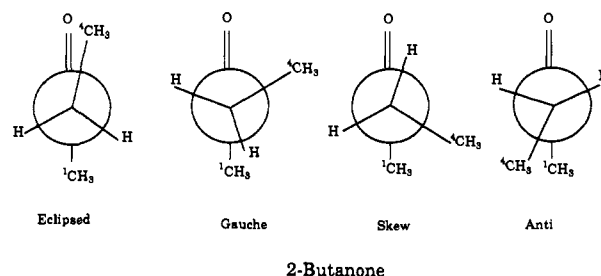
	ab initio ^{31,a}	MM3
ecl	0.00 (-17°)	0.00 (-4°)
sym	0.09 (-61°)	0.44 (-60°)
gauche	1.64 (62°)	1.61 (65°)
anti	1.22 (117°)	1.39 (118°)

^a Using 6-31G**/6-31G*(MP3) basis set.

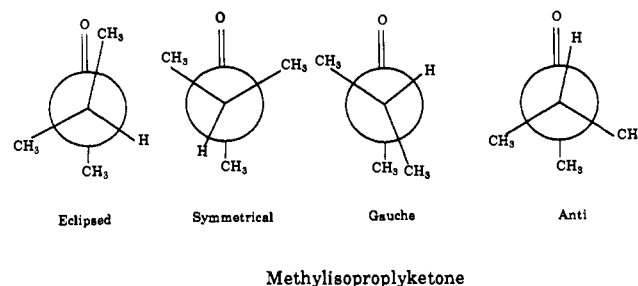
Table XIII. Structures and Energies of Diisopropyl Ketone

	Structure		
	ED ⁷⁸	MM3	diff
C=O	1.215 (5)	2.1113	-0.004
C-C _{av}	1.535 (2)	1.5378	0.003
C-H _{av}	1.118 (3)	1.1137	-0.004
∠C ₂ C ₃ C ₄	116.6 (17)	116.57	-0.03
∠CCC	110.8 (4)	110.53	-0.27
∠CCH _{Me}	111.1 (9)	111.63	0.53
Percentages (Energies)			
	exptl ⁷⁸	ab initio ⁷⁸	MM3
C ₁	45% (31)	66% (0.00)	67% (0.00)
C _s	31% (12)	4% (1.17)	3% (1.41)
C ₂	24% (22)	29% (0.09)	30% (0.08)

fraction,³³ and Raman spectroscopy agree that the eclipsed form (with respect to the carbonyl oxygen and a methyl carbon) is the most stable.



6. Methylisopropyl Ketone. The title molecule has been studied by K. B. Wiberg by using the ab initio method with 6-31G**/6-31G*(MP3)³¹ basis set. It was found that the most stable conformation has an eclipsed C-C-C=O dihedral angle. The MM3 calculated relative energies of four conformations, eclipsed, symmetrical, gauche, and anti, are summarized in Table XII, together with ab initio values.



7. Diisopropyl Ketone. A gas-phase electron diffraction study of diisopropylketone has been reported.⁷⁸ Three conformers with C₁, C_s, and C₂ symmetries were found, with the first being the most stable. An ab initio calculation with a 4-21G basis set at the SCF level⁷⁸ indicated that the C₂ and C_s conformers are 0.09 and 1.17 kcal/mol higher in energy than the C₁ conformer, respectively. The MM3 calculated mole fractions of the three conformers agree well with the values from an ab initio calculations but not as well with the experimental values⁷⁸ (Table XIII).

Cyclic Compounds. 8. Cyclopropanone. Cyclopropanone has been studied by microwave³⁴ and gas-phase infrared spectroscopy.³⁵

(32) Pierce, L.; Chang, C. K.; Hayashi, M.; Nelson, R. *J. Mol. Spectrosc.* **1969**, *5*, 449.

(33) Abe, M.; Kuchitsu, K.; Shimanouchi, T. *J. Mol. Struct.* **1969**, *4*, 245.

Table XIV. Structure of Cyclopropanone

Structures	Structures		
	MW ³⁴	MM3	diff
C=O	1.191 (20)	1.1959	0.005
C ₁ -C ₂	1.475 (17)	1.4797	0.005
C ₂ -C ₃	1.575 (12)	1.5768	0.002
C-H	1.086 (25)	1.8069	0.001
∠C ₁ C ₂ C ₃	57.7 (4)	57.81	0.11
∠C ₂ C ₁ C ₃	64.6 (8)	64.39	-0.21
∠HCH	114.8 (20)	114.38	-0.42
β ^a	29.7 (2)	28.7	1.0
Moments of Inertia			
	exptl ³⁴	MM3	error (%)
I _x	25.082	25.141	0.24
I _y	67.706	68.156	0.66
I _z	86.094	86.568	0.55
Dipole Moment			
	exptl ³⁴	MM3	
	2.67	2.757	

^aThe angle between the HCH plane and C₂-C₃ axis.

Table XV. Structure of Cyclobutanone

Structures	Structures				
	ED + MW (r _g) ³⁶	ED (r _g) ³⁶	MW (r _g) ³⁸	MM3	diff
C=O	1.202 (4)	1.202 (2)	1.202 (2)	1.2041	0.002
C ₁ -C ₂	1.534 (3)	1.533 (5)	1.527 (3)	1.5290	-0.005
C ₂ -C ₃	1.567 (5)	1.569 (5)	1.556 (1)	1.5735	0.007
C-C _{av}	1.551	1.551	1.542	1.5513	
C-H	1.100 (4)			1.1119	0.012
∠CCO				133.24	
∠CCH				113.59	
∠C ₂ C ₁ C ₄	92.8 (3)	92.2 (5)	93.1 (3)	93.53	0.73
∠C ₁ C ₂ C ₃	88.3 (2)	89.11 (6)	88.0 (3)	88.17	-0.13
∠C ₂ C ₃ C ₄	90.3 (4)	89.4 (8)	90.9 (2)	90.13	-0.17
Moments of Inertia					
	exptl ³⁸	MM3	error (%)		
I _x	46.873	47.089	0.46		
I _y	105.172	105.851	0.65		
I _z	142.064	142.680	0.43		
Dipole Moment					
	exptl (MW) ³⁸	MM3			
	2.89	2.887			

The C=O stretching mode was determined to be 1815 cm⁻¹ by A. Ohno and co-workers.^{35a} But van Tilborg^{35b} found four absorption bands, 1980, 1906, 1867, and 1816 cm⁻¹. With further evidence from theoretical calculations, he assigned the carbonyl absorption of cyclopropanone as 1906 cm⁻¹. The MM3 calculated value is 1901 cm⁻¹, which was fit to the van Tilborg value. The correctness of the experimental assignment is uncertain. Table XIV lists the calculated and observed structures.

9. Cyclobutanone. The molecular structure of cyclobutanone has been investigated by combined analysis of electron diffraction and spectroscopic data.³⁶ This molecule was found to have a large-amplitude ring puckering motion with two potential minima. There was a small potential barrier at the planar ring configuration. But infrared and Raman spectroscopic studies, by Frei et al.,^{37a} and a microwave investigation,^{37b} by Bauder et al., both

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(35) (a) Ohno, A.; Grosse, D. J.; Davis, R. E. *Tetrahedron Lett.* **1968**, 959. (b) van Tilborg, W. J. M. *Tetrahedron Lett.* **1973**, 523.

