Table XII. Entropy Factors for Individual Conformers

Conformer	Symmetry no. factor[a]	*dl* pair factor	Total symmetry factor
Y	1	1	1
Z	4	2	8
X	2	1	2
W	2	2	4

[a] Proportional to the reciprocal of symmetry no. (see ref 21).

Table XIII. Activation Energy Barriers by ^1H NMR for Conformational Processes in Hexahydrotetrazines[a]

Compd			Δ_{AB} ppm	J_{gem}, Hz	T_c, K	$\Delta G_c^\ddagger$, kcal mol^{-1}
No.	Ring	Substituent				
1	Mono	Me_4	0.65	12.0	254	11.8 ± 0.2
2	Mono	Et_4	1.66	12.0	226	10.5 ± 0.2
3	Mono	*i*-Pr_4	0.17	12.0	211	10.3 ± 0.2
4	Mono	Bz_4	0.51	11.0	244	11.5 ± 0.2
5	Mono	Me_2Bz_2; sym	0.53	7.5	251[b]	12.1 ± 1.0
16	Tri	Sat	0.38	9.0	370	18.4 ± 0.2
14	Tri	Unsat	1.53	11.5	303	14.2 ± 0.2

[a] Solvents are as for the corresponding compounds in Table I.
[b] Large error; much overlap at coalescence.

W. The balance is here a more subtle one, and it is still not completely clear why the tetramethyl compound takes up conformation W, the tetrabenzyl derivative conformation X, while the tetraethyl- and the dibenzyldimethyl derivatives occur as mixtures of X and W.

Barriers to Nitrogen Inversion. The barriers to nitrogen inversion have been calculated using the coalescence temperature approximation for some of the hexahydro-*s*-tetrazines (Table XIII). The barriers for the monocyclic hexahydrotetrazines are all in the region 10–12 kcal mol^{-1}; such differences between them as occur, for example the lowering of barrier between the tetramethyl and tetraethyl compounds, are due probably to raising of the ground state energy in the tetraethyl compound. The two tricyclic compounds display significantly higher barriers, due probably to increased strain in the transition state; that of the saturated compound is again significantly higher than that of the bisolefinic. The sp^2 hybridization in the latter probably results in the transition state being raised somewhat less in energy than in the case of the saturated compound.

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Conformations of Methylated Cycloheptanones

M. St-Jacques,* C. Vaziri, D. A. Frenette, A. Goursot,[1] and S. Fliszár

Contribution from the Département de Chimie, Université de Montréal, Montreal, Quebec, Canada.

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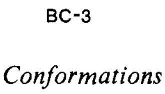
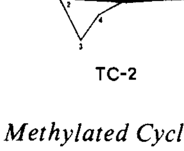
Abstract: ^1H NMR studies of dimethylcycloheptanones at low temperatures (below coalescence) together with conformational calculations using the PCILO approach indicate that the most stable conformations are twist chairs with the carbonyl group located at position 2 (i.e., TC-2,1, TC-2,4, and TC-2,5) in accord with a greater competitive conformational preference for the carbonyl group relative to the gem-dimethyl group. The above conclusion is then used to rationalize the low-temperature spectral behavior observed for two tetramethylcycloheptanones. A consistent conformational rationale, which explains all the experimental results, is formulated.

Knowledge of the conformational dynamics of a wide variety of cyclic ketones has constituted a research objective of considerable popularity over the years. Although it has been known for quite a while that both cyclohexane and cyclohexanone have similar overall chair conformations,[2] the extent of flattening caused by the carbonyl group was determined not long ago.[3] The free energy barriers for ring inversion in cyclohexanone[4] and its derivatives[5,6] have been found recently to be much smaller than that of cyclohexane and were rationalized in terms of a lower torsional energy requirement for partial rotation about the bonds next to the carbonyl group. Further insight into the conformational effect of a carbonyl group has been provided from dynamic nuclear magnetic resonance (DNMR) studies of cyclooctanone[7] whose conformation has been found to be similar to the boat-chair of cyclooctane with the carbonyl group located preferentially at position 3 as in conformation BC-3.



BC-3



TC-2

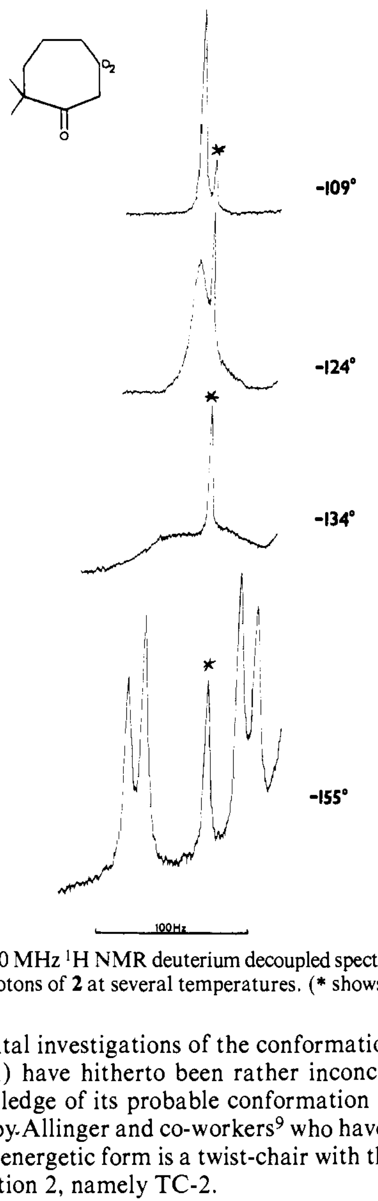


Figure 1. The 100 MHz ^1H NMR deuterium decoupled spectra of the C(7) α-methylene protons of **2** at several temperatures. (* shows impurity).

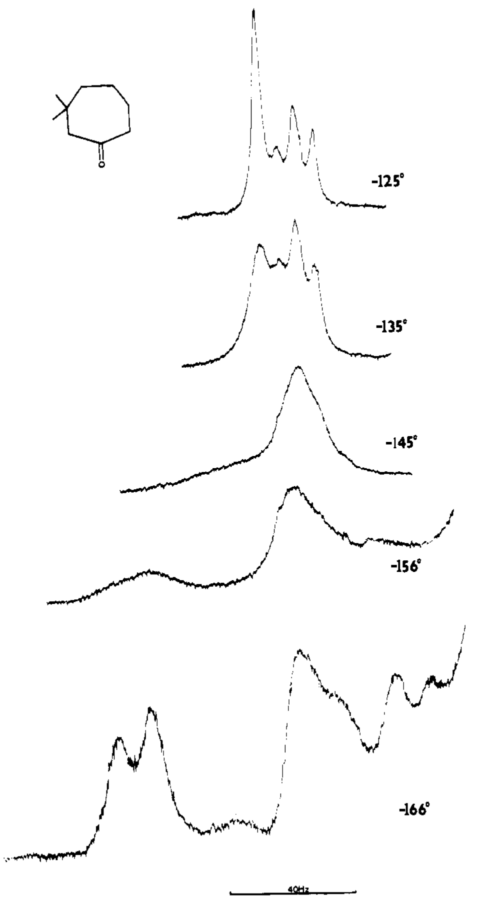
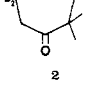


Figure 2. The 100 MHz ^1H NMR spectra of the α-methylene protons on C(2) and C(7) of **3** at several temperatures.

Experimental investigations of the conformation of cycloheptanone (**1**) have hitherto been rather inconclusive[8] and present knowledge of its probable conformation is based on calculations by Allinger and co-workers[9] who have estimated that the least energetic form is a twist-chair with the carbonyl group at position 2, namely TC-2.

Application of the DNMR method to cycloheptanone is inherently difficult because of its extremely low barrier for ring inversion which is still unknown, unlike that of cyclohexanone[4] and cyclooctanone.[7] Geminal methyl groups, however, raise the $\Delta G^{\ddagger}$ barrier significantly[10] and it was possible to observe a characteristic spectral change for 3,3,5,5-tetramethylcycloheptanone[11,12] and 3,3,6,6-tetramethylcycloheptanone.[13] Unfortunately, only tentative conclusions of limited conformational value were possible from these preliminary studies.

Our objective in the present detailed study of geminal dimethyl derivatives of cycloheptanone (**2** to **4**) was to achieve conditions of measurable $\Delta G^{\ddagger}$ values and consequently to determine some characteristic conformational properties for these molecules from the analysis of the low-temperature ^1H NMR spectra. Selective deuteration was required for certain molecules in order to simplify the signals of the protons next to the carbonyl group.



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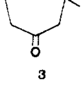

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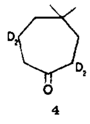

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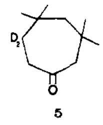

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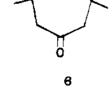

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The present investigation required the evaluation of the relative preference (or competition) of the carbonyl group vs. a gem-dimethyl group for the various positions on the stable conformation of the seven-membered ring. Conformational calculations using the PCILO method (vide infra) were found very useful for this task. The present account, therefore, contains the results and conclusions from the combined calculation and DNMR studies which provide unique information concerning the nature of the most stable conformations of compounds **2** to **6** in solution.