(36) Tamagawa, K.; Hilderbrandt, R. L. *J. Phys. Chem.* **1983**, *87*, 5508.

(37) (a) Frei, K.; Gunthard, H. H. *J. Mol. Spectrosc.* **1960**, *5*, 218. (b) Bauder, A.; Gaumann, T.; Tank, F. *Physik.-Chem. Lab., ETH. Zurich*, cited in ref 37a.

Table XVI. Structure and Energy of Cyclopentanone

Structures	Structures				
	ED + MW (r _g) ³⁹	ED (r _g) ⁴¹	MW (r _g) ⁴²	MM3	diff
C=O	1.213 (4)	1.226 (4)	1.215 (5)	1.2086	-0.004
C ₁ -C ₂	1.531 (4)	1.519	1.504 (10)	1.5259	-0.005
C ₂ -C ₃	1.542 (3)	1.532	1.557 (7)	1.5374	-0.005
C ₃ -C ₄	1.542 (3)	1.540	1.557 (7)	1.5415	-0.000
C-C _{av}	1.538	1.528 (1)		1.5336	-0.004
C-H				1.1159	
∠CCO				125.59	
∠CCH				111.00	
∠C ₂ C ₁ C ₅	108.6 (2)	112.40 (30)	110.50 (70)	108.82	0.21
∠C ₁ C ₂ C ₃	104.2 (1)	102.20 (30)	104.50 (50)	104.84	0.64
∠C ₂ C ₃ C ₄	103.4 (2)		103.00 (50)	104.21	0.81
φ ^a	24.7 (4)		23.60 (40)	26.7	2.0
Moments of Inertia					
	exptl ⁴²	MM3	error (%)		
I _x	76.36	76.978	0.81		
I _y	150.84	151.350	0.34		
I _z	209.73	211.073	0.65		
Relative Energy					
	exptl ⁴⁰	MM3			
twist	0.00	0.00			
envelope	2.4	2.50			
Dipole Moment					
	exptl (MW)	MM3			
	3.30 ²⁶	3.234			

^aAngle between C₅-C₁-C₂ plane and C₃-C₄ bond.

indicated that cyclobutanone has a planar skeleton. The MM3 calculation shows that the ground-state conformation of this molecule is planar (C_{2v} symmetry). The geometries of cyclobutanone are listed in Table XV, compared with the observed values.

10. Cyclopentanone. Cyclopentanone exists in the twist conformation (C₂ symmetry) in the gas phase,³⁹ and the envelope form with C_s symmetry is 2.4 kcal/mol higher than the twist form according to Pitzer and Donath's study.⁴⁰ The MM3 calculations are in good agreement with the earlier work. Concerning the geometries, the average bond length of the ring skeleton is calculated to be too short by about 0.004 Å. Table XVI shows the MM3 and observed results.

11. Cyclohexanone. The geometry of this molecule has been studied intensively, including being studied by the methods of electron diffraction and microwave spectroscopy.⁴²⁻⁴⁹ The chair form was found to be the most stable. The torsional barrier was first determined to be 4.9 kcal/mol by Jensen and Beck by using dynamic NMR.⁴⁶ But later, Anet repeated the experiment and found that the barrier (ΔG[‡]) is no more than 4.0 ± 0.1 kcal/mol.⁴⁸ MM3 calculation gives 4.50 kcal/mol (ΔH[‡]). The individual C-C bond lengths of type 1-3 are calculated too large by 0.017 Å, and type 1-1 are calculated too short. But the average bond length, which is what is really determined experimentally, is calculated

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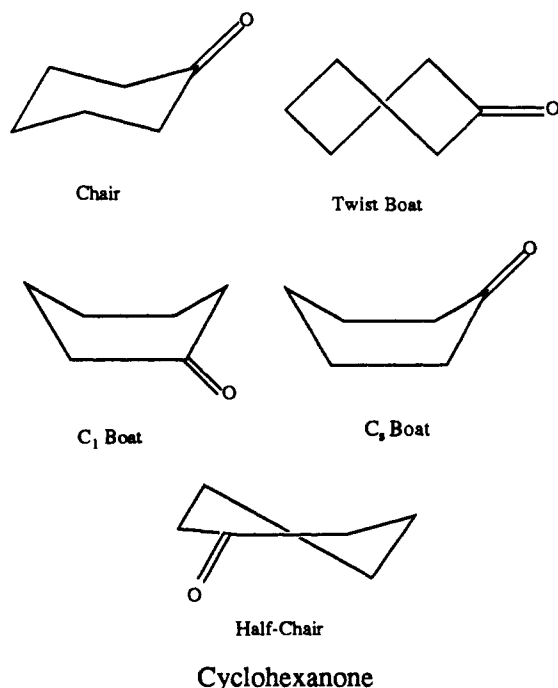
(48) Anet, F. A. L.; Chmurny, G. N.; Krane, J. *J. Am. Chem. Soc.* **1973**, *95*, 4423.

(49) Dillen, J.; Geise, H. J. *J. Mol. Struct.* **1980**, *69*, 137.

Table XVII. Structure and Energy of Cyclohexanone

Structures	ED +			
	MW (r_g) ⁴⁹	MW ⁴³	MM3	diff
C=O	1.229 (3)	1.222	1.2108	-0.018
C ₁ -C ₂	1.503 (4)	1.516	1.5199	0.017
C ₂ -C ₃	1.542 (2)	1.535	1.5362	-0.006
C ₃ -C ₄	1.545		1.5345	-0.010
C-C _{av}	1.530		1.5302	0.000
C-H			1.1157	
∠CCO			121.96	
∠C ₂ C ₁ C ₆	115.3 (3)	116.20	116.08	0.78
∠C ₁ C ₂ C ₃	111.5 (1)	110.40	111.59	0.09
∠C ₂ C ₃ C ₄	110.8 (2)	114.60	111.66	0.86
∠C ₃ C ₄ C ₅	110.8 (2)	110.70	111.06	0.26
∠OC ₁ C ₂ C ₃	128.3		134.9	6.6
∠C ₆ C ₁ C ₂ C ₃	52.7		48.2	-4.5
∠C ₁ C ₂ C ₃ C ₄	53.0		51.5	-1.5
∠C ₂ C ₃ C ₄ C ₅	56.3		56.8	0.5
Moments of Inertia				
	exptl ⁴³	MM3	error (%)	
I _x	120.48	120.901	0.20	
I _y	202.00	203.359	0.67	
I _z	288.09	292.117	1.40	
Conformational Energies				
	exptl	MM3		
chair	0.00	0.00		
twist		3.09		
boat(C ₁)		3.52		
boat(C ₂)		4.11		
half-chair	<4.00 ± 0.1 ⁴⁸	4.38		
Dipole Moment				
	exptl (MW) ²⁶	MM3		
	3.08	2.929		

close to the experimental value. The moments of inertia show that the calculated molecule is a bit too flat.



The experimental value for the ΔH of the equatorial-axial equilibrium for the 2-methylcyclohexanone is 2.10 kcal/mol.⁵⁰ The MM3 calculation of the energy difference between the conformers is 2.08 kcal/mol. We also calculated the energies of the corresponding conformers of 3-methyl- and 4-methylcyclo-

Table XVIII. Relative Energies of the Methylcyclohexanone Conformations

	2-Me		3-Me		4-Me	
	eq	ax	eq	ax	eq	ax
exptl ⁵⁰	0.00	2.10	0.00	1.36 ^a	0.00	1.75 ^b
MM3	0.00	2.08	0.00	1.44	0.00	1.65

^a Measured in the liquid phase on 3,5-dimethylcyclohexanone. ^b Assumed the same as for methylcyclohexane (liquid phase).