Results

Compound **2** was prepared by α deuteration of 2,2-dimethylcyclohexanone in the presence of deuterium oxide and potassium carbonate followed by ring expansion[14] with diazomethane and boron trifluoride etherate which gave a mixture of ketones[15] from which **2** was obtained pure. Compound **3** was obtained from a ring expansion of 2,2-dimethylcyclohexanone, while **4** was prepared by α deuteration of 4,4-dimethylcyclohexanone followed by ring expansion. Finally, **5** was prepared by α deuteration of 3,3,5,5-tetramethylcyclohexanone, followed by ring expansion and then by the removal of the α deuterons with water and potassium carbonate.

Spectral Analysis. Figure 1 illustrates the only ^1H NMR spectral change observed for **2** at low temperatures. The α-methylene protons singlet (δ 2.50) broadens and becomes an AB quartet below −134 °C, the coalescence temperature (T_c). Spectral analysis provided the following parameters: $^2J_\alpha$ = −10.4 Hz and $\Delta\nu_\alpha$ = 71.5 Hz. The use of standard equations[16] yields $\Delta G^{\ddagger}$ = 6.5 kcal/mol for this spectral change.

The 100 MHz ^1H NMR spectrum of **3** showed spectral changes in two regions. The methyl singlet (δ 0.957) changed into a doublet separated by 16.8 Hz at −165 °C ($T_c \approx -162$ °C) while Figure 2 illustrates the spectral behavior of the singlet (δ 2.444) for the α-methylene protons on C(2) and the

Table I. Summary of the Spectral Parameters Obtained for the Methylated Derivatives of Cycloheptanone

Compd	Signals obsd	$\Delta\nu$, Hz	T_c,[a] °C	k, s^{-1}	$\Delta G^{\ddagger}$,[b] kcal/mol	$^2J_{HH}$, Hz
2,2,7,7-Tetradeuterio-cycloheptanone	Methylene on C(3), C(4), C(5), and C(6)		<−172		<5.0	
2	Methylene on C(7)	71.5	−134	169	6.5	−10.4[d]
3	Methylene on C(2)	86.0	−148	201	5.8	−11.0[c]
4	Methylene on C(3) or C(5)	21.0	−149	93	5.9	−14.6[c]
5	Methylene on C(2)	90.4	−138	202	6.3	−10.1[d]

[a] ±2 °C. [b] Calculated using a transmission coefficient of 1; ±0.3 kcal/mol. [c] ±0.5 Hz. [d] ±0.2 Hz.

triplet (δ 2.360) for the α-methylene protons on C(7). The singlet broadens and changes below −148 °C (T_c) into an AB pattern characterized by $^2J_\alpha = -11.0$ Hz and $\Delta\nu_\alpha = 86.0$ Hz at −165 °C. Very little change besides broadening is observed for the C(7) protons triplet. Values of $\Delta G^{\ddagger} = 5.5$ kcal/mol at −162 °C and $\Delta G^{\ddagger} = 5.8$ kcal/mol at −148 °C were calculated for the changes in the methyl and methylene signals, respectively.

Figure 3 illustrates the only spectral change observed for **4**. The singlet at δ 1.48 (methylene protons on either C(3) or C(5)) changes into an AB pattern below −149 °C (T_c) for which the two upfield lines are clearly resolved. A value of $^2J_{HH} = -14.6$ Hz is measured while $\Delta\nu = 21.0$ Hz is estimated assuming symmetrical splitting about δ 1.48. A value of $\Delta G^{\ddagger} = 5.9$ kcal/mol was calculated at −149 °C.

It is particularly significant to note that the α-methylene protons singlet (δ 2.400) of **4** does not change because the ratio $\Delta\nu_\alpha/^2J_\alpha$ is relatively small and consequently $\Delta\nu_\alpha$ is also small in the stable conformation of this molecule.

The 100 MHz ^{1}H NMR spectral change observed for **5**, which was previously reported in a preliminary communication,[11] will be summarized briefly here. Of the two α-methylene singlets (δ 2.437 for C(2) and δ 2.362 for C(7)), only that of C(2) changes into an AB quartet below −138 °C (T_c) characterized by $^2J_\alpha = -10.1$ Hz, $\Delta\nu_\alpha = 90.4$ Hz at −155 °C, and $\Delta G^{\ddagger} = 6.3$ kcal/mol at −138 °C. The absence of a change for the signal of the protons on C(7) suggests that the two methylene protons are characterized by a small $\Delta\nu_\alpha$ in the stable conformation of this molecule.

Table I contains a summary of the pertinent data obtained from the spectral studies.

Conformational Calculations. Because of its speed and recognized successes,[17] the PCILO (Perturbative Configuration Interaction of Localized Orbitals) method,[18] a semiempirical conformational energy calculation procedure, was selected in this work. This semiempirical all valence electron method considers, from a conceptual point of view, that the chemical formula is a good zeroth order approximation and looks at the molecule as an assembly of interacting chemical bonds, the interaction being treated by perturbation theory. This method lies beyond the SCF approximation and uses the CNDO/2 hypotheses[19] for the integrals. In PCILO, the hybrid atomic orbitals are constructed following Del Re's method,[20] i.e., hybrids with maximum overlap on the chemical bonds, adding to the strong chemical character of PCILO. The program uses a polarity parameter δ for each bond, such that the coefficients C_{i1} and C_{i2} of the bonding orbitals are $C_{i1} = [(1 + \delta)/2]^{1/2}$ and $C_{i2} = [(1 - \delta)/2]^{1/2}$. While the bond polarities were originally determined empirically from bond dipole moments, these are optimized in the present PCILO calculations.

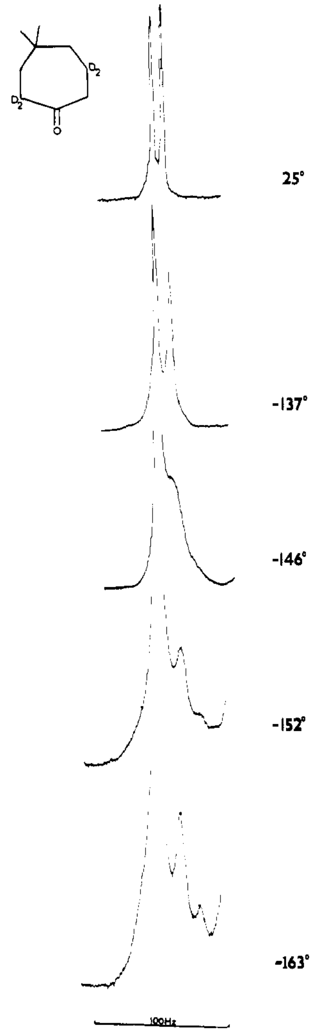


Figure 3. The 100 MHz ^{1}H NMR deuterium decoupled spectra of the methylene protons on C(3) and C(5) of **4** at several temperatures.

Instead of optimizing the conformational minimal energies by varying, one at a time, the various geometrical parameters as commonly done, a modified procedure was developed based on the more powerful technique of Powell,[21] later improved by Zangwill,[22] for finding the minimum of a function of several variables through the simultaneous treatment of all variational parameters. This optimization technique chooses conjugate or successively orthogonal directions in the parameter space to ensure a faster rate of convergence even from a bad starting approximation. This optimization technique has been extensively tested for its ability of reproducing correctly experimental results.[23]

It has been noticed earlier[24] that interatomic distances are not reproduced accurately in PCILO calculations, whereas angular parameters are in good agreement with experimental results. Since in the present study angular parameters are the

Table II. Relative Energies of the Dimethylcycloheptanones **2**, **3**, and **4**

Molecule	Conformer (TC-*m*,*n*)	Rel energy, kcal/mol
Dimethyl-2,2-cycloheptanone (**2**)	TC-1,2	2.2
	TC-2,1	0.0
	TC-2,3	1.5
	TC-3,2	3.3
	TC-3,4	1.6
	TC-4,3	1.2
	TC-4,5	2.6
Dimethyl-3,3-cycloheptanone (**3**)	TC-1,3	1.1
	TC-2,7	2.3
	TC-2,4	0.0
	TC-3,1	0.9
	TC-3,5	1.2
	TC-4,2	2.0
	TC-4,6	0.9
Dimethyl-4,4-cycloheptanone (**4**)	TC-2,5	0.0
	TC-4,1	0.6

prime factors determining the conformations, all valence and dihedral angles were included in the set of variational parameters, while bond lengths were selected from microwave results obtained for molecules of similar structure. By analogy with cyclohexanone,[25] the following interatomic distances were assumed (in Å): r(CC) = 1.535 (sp^3-sp^3), r(CC) = 1.516 (sp^3-sp^2), r(CO) = 1.222, and r(CH) = 1.096.

The calculations were carried out as follows: First, the energy of cycloheptane in the twist-chair conformation was calculated assuming r(CC) = 1.535 Å and $\angle$CCC = 116°. Next, a cycloheptanone initial geometry was generated from the above geometry by replacing a methylene group by a carbonyl group and changing the sp^3-sp^2-sp^3 CCC angle until the sp^3-sp^2 CC distance of 1.516 Å was obtained while keeping the three C and the O atoms in the same plane as originally present in the cycloheptane model. All methylenic HCC angles were kept at 108.5°, an angle which has been indicated by preliminary test calculations to be reasonably close to its optimum value. Starting geometries for cycloheptanone were, of course, generated for each of the nonequivalent possible forms of the twist-chair ring, thus defining the carbon skeletons of the various possible conformers. Finally, dimethyl-substituted cycloheptanones were generated, assuming methyl HCC angles of 109.5°. In this way, the starting geometries for all seven possible twist-chair conformations of dimethyl-2,2-cycloheptanone were generated. The starting geometries of dimethyl-3,3- and dimethyl-4,4-cycloheptanone were generated in a similar way.