Table XX. Structure and Energy of Cycloheptanone

Structures	ED (r_g) ⁵³			
	MM3 ^a	diff		
C=O	1.219 (12)	1.2114	-0.008	
C-C(1-1) _{av}	1.536 (3)	1.5382	0.002	
C-C(1-3) _{av}	1.517 (fixed)	1.5213	0.004	
C-H _{av}	1.124 (7)	1.1157	-0.008	
∠CCC(1-3-1)	117.3 (18)	117.59	0.29	
∠CCC _{av}	115.5 (5)	114.06	-1.44	
∠HCH(5-1-5) _{av}	103.2 (26)	105.93	2.73	
Conformational Energies				
	symm	2-sub	3-sub	4-sub
MM3	0.29	0.00	1.12	1.97

^a Structure of the 2-substituted conformer.

hexanone, and the results are summarized in Table XVIII.

12. 4-*tert*-Butylcyclohexanone. The X-ray structure of this molecule was determined at room temperature.⁵¹ The cyclohexane ring showed a chair conformation. The MM3 calculation agrees with the experiment, and both show that the *tert*-butyl group is in the expected equatorial position. The average bond distances calculated by MM3 are apparently too large by 0.017 Å (Table XIX (supplementary material)). In the MM3 force field, bond lengths are, by definition, of the r_g type; i.e., the bond length is defined as the average distance between atoms. However, this is not the distance measured by X-ray crystallography. Rather, in crystallography the average distances between the atomic positions, r_{av} , are measured. Furthermore, a molecule in a crystal lattice at room temperature undergoes sizable thermal librations, which lead to apparent bond shortenings. The thermal corrections to X-ray bond lengths are typically 0.005–0.015 Å at room temperature.⁵² The discrepancies here are, we believe, primarily due to experimental errors, especially thermal motions.

13. Cycloheptanone. This molecule has been investigated by gas-phase electron diffraction⁵³ at 371 K. Unfortunately, it is too complicated to be analyzed without some assumptions. The most stable conformation of the molecule was assumed to be the symmetrical twist-chair form. But, the 2-substituted conformer was found to be of lowest energy by the MM3 study, and the symmetrical one is 0.29 kcal/mol higher. The MM3 prediction is that the compound will be found as a Boltzmann distribution over four twist-chair conformations. The observed and calculated structures are listed in Table XX.

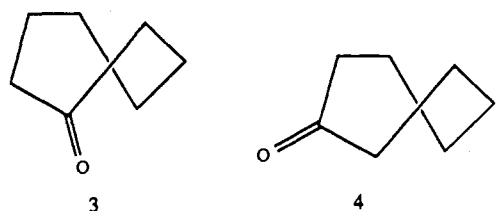
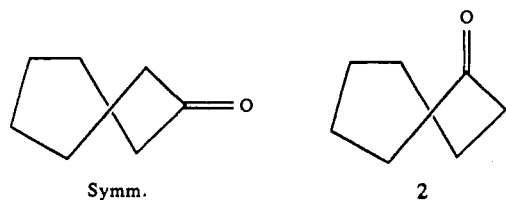
14. Cyclooctanone. In cyclooctane, the boat-chair (C_2 symmetry) conformation is much lower in energy than other possible conformations. It was assumed that the cyclooctanone would have the same skeletal structure. From NMR studies, Roberts and Anet concluded that conformer 3 was the lowest energy confor-

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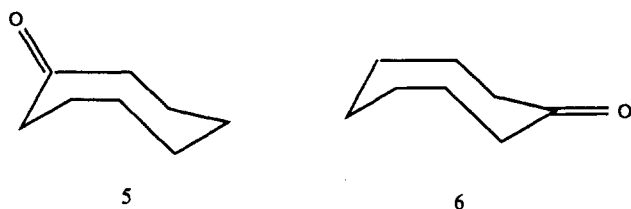
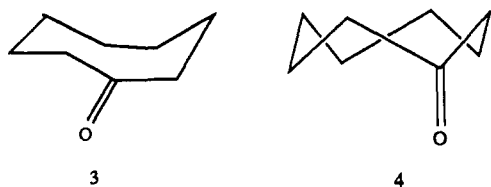
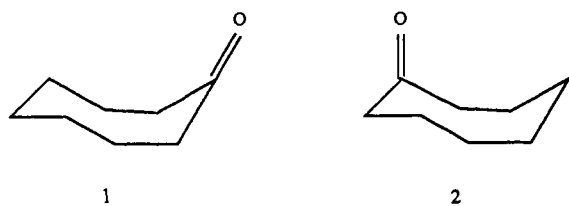
(51) Lectard, A.; Lichanot, A.; Metras, F.; Gaultier, J.; Hauw, C. *Cryst. Struct. Commun.* **1975**, *4*, 527.

(52) This version uses the quadratic approximation of Schomaker and Trueblood (*Acta Crystallogr., Sect. B* **1968**, *24*, 63) for the rigid-body motion and the approximation of Dunitz and White (*Acta Crystallogr., Sect. A* **1973**, *29*, 93) for the libration of attached rigid groups on the molecule, including correlations of the internal and overall motion (Schomaker, V.; Trueblood, K. **1984**, 1986. Personal communication from Dr. Trueblood).

(53) Dillen, J.; Geise, H. J. *J. Mol. Struct.* **1981**, *72*, 247.



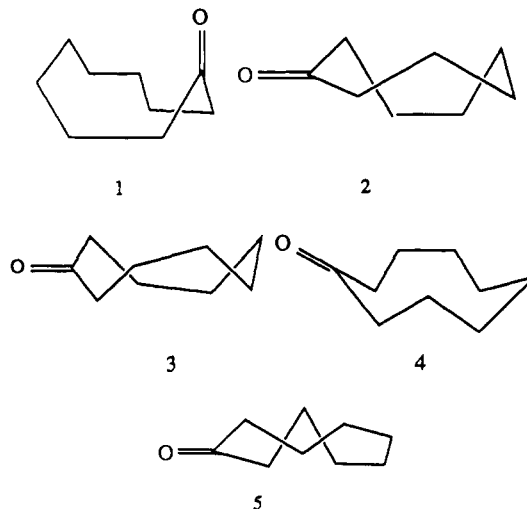
Cycloheptanone



Cyclooctanone

mation of this molecule.^{54,55} Infrared studies by Strauss⁵⁶ agreed. The MM3 calculations confirm their conclusions.