The best conformational energies and geometries were obtained after an energy minimization resulting from the simultaneous optimization of all angular parameters, including the dihedral angles of the oxygen lone pair electrons.[26] The final geometries which are obtained in this manner represent local minima, i.e., structures possessing an energy minimum in the neighborhood of the assumed starting geometry.

The results obtained for the various twist-chair conformations of **2**, **3**, and **4** are summarized in Table II. The various forms are represented symbolically by TC-*m*,*n* where *m* denotes the position of the carbonyl group on the twist-chair skeleton and *n* denotes the position of the gem-dimethyl group; the isoclinal carbon always bears number one.[10] In contrast, the various carbon positions on the cycloheptanone structure are represented by C(x) where x denotes the substituent position with respect to the carbonyl carbon bearing number one.

Previous work[23,27] has shown that the PCILO calculations predict reliably the most stable conformations but that higher energy forms are somewhat underestimated most probably because of an underestimation of repulsive terms. Accordingly, more weight should be given to the order of stabilities than to the absolute energy difference magnitudes between the various forms in Table II.

Discussion

The conformational dynamics of cycloheptane is still a subject of current interest[28] and it appears fairly well established that its most stable conformation is the twist-chair. Experimental verification through low-temperature studies[10] of 1,1-difluoro-*trans*-4,5-dibromocycloheptane has shown that this derivative exists as TC while x-ray results[29] have shown that "dimeric cycloheptanone peroxide" exists in the chair (C) form. Since the interconversion between C (**7**) and TC (**8**) involves only a slight twisting (pseudorotation motion of the ring skeleton), the different results in solution and in the solid state can be explained by assuming that crystal lattice forces are responsible for the conformational change.

C(7) TC(8)

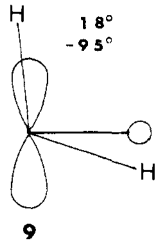
The most stable conformation of cycloheptanone has been predicted[9] to be TC-2 whereas experimental results on this ring system are scarce. It has been reported that 4-bromo-6,10-dimethylbicyclo[5.3.0]decan-3-one[30] exists as a chair in the solid state while ^{13}C magnetic resonance results on methylcycloheptanones in solution at room temperature were reported to be generally in good agreement with predictions based on the TC form.[8] It was not possible, however, to specify the positions of the carbonyl and methyl groups on TC.

The results of our systematic study are more comprehensive since the theoretical prediction that the most stable conformations of **2**, **3**, and **4** (Table II) should be TC-2,1, TC-2,4, and TC-2,5, respectively, is verified experimentally through interpretation of the low-temperature ^{1}H NMR.

The experimental confirmation of the predicted stable conformations rests upon the rationalization of the coupling constants ($^2J_\alpha$) and chemical shift differences ($\Delta\nu_\alpha$) determined at low temperatures for the methylene protons on C(2) and/or C(7) of the various compounds. The magnitude of both of these parameters is know to depend on the angular relationship between the α-CH$_2$ and the carbonyl groups[31,32] of the most stable conformations which is characterized by the low-temperature spectra.

Table I reveals a constant relationship: $|^2J_\alpha|$ = 10–11 Hz and $\Delta\nu_\alpha$ = 70–90 Hz. This interval for $^2J_\alpha$ corresponds to an angle θ value near 120°.[31] For the purpose of conformational comparisons, it is useful to define dihedral angles (χ) between the carbonyl group and each α-methylene proton such that $\theta = \chi + 90°$. Consequently, the range of 10–11 Hz for $^2J_\alpha$ corresponds to a $\chi \approx 30°$ (the clockwise direction is indicated by a positive sign).

Structures **9**, **10**, **11**, and **12** represent the projections about the 1-2 (and 2-1), 2-3 (and 3-2), 3-4 (and 4-3), and 4-5 (and 5-4) bonds of TC, respectively, for which the carbonyl group



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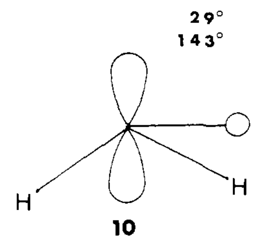

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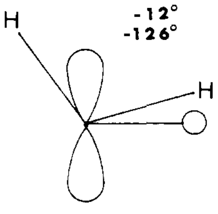

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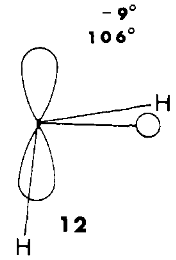

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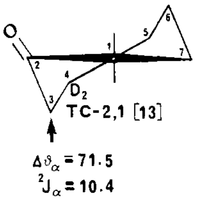
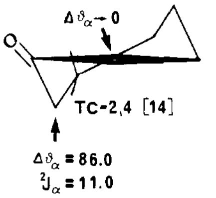
is located by convention at the front of the projected bonds. Examination of the various dihedral angles (±2–3°) for the different projections shows that only **10** has a χ value compatible with the experimentally observed $^2J_\alpha$ values. Consequently, the ^1H MMR parameters are compatible with the geometrical characteristics of the α-methylene protons at position 3 of TC-2.

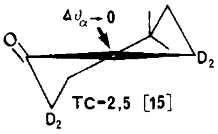
Structures **13**, **14**, and **15** depict the geometries of the most stable conformations calculated for **2**, **3**, and **4** together with the pertinent $\Delta\nu_\alpha$ and $^2J_\alpha$ which, for position 3 of TC-2,1 and TC-2,4, correspond to the χ angle of 29° depicted in **10**, while for position 1 of TC-2,5 both χ angles are very different from 30° as seen in **9**. The similarly large $\Delta\nu_\alpha$ values observed for position 3 of conformations **13** and **14** and the similarly small $\Delta\nu_\alpha/^2J_\alpha$ for position 1 of **14** and **15** are internally consistent.



TC-2,1 [13]



TC-2,4 [14]



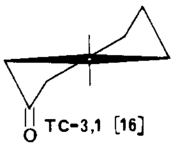
TC-2,5 [15]

Because, in the absence of substituents, the two isoclinal protons at position 1 are equivalent, it would appear that the combined anisotropies of the carbonyl group and the gem-dimethyl group in **14** and **15** produce a small $\Delta\nu_\alpha/^2J_\alpha$ value such that the ^1H NMR signal of the protons on C(7) for **3** does not show clear splitting while the protons on C(7) of **4** remain a singlet, even below coalescence, thus making the measurement of $^2J_\alpha$ impossible.

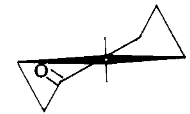
It is significant to note that the carbonyl group in **13**, **14**, and **15** adopts the most preferred position according to the order calculated by Allinger:[9] $2 \gtrsim 1 > 4 \gtrsim 3$. The gem-dimethyl group also takes up the least energetic positions (i.e., 1, 4, and 5) according to the order calculated by Hendrickson:[33] $2 > 4$ $(5) > 2 \gtrsim 3$.

The consideration of the alternative ensemble of conformations TC-1,2, TC-1,3, and TC-1,4 which maintain the carbonyl group at position 1 is not compatible with our observations. First, the conformational energies of TC-1,2 and TC-1,3 are not calculated to be the lowest ones as reported in Table II. Second, the χ values for the methylene protons at position 7 of TC-1,2 and position 2 of TC-1,3 (given in **9**) are incompatible with the $^2J_\alpha$ values of -10.4 and -11.0 Hz observed.[31] Furthermore, the results of Hendrickson's calculations[33] suggest that the gem-dimethyl group in TC-1,3 should be very energetic while in TC-1,2 both the carbonyl group and the gem-dimethyl group are located at more energetic positions than in TC-2,1.

Because it has been shown that a gem-dimethyl group takes up position 1 of the TC conformation of cycloheptane,[10] it is important to consider the ensemble of conformations TC-2,1 (**13**), TC-3,1 (**16**), and TC-4,1 (**17**) which also maintain the gem-dimethyl group at position 1 of TC for the various dimethylcycloheptanones. While the conformational energies reported in Table II argue against TC-3,1 and TC-4,1 being most stable for **3** and **4**, it is not possible to exclude them on the basis of incompatibility between $^2J_\alpha$ and χ values.



TC-3,1 [16]

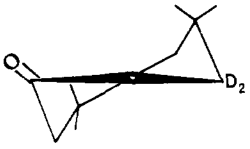


TC-4,1 [17]

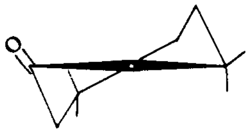
Consequently, the excellent agreement between the calculations and the conformational interpretation of the ^1H NMR parameters indicates that the stable conformations of **2**, **3**, and **4** are TC-2,1, TC-2,4, and TC-2,5, respectively, thus implying that *the competitive conformational preference of a carbonyl group is stronger than that of a gem-dimethyl group on the cycloheptane TC skeleton.*

The above suggestion can be used advantageously to explain the conformational properties of tetramethylcycloheptanones as revealed by spectral changes observed at low temperatures for **5** and **6**.

First, the ^1H NMR parameters obtained for 3,3,5,5-tetramethyl-6,6-dideuteriocycloheptanone[11] (**5**) reported in Table I are compatible with the form TC-2,4,6 (**18**) (where the third number defines the position of the second gem-dimethyl group) for which $\Delta\nu_\alpha = 90.4$ Hz and $^2J_\alpha = -10.1$ Hz are characteristic of the methylene group at position 3, in accord with similar parameters for the same position in TC-2,1 of **2** and in TC-2,4 of **3** which serve as models. In addition, the nonchanging singlet of the methylene protons on C(7) is in accord with the small $\Delta\nu_\alpha/^2J_\alpha$ expected for position 1 in agreement with similar observations for position 1 of conformations TC-2,4 of **3** and TC-2,5 of **4**.