15. Cyclononanone. Cyclononanone has been studied by X-ray crystallography⁵⁷ as a complex. The crystals are monoclinic with space group $P2_1/c$. The unit cell contains four cyclononanone and four mercuric chloride molecules. We generated (from the hydrocarbon conformations by placing a carbonyl in various positions) a series of five low-energy conformations for the ketone (structures shown). The conformer 4, a twist boat-chair form, was found to correspond to the conformation found in the crystal. The four molecules in the unit cell can be separated into two asymmetric units. There are two independent cyclononanone molecules with enantiomeric conformations in the asymmetric unit. The experimental geometries of two cyclononanone molecules are different. We generated the crystal structures of the two molecules from the published fractional unit cell coordinates and found that the geometries were not the same as those cited in the paper, especially the dihedral angles. The experimental structures were pretty rough ($R = 11.6\%$), and we assume that the structures from the fractional coordinates should be better. The out-of-plane bending angles of type 1-3-1 and 1-3-7 are about 5° for one



Cyclononanone

molecule (2), and only 0.5° for the other (1). This difference might be due to the interactions between the carbonyl oxygens and mercuric chloride molecules and/or to crystal packing forces. These two molecules minimized to the same energy point with MM3 as isolated molecules, and the out-of-plane bending angles are about 1° .

More recently the stochastic search procedure of M. Saunders has become available,⁷⁷ so the potential surface of cyclononanone as calculated by MM3 was explored by using this method. The search was allowed to run for 10 h on the VAX 750 and appeared to be complete. Because there are two ways to number the molecule starting with the carbonyl carbon as one, all of the conformations should be found in duplicate. We found 17 conformations with conformational energies of less than 3 kcal/mol, many more than found by trial and error. Conformations 6, 8, and 9 of this set (Table XXI, note conformational numbering is not the same as in previous discussion) were found only as single conformations, and the others (including 1-5) were all found in duplicate. It therefore seems unlikely that any conformation lying below 4 has been missed. What the results showed (Table XXI) was that there are three conformations lying within 0.2 kcal/mol of the minimum energy, and the one found in the crystal is the third highest in energy. Because these energy differences are so small, one does not necessarily expect to find the lowest energy conformation in the crystal, but one expects to find a conformation which is at least close to the low energy.

The importance of doing some type of systematic search of the conformational surface of a molecule of this complexity is clear from the above.

With the 4,4,7,7-tetramethyl derivative (generated by methylation of structures 1-5), the conformation corresponding to 2 in the parent was found to be the most stable, which is analogous to what was found with cyclononane and 1,1,4,4-tetramethylcyclononane.^{58,59} Table XXII (supplementary material) summarizes the molecular structures of the title compound and the relative energies of different conformers.

16. Cyclodecanone. The X-ray diffraction was carried out by P. Groth at -160°C for cyclodecanone.⁶⁰ The X-ray structure shows a 3-keto conformation as predicted.⁹ Anet's low-temperature NMR evidence also points to a single conformer, which is most likely a 3-keto form.⁶¹ The MM3 calculations give similar results; conformers 1 and 2 are 2.50 and 4.37 kcal/mol above conformer 3. We also calculated the thermal librations of the heavy atoms in Groth's crystal by using the THMA10 program,⁵² and we included the $r_\alpha-r_\beta$ conversion (0.002 \AA).⁶² Table XXIII

(54) Anet, F. A. L.; St. Jacques, M.; Henrichs, P. M.; Cheng, A. K.; Krane, J.; Wong, L. *Tetrahedron* **1974**, *30*, 1629 and references therein.
 (55) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 1347.
 (56) Strauss, H. L., private communication.
 (57) Dahl, S.; Groth, P. *Acta Chem. Scand.* **1971**, *25*, 1114.

(58) Anet, F. A. L.; Wagner, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 5266.
 (59) Borgen, G.; Dale, J. *Chem. Commun.* **1970**, 1105.
 (60) Groth, P. *Acta Chem. Scand. (A)* **1976**, *30*, 294.
 (61) Anet, F. A. L.; Cheng, A. K.; Krane, J. *J. Am. Chem. Soc.* **1973**, *95*, 7877.

Table XXI. The Conformations of Cyclononane

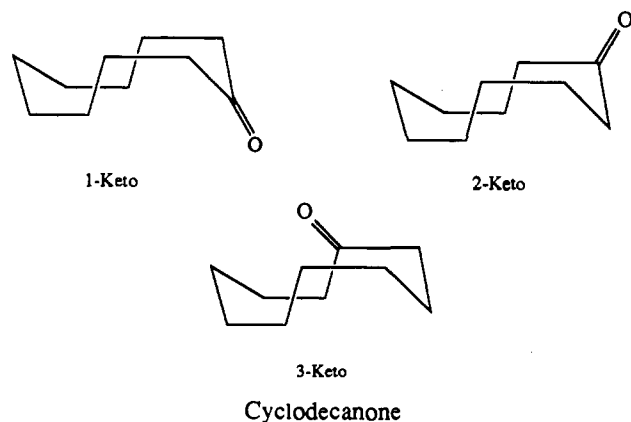
conformation	energy	conformation	energy
1	0.00	5	0.72
2	0.13	6	0.79
3	0.18	7	0.84
4	0.45	8	1.31

Table XXIII. The Structures of Cyclodecanone^a

	X-ray ⁶⁰		
	1 ^b	2 ^b	
	Structures		
C ₁ =O	1.220	1.224	1.212
C ₁ -C ₂	1.518	1.522	1.525
C ₂ -C ₃	1.537	1.541	1.545
C ₃ -C ₄	1.531	1.536	1.542
C ₄ -C ₅	1.530	1.535	1.538
C ₅ -C ₆	1.534	1.538	1.542
C ₆ -C ₇	1.533	1.539	1.538
C ₇ -C ₈	1.535	1.540	1.542
C ₈ -C ₉	1.534	1.539	1.543
C ₉ -C ₁₀	1.535	1.540	1.540
C ₁ -C ₁₀	1.513	1.517	1.526
C-C(1-3) _{av}	1.516	1.520	1.526
C-C(1-1) _{av}	1.534	1.539	1.541
∠C ₂ C ₁ C ₁₀	119.1		117.30
∠C ₁ C ₂ C ₃	118.7		116.34
∠C ₂ C ₃ C ₄	115.2		116.37
∠C ₃ C ₄ C ₅	114.9		116.13
∠C ₄ C ₅ C ₆	114.2		114.08
∠C ₅ C ₆ C ₇	114.7		114.46
∠C ₆ C ₇ C ₈	117.4		117.00
∠C ₇ C ₈ C ₉	117.9		117.76
∠C ₈ C ₉ C ₁₀	117.0		118.24
∠C ₁ C ₁₀ C ₉	114.9		114.67
∠C ₁₀ C ₁ O	120.6		121.69
∠C ₂ C ₁ O	120.2		121.01
∠CCC _{av}	116.4		116.24
ω _{C₁C₂C₃C₄}	-70.2 (5)		-66.5
ω _{C₂C₃C₄C₅}	59.6		61.5
ω _{C₃C₄C₅C₆}	65.2		61.0
ω _{C₄C₅C₆C₇}	-158.6		-157.4
ω _{C₅C₆C₇C₈}	51.4		56.2
ω _{C₆C₇C₈C₉}	66.1		64.2
ω _{C₇C₈C₉C₁₀}	-64.6		-68.0
ω _{C₁C₁₀C₉C₈}	-56.0		-48.2
ω _{C₉C₁₀C₁C₂}	152.3		154.0
ω _{C₃C₂C₁C₁₀}	-49.1		-58.5

^a Numbering as shown on structure. ^b Column 1 gives Groth's bond lengths uncorrected. Column 2 includes corrections for thermal motion and to r_g .

shows the calculated and observed (with these corrections) molecular structures of cyclodecanone.