TC-2,4,6 [18]



TC-2,4,7 [19]

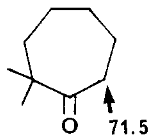
The striking internal consistency observed between the values of the ^1H NMR parameters for similar TC positions for the dimethyl and tetramethyl derivatives thus enhances the credibility of the overall conformational conclusion.

Methyl group anisotropy has not been considered explicitly in the above conformational interpretation even though it is known to produce significant chemical shift changes on methylene protons Δ and β to gem-dimethyl groups in methylcyclohexanes.[34]

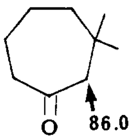
At the outset it is important to stress that although methyl anisotropy can affect $\Delta\nu_\alpha$ significantly, it does not influence the $^2J_\alpha$ magnitudes which also constitute a basic set of experimental parameters in our work.

Since a quantitative evaluation of the combined carbonyl and methyl group anisotropies from first principles would be of doubtful value in a complex conformational problem involving seven-membered rings, our objective will be to show that methyl group anisotropy is not the dominant contribution to $\Delta\nu_\alpha$ and consequently that other conformational factors are more important.

For this purpose it is useful to examine structures **20**, **21**, and **22** which illustrate the observed changes in $\Delta\nu_\alpha$. The 5,5-dimethyl group in **22** should have a very small effect on $\Delta\nu_\alpha$ of the methylene group identified because of the large distance involved.[34] Furthermore the similar magnitudes for **21** and **22** suggest a comparable relationship between α-CH$_2$ and the 3,3-dimethyl groups. The comparison of **20** and **21** shows that the chemical shift change brought about by the change in



20



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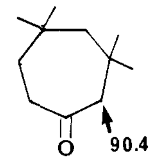

22

α-CH$_2$ and gem-dimethyl relationship (1,3 in **20** and 1,2 in **21**) has not modified $\Delta\nu_\alpha$ drastically, so that it is not unreasonable to conclude that the α-CH$_2$ of all three compounds possess comparable environments in accord with our previous conclusion.

The success of our approach and its clear-cut conclusion has led us to reconsider the conformational interpretation of the low-temperature spectral change already reported[13] for 3,3,6,6-tetramethylcycloheptanone (**6**).

It has been reported that at −115 °C the methyl singlet has split into a doublet, the CH$_2$CH$_2$ singlet has become a multiplet, while the α-CH$_2$ singlet has remained unchanged. To explain these results, the authors[13] proposed a TC-3,1,5 conformation capable of undergoing two exchanging processes: one characterized by a $\Delta G^{\ddagger} = 8.5$ kcal/mol responsible for the spectral modification and the other still rapid at low temperatures to account for the apparent simplicity of the spectrum at −115 °C. The choice of TC-3,1,5 did not consider the strong conformational preference of the carbonyl group but resulted from the minimization of methyl interactions.

Assuming that **6** also possess a basic TC skeleton, our results suggest that another plausible explanation could involve TC-2,4,7 (**19**) as the most stable form. The partial pseudorotation TC-2,4,7 $\rightleftharpoons$ C $\leftharpoondown$ TC-1,3,6 $\rightleftharpoons$ C′ $\rightleftharpoons$ TC′-2,4,7 (where the primes indicate inverted forms) averages partially the various methyl and methylene proton environments since the rapidly equilibrating TC conformations possess an average symmetry equivalent to that of TC-1,3,6 which contains a C_2 symmetry axis through the carbonyl group. Thus only two averaged methyl environments would result in accord with the two lines observed and only two averaged α-methylene proton environments would be expected. The α-CH$_2$ would be characterized by a small average $\Delta\nu_\alpha/{}^2J_\alpha$ in order to give rise to the singlet observed down to −130 °C. At high temperatures, when complete pseudorotation or any other exchange process (possibly a ring inversion through boat forms) becomes rapid on the ^{1}H NMR time scale, all methyl groups would average out to give a singlet as observed.

Experimental Section

The VPC analyses and separations were carried out on a Varian-Aerograph A90-P3 instrument using 0.25-in. columns.

Routine analytical ^{1}H NMR spectra were recorded on a JEOL C-60H spectrometer operating at 60 MHz in the external lock made. The low-temperature ^{1}H NMR spectra were obtained at 100 MHz using a JEOL JNM-4H-100 spectrometer. The samples studied were solutions in chlorodifluoromethane (10% by volume) with the exception of **5** which was examined as a 5% solution. All solutions containing a small quantity of TMS were degassed and sealed. Deuterium decoupling, when required, was effected by means of the JEOL Hetero Spin Decoupler Model JNM-SD-HC.