17. Cycloundecanone. The crystal structure of this molecule was determined at -165°C by P. Groth.⁶³ The crystals are

(62) *Molecular Structure by Diffraction Methods*; Sim, G. A.; Suttén, L. E.; Eds.; The Chemical Society: London, 1975, Vol. 3.

Table XXV. Carbonyl Frequencies Calculated for Cycloalkanones

n^a	C=O (cm ⁻¹)		
	MM3	exp. (gas)	exp. (liq) ^{c,e}
3	1901	1906 ^{35b}	1820
4	1816	1816 ²⁹	1780
5	1763	1770	1745
6	1740	(1743) ^d	1718 ^b
7	1731		1702 ^e
8	1725		
9	1723		
10	1720		
11	1714		

^a Number of carbons in the ring. ^b A liquid-phase datum: Fuhper, H.; Katha, V. B.; Krueger, P. J.; Mantsch, H. M.; Jones, R. N. *Chem. Rev.* 1972, 72, 437. ^c See for example, ref 79. ^d Estimated from the liquid-phase value. ^e Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience-Wiley: 1965.

Table XXVI. Relative Energies of Cyclohexane-1,4-dione

	chair (C _{2h})	twist (D ₂)	boat (C _{2v})	boat (C ₂)
exptl ⁶⁷	2.0 ± 0.7	0.00		
ab initio	0.00	0.50		
MM3	0.00	0.12	4.85	0.80

Table XXVII. Conformations and Energies of 19 (kcal/mol)

conformers	energy population	
	1.29	7.4%
	0.00	65.5%
	3.51	0.2%
	0.70	20.1%
	1.62	4.3%
	1.92	2.6%

monoclinic with the space group $P2_1/c$. A temperature-dependent NMR spectra study of cycloundecanone indicated a single

Table XXVIII. Heats of Formation for Carbonyl Compounds (MM3)^a

compound	wt	H_f°	sumh	steric	pop	tors	T/R
acetaldehyde	10	-39.73	-13.77	0.44	0.00	0.00	2.40
propanal	10	-45.45	-19.46	1.60	0.27	0.42	2.40
butanal	8	-48.94	-26.20	2.70	0.52	0.84	2.40
pentanal	5	-54.45	-32.93	3.75	0.87	1.26	2.40
hexanal	5	-59.37	-39.66	4.80	1.22	1.68	2.40
2-methylpropanal	8	-52.25	-25.15	3.98	0.17	0.42	2.40
2-ethylhexanal	0	-71.60	-52.08	10.38	1.22	2.10	2.40
acetone	10	-51.90	-27.54	0.59	0.00	0.00	2.40
2-butanone	10	-57.02	-33.23	1.81	0.00	0.42	2.40
2-pentanone	10	-61.92	-39.97	2.90	0.27	0.84	2.40
3-pentanone	9	-61.65	-38.92	3.03	0.00	0.84	2.40
2-hexanone	9	-6.70	-46.70	3.94	0.62	1.26	2.40
3-hexanone	9	-66.51	-45.65	4.11	0.27	1.26	2.40
4-heptanone	9	-71.30	-52.38	5.19	0.54	1.68	2.40
5-nonanone	6	-82.03	-65.85	7.27	1.24	2.52	2.40
6-undecanone	0	-92.55	-79.31	9.35	1.94	3.36	2.40
3-methyl-2-butanone	10	-62.76	-38.92	4.72	0.06	0.42	2.40
3,3-dimethyl-2-butanone	10	-69.47	-44.61	7.87	0.00	0.42	2.40
3-methyl-2-pentanone	8	-67.90	-45.65	6.91	0.27	0.84	2.40
3,3-dimethyl-2-pentanone	6	-72.60	-51.34	10.89	0.27	0.84	2.40
4-methyl-2-pentanone	7	-69.60	-48.28	5.11	0.00	0.84	2.40
4,4-dimethyl-2-pentanone	8	-76.60	-57.98	8.09	0.00	0.84	2.40
2-methyl-3-pentanone	9	-68.38	-44.61	5.97	0.00	0.84	2.40
2,2-dimethyl-3-pentanone	7	-74.99	-50.29	9.17	0.00	0.84	2.40
2,4-dimethyl-3-pentanone	8	-74.40	-50.29	9.07	0.11	0.84	2.40
3,3,4-trimethyl-2-pentane	6	-78.50	-59.65	15.28	0.00	0.84	2.40
3,3,4,4-tetramethyl-2-pentanone	5	-83.10	-69.36	19.99	0.03	0.84	2.40
2,6-dimethyl-4-pentanone	5	-85.49	-69.01	9.54	0.54	1.68	2.40
di- <i>tert</i> -butyl ketone	8	-82.64	-61.67	20.23	0.00	0.84	2.40
<i>tert</i> -butylneopentyl ketone	6	-94.15	-75.04	15.30	0.27	1.26	2.40
dineopentyl ketone	2	-100.67	-88.41	15.49	0.54	1.68	2.40
cyclopentanone	8	-46.03	-34.89	15.35	0.00	0.42	2.40
cyclohexanone	6	-54.04	-36.11	7.94	0.00	0.42	2.40
cycloheptanone	0	-59.10	-42.84	13.74	0.08	0.42	2.40
cyclooctanone	0	-64.90	-49.58	18.05	0.02	0.00	2.40
<i>cis</i> -hyd-2-one	5	-59.30	-55.44	23.76	0.00	0.00	2.40
<i>trans</i> -hyd-2-one	5	-59.70	-55.44	23.16	0.00	0.00	2.40
<i>trans</i> -8-Me-hyd-2-on	3	-65.74	-65.16	28.90	0.00	0.00	2.40
<i>cis</i> -8-Me-hyd-2-one	2	-68.56	-65.16	26.28	0.00	0.00	2.40
norbornan-2-one	0	-40.20	-44.87	38.65	0.00	0.00	2.40
norbornan-7-one	0	-32.00	-42.24	47.97	0.00	0.00	2.40
bicyclo[3.2.1]octan-2-one	0	-51.80	-46.10	27.24	0.00	0.00	2.40
bicyclo[3.2.1]octan-3-one	0	-52.90	-48.71	25.42	0.00	0.00	2.40
bicyclo[3.2.1]octan-8-one	0	-46.20	-43.46	31.99	0.00	0.00	2.40
bicyclo[3.3.1]nonan-3-one	0	-63.80	-49.93	17.58	0.00	0.00	2.40
bicyclo[3.3.1]nonan-9-one	0	-57.30	-44.68	23.28	0.00	0.00	2.40
adamantanone	0	-55.10	-45.04	22.78	0.00	0.00	2.40
diadamantanone	0	-56.63	-59.23	33.83	0.00	0.00	2.40
camphor	0	-63.90	-68.58	46.48	0.00	0.00	2.40
2,2-dimethylpropanal	0	0.00	-30.84	6.49	0.00	0.42	2.40
3,3-dimethylbutanal	0	0.00	-44.21	7.78	0.02	0.84	2.40
3-methylbutanal	0	0.00	-34.50	4.96	0.07	0.84	2.40

^a Input.

asymmetric conformation.⁶⁴ Considering that Groth's bond lengths are uncorrected (see under cyclodecanone, above), the MM3 calculated conformation agrees with the observed (Table XXIV (supplementary material)).

From the above calculations, we found a systematic error with angle type 1-3-1 for cyclic compounds of ring size 9-11. We calculated these angles too small by about 2-6°. Some of the discrepancy may be a result of crystal packing. We cannot improve this situation without adversely affecting the open chain molecules and rings of size 6-8, however.

A few comments regarding the spectroscopic calculations seem pertinent here. One might wonder why the rms error is as large as it is. This could certainly be reduced by introducing more cross terms into the calculation. For example, by a coupling between the HCH bending and the CO stretching in formaldehyde, these two frequencies could be brought much closer together. This is

an interaction unique to formaldehyde, however, and it did not seem worth very much effort to improve the fit for this single compound.⁶⁵ The other carbonyl frequencies are calculated with errors of 5-15 cm⁻¹ and seem reasonably adequate.

It is of interest that the CH stretching frequencies are systematically low (on average by about 20 cm⁻¹) when the carbon is adjacent to a carbonyl group, as in acetone or an acetaldehyde. It is also known that these CH bonds are shorter than usual,⁶⁶ so it is reasonable that they are also stronger than usual. Further, their lengths and, so presumably, stretching constants also should

(65) A brief study of this problem was carried out by Dr. H. D. Thomas here. He found that if a constant of -0.1 was assigned to the cross term mentioned the calculated errors in the two frequencies mentioned were reduced from +34, -83 to +6, -64, and the rms error was reduced from 46 to 39 cm⁻¹. Similar interactions occur with HCH, HCC, and CCC groups in ethylene, acetaldehyde, acetone, etc., but it was found the improvements in these compounds were much smaller than in formaldehyde, and it was decided not to incorporate them into the program, at least for now.

(66) (a) McKean, D. C.; Boggs, J. E. Schafer, L. *J. Mol. Struct.* **1984**, *116*, 313. (b) Allinger, N. L.; Schafer, L.; Siam, K.; Klimkowski, V. J.; Van Alsenoy, C. *J. Comput. Chem.* **1985**, *6*, 331.

(63) Groth, P. *Acta Chem. Scand. (A)* **1974**, *28*, 294.

(64) Anet, F. A. L.; Cheng, A. K.; Wagner, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 9250.

Table XXIX. Heats of Formation for Carbonyl Compounds (MM3)^a

compound	C=O	C-C	Me	sec	tert	neo	iso	C-H
acetaldehyde	1	1	1	0	0	0	0	1
propanal	1	1	0	0	0	0	0	1
butanal	1	1	0	0	0	0	0	1
pentanal	1	1	0	0	0	0	0	1
hexanal	1	1	0	0	0	0	0	1
2-methylpropanal	1	1	0	1	0	0	0	1
2-ethylhexanal	1	1	0	1	0	0	0	1
acetone	1	2	2	0	0	0	0	0
2-butanone	1	2	1	0	0	0	0	0
2-pentanone	1	2	1	0	0	0	0	0
3-pentanone	1	2	0	0	0	0	0	0
2-hexanone	1	2	1	0	0	0	0	0
3-hexanone	1	2	0	0	0	0	0	0
4-heptanone	1	2	0	0	0	0	0	0
5-nonanone	1	2	0	0	0	0	0	0
6-undecanone	1	2	0	0	0	0	0	0
3-methyl-2-butanone	1	2	1	1	0	0	0	0
3,3-dimethyl-2-butanone	1	2	1	0	1	0	0	0
3-methyl-2-pentanone	1	2	1	1	0	0	0	0
3,3-dimethyl-2-pentanone	1	2	1	0	1	0	0	0
4-methyl-2-pentanone	1	2	1	0	0	0	1	0
4,4-dimethyl-2-pentanone	1	2	1	0	0	1	0	0
2-methyl-3-pentanone	1	2	0	1	0	0	0	0
2,2-dimethyl-3-pentanone	1	2	0	0	1	0	0	0
2,4-dimethyl-3-pentanone	1	2	0	2	0	0	0	0
3,3,4-trimethyl-2-pentanone	1	2	1	0	1	0	1	0
3,3,4,4-tetramethyl-2-pentanone	1	2	1	0	1	1	0	0
2,6-dimethyl-4-pentanone	1	2	0	0	0	0	2	0
di- <i>tert</i> -butyl ketone	1	2	0	0	2	0	0	0
<i>tert</i> -butyl neopentyl ketone	1	2	0	0	1	1	0	0
dineopentyl ketone	1	2	0	0	0	2	0	0
cyclopentanone	1	2	0	0	0	0	0	0
cyclohexanone	1	2	0	0	0	0	0	0
cycloheptanone	1	2	0	0	0	0	0	0
cyclooctanone	1	2	0	0	0	0	0	0
<i>cis</i> -hyd-2-one	1	2	0	0	0	0	2	0
<i>trans</i> -hyd-2-one	1	2	0	0	0	0	2	0
<i>trans</i> -8-Me-hyd-2-one	1	2	0	0	0	1	1	0
<i>cis</i> -8-Me-hyd-2-one	1	2	0	0	0	1	1	0
norbornan-2-one	1	2	0	1	0	0	1	0
norbornan-7-one	1	2	0	2	0	0	0	0
bicyclo[3.2.1]octan-2-one	1	2	0	1	0	0	0	0
bicyclo[3.2.1]octan-3-one	1	2	0	0	0	0	2	0
bicyclo[3.2.1]octan-8-one	1	2	0	2	0	0	0	0
bicyclo[3.3.1]nonan-3-one	1	2	0	0	0	0	2	0
bicyclo[3.3.1]nonan-9-one	1	2	0	2	0	0	0	0
adamantanone	1	2	0	2	0	0	0	0
diadamantanone	1	2	0	2	0	0	2	0
camphor	1	2	0	0	1	1	1	0
2,2-dimethylpropanal	1	1	0	0	1	0	0	1
3,3-dimethylbutanal	1	1	0	0	0	1	0	1
3-methylbutanal	1	1	0	0	0	0	1	1

^a Input.

be torsion angle dependent.^{66b} Since these frequencies do not affect the structure, or much of anything else, they could be, but have not been improved in the present work.

As we remarked with the hydrocarbons, one can fit the frequencies better than we have done if one really wants to do so. However, the work is labor intensive, and it requires complicating the calculations, so that more computer time will be required if such complications are introduced. These factors have to be weighted against the higher accuracy which can be obtained from the calculations. We have compromised at this point for now.

The aldehydic hydrogen is also worthy of some comment. This hydrogen is attached to the very positive carbonyl carbon, and hence the electron density in the CH bond is quite low. This low electron density leads to a number of unique features for this type of CH bond. This proton is observed at extremely low field in the proton NMR spectrum, which makes it useful for identification purposes. Also, the CH stretching frequency is unusually low, the force constant is low, and the bond length is long. These vibrational characteristics are reproduced here, because the type 3-5 bond is assigned a lower force constant than the 1-5 and also

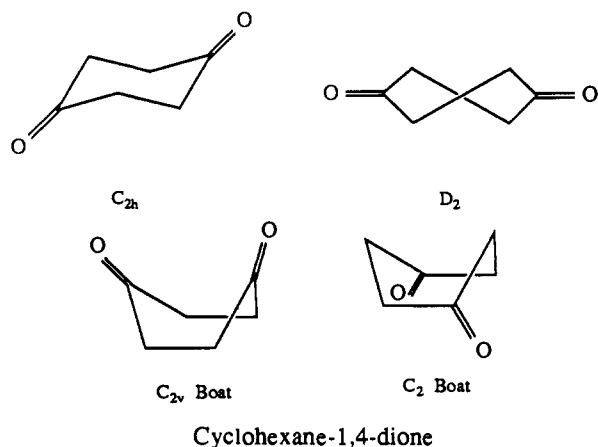
a longer I_0 . The aldehydic hydrogen can also be located easily enough in the infrared spectrum in most cases.

Something which is of great diagnostic value to organic chemists is the stretching frequency of the CO bond in the infrared.⁷⁹ This frequency is quite sensitive to ring size for ketones⁸⁰ (and also to other things, such as conjugation, or whether the compound is a ketone or an ester, an amide, etc.). The variation of frequency with ring size, according to our model, stems from two different features. The primary cause of this effect is mechanical. The C-C stretching vibrations are coupled with the C=O stretching, and, as the ring gets smaller, the C-C vibrations become more parallel to the C=O vibration, and they couple with it more strongly. As the ring gets larger, these vibrations become more nearly perpendicular, and they do not couple effectively. This coupling is a purely mechanical effect, which tends to make the high frequency higher and the low frequency lower. Ordinarily we do not observe the C-C stretching frequency (which is coupled with many other bendings, etc.), but the C=O frequency in fact goes higher as the ring gets smaller.⁸⁰ The effect is quite noticeable in practice for ketones which contain five- to seven-membered

rings, and this trend in frequencies is well reproduced. It is further known that the four- and three-membered rings show the effect in an even more pronounced way, and the frequencies for those compounds are much higher yet. The variation of stretching frequency with ring size is often explained in terms of a hybridization model.⁷⁹ More p character goes into the CC vibrations in a small ring, leaving less of it in the CO vibration. The higher percentage s character in the CO vibration leads to a stronger bond and a higher vibrational frequency. According to our model, however, this hybridization effect is insignificant (except possibly for cyclopropanone). Our mechanical effect reproduces the observed stretching frequencies well. The stretching parameters for the CO bond are essentially the same in cyclobutanone and in larger rings. (We use a larger constant in cyclopropanone, but the experimental value we are trying to fit is uncertain.) MM3 should be capable of calculating rather good shifts in this carbonyl frequency for arbitrary geometries of ketones. One should compare the shifts relative to a standard compound, however, rather than the absolute numbers, because our absolute numbers are not as good as we would like, and these frequencies are also changed a good bit from solvation if the spectra are determined in solution. The calculations and experimental results for the cycloalkanones are summarized in Table XXV.

We also carried out the calculation for 2-norbornanone, 7-norbornanone, and 2-bicyclo[2.2.2]octanone. The first two are five-membered ring ketones, while the latter is in a six-membered ring. These compounds are strained, however, in the direction of reducing the C-C-C angles. Compared with the parent compounds, therefore, these should, and do, show positive shifts in the C=O frequencies. Those are found to be at 1779, 1824, and 1754 cm⁻¹, respectively, corresponding to shifts of +34, +79, and +39 cm⁻¹ from the parent ring compounds⁷⁹ and in line with what is expected from bond angle considerations.

18. Cyclohexane-1,4-dione. There have been a number of experimental studies on the conformations of this molecule. The D₂ twist form was found to be the most stable form by temperature-dependent Raman spectra⁶⁷ in the liquid phase. The chair form with C_{2h} symmetry is 2.0 ± 0.7 kcal/mol (Δ*H*) above the twist form. Ab initio calculations showed that the chair form is 0.5 kcal/mol (E_c) more stable than the twist form with the 3-21G basis set. According to our MM3 calculations, the twist form is 0.12 kcal/mol above the chair⁶⁷ form. The relative energies of the four conformations are summarized in Table XXVI.



Decalin Diones. The isomerization equilibrium ratio of the trans and cis isomers of a decalin-1,4-dione (19) has been determined experimentally as 76:24 (in chloroform).¹³ Two conformations with the trans ring juncture and four conformations with the cis fusion were considered. The predominant conformation of the trans isomer has the B-ring in the boat form. On the contrary, the chair form is more favorable in the cis isomer. The MM3

Table XXV. Heats of Formation for Carbonyl Compounds (MM3)^{a-c}

	best values	best values	fixed values		
C=O =	-21.700	C-C =	-3.693	C-H =	-4.590
Me =	0.864	sec =	-3.755		
tert =	-7.665	neo =	-1.622		
iso =	-0.771				

compound	wt	H _f ^o calc	H _f ^o exptl	diff (calc - exptl)
acetaldehyde	10	-40.05	-39.73	-0.32
propanal	10	-44.75	-45.45	0.70
butanal	8	-49.72	-48.94	-0.78
pentanal	5	-54.63	-54.45	-0.18
hexanal	5	-59.54	-59.37	-0.17
2-methylpropanal	8	-51.92	-52.25	0.33
2-ethylhexanal	0	-69.72	-71.60	1.88
acetone	10	-51.91	-51.90	-0.01
2-butanone	10	-56.82	-57.02	0.20
2-pentanone	10	-61.78	-61.92	0.14
3-pentanone	9	-61.74	-61.65	-0.09
2-hexanone	9	-66.70	-66.70	0.00
3-hexanone	9	-66.70	-66.51	-0.19
4-heptanone	9	-71.66	-71.30	-0.36
5-nonanone	6	-81.51	-82.03	0.52
6-undecanone	0	-91.35	-92.55	1.20
3-methyl-2-butanone	10	-63.30	-62.76	-0.54
3,3-dimethyl-2-butanone	10	-69.81	-69.47	-0.34
3-methyl-2-pentanone	8	-67.21	-67.90	0.69
3,3-dimethyl-2-pentanone	6	-72.83	-72.60	-0.23
4-methyl-2-pentanone	7	-68.92	-69.60	0.68
4,4-dimethyl-2-pentanone	8	-76.49	-76.60	0.11
2-methyl-3-pentanone	9	-68.24	-68.38	0.14
2,2-dimethyl-3-pentanone	7	-74.63	-74.99	0.36
2,4-dimethyl-3-pentanone	8	-74.47	-74.40	-0.07
3,3,4-trimethyl-2-pentanone	6	-77.79	-78.50	0.74
3,3,4,4-tetramethyl-2-pentanone	5	-83.61	-83.10	-0.51
2,6-dimethyl-4-heptanone	5	-85.48	-85.49	0.01
di-tert-butyl ketone	8	-82.62	-82.64	0.02
tert-butyl neopentyl ketone	6	-94.18	-94.15	-0.03
dineopentyl ketone	2	-100.63	-100.67	0.04
cyclopentanone	8	-45.81	-46.03	0.22
cyclohexanone	6	-54.44	-54.04	-0.40
cycloheptanone	0	-55.29	-59.10	3.81
cyclooctanone	0	-58.20	-64.90	6.70
cis-hyd-2-one	5	-59.91	-59.30	-0.61
trans-hyd-2-one	5	-60.51	-59.70	-0.81
trans-8-Me-hyd-2-one	3	-65.34	-65.74	0.40
cis-8-Me-hyd-2-one	2	-67.69	-68.56	0.60
norbornan-2-one	0	-37.43	-40.20	2.77
norbornan-7-one	0	-28.47	-32.00	3.53
bicyclo[3.2.1]octan-2-one	0	-49.30	-51.80	2.50
bicyclo[3.2.1]octan-3-one	0	-51.52	-52.90	1.38
bicyclo[3.2.1]octan-8-one	0	-45.67	-46.20	0.53
bicyclo[3.3.1]nonan-3-one	0	-60.58	-63.80	3.22
bicyclo[3.3.1]nonan-9-one	0	-55.60	-57.30	1.70
adamantanone	0	-56.46	-55.10	-1.36
diadamantanone	0	-61.14	-56.63	-4.51
camphor	0	-58.84	-63.90	5.06
2,2-dimethylpropanal	0	-59.18		
3,3-dimethylbutanal	0	-64.77		
3-methylbutanal	0	-56.98		

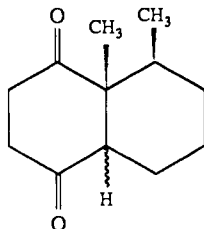
^a The standard deviation = 0.412. Based on 35 equations optimization and analysis ignores all equations whose weight is zero. ^b Output.

^c After the least-squares fit was carried out and all of the parameters fit, a few small typographical errors were found in the input. Since changes at this point, which would have been very small, would have involved redoing essentially all of the previous calculations, we decided to keep the parameter set as it was. This table was printed without actually reoptimizing the parameters but with the use of all of the numerically corrected values in the above table. The standard deviation overall actually reduced from 0.414 to 4.111, but we do not regard this change as significant: C-C = bond increment of type 1-3, C-H = bond increment of type 3-5, C=O = bond increment of type 3-7, Me = structural feature in which the α-carbon is a methyl group, sec = structural feature in which two alkyl groups are attached to the α-carbon, tert = structural feature in which three alkyl groups are attached to the α-carbon, iso = structural feature in which two alkyl groups are attached to the β-carbon, neo = structural feature in which three alkyl groups are attached to the β-carbon.

Table XXXI. Heats of Formation for Carbonyl Compounds (MM3, Stainless)

compound	wt	H_f°	sumh	steric	pop	tors	T/R	C=O	C-C	Me	sec	tert	neo	iso	C-H
Acetaldehyde	10	-40.05	-13.77	0.00	0.00	0.00	2.40	1	1	1	0	0	0	0	1
propanal	10	-44.75	-18.44	0.00	0.27	0.42	2.40	1	1	0	0	0	0	0	1
2-methylpropanal	10	-51.92	-23.12	0.00	0.17	0.42	2.40	1	1	0	1	0	0	0	1
acetone	10	-51.91	-27.54	0.00	0.00	0.00	2.40	1	2	2	0	0	0	0	0
2-butanone	10	-56.82	-32.21	0.00	0.00	0.42	2.40	1	2	1	0	0	0	0	0
2,2-dimethylpropanal	10	-59.18	-27.80	0.00	0.00	0.42	2.40	1	1	0	0	1	0	0	1
3,3-dimethylbutanal	10	-64.77	-39.88	0.00	0.02	0.84	2.40	1	1	0	0	0	1	0	1
3-methylbutanal	10	-56.98	-31.30	0.00	0.07	0.84	2.40	1	1	0	0	0	0	1	1

calculations give the trans/cis ratio of 73:27. The latter results from a mixture of six conformations, as detailed in Table XXVII.



Decalin Dione

Heats of Formation of Carbonyl Compounds. Heats of formation are fundamental properties of molecules. The molecular mechanics method has successfully calculated the heats of formation for several classes of compounds. In the hydrocarbon case, there are many accurate experimental data available. There are rather fewer good experimental values for the carbonyl compounds.⁶⁸⁻⁷⁶

Similar to the treatment used for hydrocarbons, we introduced structural parameters for substitution at the α -carbon for carbonyl compounds. But, we found that substitution at the carbon atom β to the carbonyl group also stabilizes the molecule to a remarkable extent. So we include two new parameters to account for this interesting effect. Our physical interpretation of the effect is as follows. Alkyl groups are more polarizable than hydrogen, in proportion to their size. The carbonyl dipole is quite large, and it strongly polarizes neighboring alkyl groups. This polarization lowers the energy of the system, with the energy lowering depending on the size of the alkyl group and its distance from the carbonyl. For a methyl ketone, the parameter is positive (0.8 kcal/mol), relative to the case of a normal alkyl chain, (such as an ethyl group) as zero. The secondary and tertiary centers at the α carbon lead to increasingly greater stabilization (-3.7, -7.7 kcal/mol). If the branch is moved to the β position, the effect is much less, but still a quaternary center lowers the energy 1.6 kcal/mol, while a tertiary center lowers it 0.8 kcal/mol. The

Table XXXII. Heats of Formation for Carbonyl Compounds (MM3, Stainless)^{a,b}

	best values	best values	fixed values
C=O =	-21.455	C-C = -3.340	C-H = -4.590
me =	0.690	sec = -2.405	
tert =	-4.815	neo = 1.235	
iso =	0.395		

compound	wt	H_f° calc	H_f° exptl	diff (calc - exptl)
acetaldehyde	10	-40.07	-40.05	-0.01
propanal	10	-44.74	-44.75	0.01
2-methylpropanal	10	-51.92	-51.92	0.00
acetone	10	-51.90	-51.91	0.01
2-butanone	10	-56.84	-56.82	-0.01
2,2-dimethylpropanal	10	-59.18	-59.18	0.00
3,3-dimethylbutanal	10	-64.77	-64.77	0.00
3-methylbutanal	10	-56.98	-56.98	0.00

^aThe standard deviation = 0.011. Based on eight equations optimization and analysis ignores all equations whose weight is zero. ^bSee footnote c to Table XXX.

parameters were determined by a least-squares fitting to the experimental data. The values for the weights in the fitting were determined by inverse scaling according to the experimental errors. The heats of formation for a few compounds were calculated in very poor agreement with the experimental values. We suspect that for these compounds the experiments are likely to be in error. Those compounds are 2-ethylhexanal, cycloheptanone, cyclooctanone, and some bridged bicyclic compounds. It could, of course, be that the present method simply works poorly for these compounds for reasons that we do not yet understand. With the bridged bicyclics, this is conceivably true, but it seems unlikely for the other compounds, which are quite ordinary. This group of compounds was accordingly weighted zero in determining the heat of formation parameters. Ab initio calculations are in progress to determine the nature of the discrepancies for these compounds. The input and output data are shown in Tables XXVIII-XXXII. For further details see ref 17.

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Registry No. *trans*-19, 106588-81-2; *cis*-19, 106588-80-1; MeCOCH-(CH₃)₂, 563-80-4; cycloheptanone, 502-42-1; cyclononanone, 3350-30-9; 4,4,7,7-tetramethylcyclononanone, 29416-00-0; 2-norbornanone, 497-38-1; 7-norbornanone, 10218-02-7; 2-bicyclo[2.2.2]octanone, 2716-23-6; 2,3-dimethylpropanal, 630-19-3; 3,3-dimethylbutanal, 2987-16-8; 3-methylbutanal, 590-86-3.

Supplementary Material Available: Tables XIX, XXII, and XXIV and a figure showing the rotational potential profile for methyl isopropyl ketone (6 pages). Ordering information is given on any current masthead page.

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