Temperatures were monitored by means of a JEOL temperature control unit Model JES-VT-3 and determined accurately with a calibrated thermocouple placed inside a solvent-containing dummy NMR tube. A precision of ±1 °C is expected.

The computer calculations were carried out on the CDC CYBER 74 computer at the Université de Montréal computing center.

2,2-Dimethyl-6,6-dideuteriocycloheptanone (2). 2,2-Dimethylcyclohexanone (2.0 g), 15 ml of deuterium oxide, and 1.5 g of potassium carbonate were refluxed for 36 h after which the product was extracted with ether. ^{1}H NMR analysis revealed complete absence of the α-methylene signal.

Ring expansion was accomplished with diazomethane according to the procedure published earlier for the nondeuterated analogue.[14] The desired product was separated from the mixture and purified by preparative VPC using a carbowax 20 M column at 170 °C.

Compound **2** was identified by its identical retention time to the known nondeuterated analogue and its characteristic ^{1}H NMR spectrum in dimethyl sulfide: a singlet at δ 1.00 (6 H), a multiplet centered at δ 1.55 (6 H), and a singlet at δ 2.35 (2 H).

3,3-Dimethylcycloheptanone (3). Compound **3** was prepared by a procedure already published.[14] It was purified by preparative VPC using a carbowax 20 M column at 170 °C and found to have the same ^{1}H NMR spectrum as in the literature.[15]

4,4-Dimethyl-2,2,6,6-tetradeuteriocycloheptanone (4). The preparation of compound **4** has already been published.[14] It was shown that it could be obtained pure through VPC purification using a UCW-98 column at 180 °C.

3,3,5,5-Tetramethyl-6,6-dideuteriocycloheptanone (5). 3,3,5,5-Tetramethylcyclohexanone[35] (34 g), 100 ml of deuterium oxide, and 10 g of potassium carbonate were refluxed for 24 h. Three similar exchanges were required to prepare the tetradeuterated cyclohexanone with a deuterium content greater than 99% as revealed by ^{1}H NMR analysis.

Ring expansion was accomplished with diazomethane using the procedure already published.[14] The desired product was separated from the mixture and purified by preparative VPC using a carbowax 20 M column at 200 °C.

3,3,5,5-Tetramethyl-2,2,6,6-tetradeuteriocycloheptanone (0.06 g), 50 ml of water, and 5 g of potassium carbonate were refluxed for 24 h. The product (**5**) was then purified as above and found to have a retention time identical with the nondeuterated analogue already published.[14] Its ^{1}H NMR spectrum taken as a 5% solution in chlorodifluoromethane showed the following signals: a singlet at δ 0.98 (6 H), a singlet at δ 1.00 (6 H), a singlet at δ 1.44 (2 H); a singlet at δ 2.36 (2 H on C(7)), and a singlet at δ 2.44 (2 H on C(2)).

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Model of Hydrogen-Bond Interactions near the Equilibrium Configuration. Application to Vibrational Energy Transfer in DF($v = n$) + DF($v = 0$)[1a]

Hyung Kyu Shin

Contribution from the Department of Chemistry,[1b] University of Nevada, Reno, Nevada 89507. *Received November 24, 1975*

Abstract: A model is developed in order to study near-equilibrium behavior of hydrogen-bond systems, in which individual molecules are considered to undergo hindered rotational motion and back-and-forth translational motion. The hindered rotational motion is described quantum mechanically, while the translational motion is analyzed in classical dynamics. Application of the model is made to calculate energy transfer probabilities of DF($v = n$) + DF($v = 0$) $\rightarrow$ DF($v = n - 1$) + DF($v = 1$) + ΔE for n = 2–5 at low temperatures, where the energy mismatch ΔE is transferred to the back-and-forth translational motion. As temperature increases, the formation of hydrogen bonds becomes less important, and energy transfer probabilities decrease sharply. The model is extended for the discussion of the self-deexcitation process DF($v = 1$) + DF($v = 0$) $\rightarrow$ DF($v = 0$) + DF($v = 0$) + ΔE at low temperatures, where ΔE is large and is now considered to be transferred to both the hindered rotational motion and back-and-forth translational motion. The model gives a strong negative temperature dependence of the deexcitation probability, which is in agreement with experiment.

The formation of hydrogen bonds is involved in many important phases of chemical and physical processes.[2-4] Hydrogen bonding in molecules such as H_2O, HF, and NH_3 is responsible for many of their most important properties and is quite common in proteins because of the presence of the carbonyl oxygen and amine hydrogen in the polypeptide chain. Unless they are formed between molecules in the rigid state, the molecules can have a significant degree of freedom in the near-equilibrium configuration. Then, such nonrigid bonds can affect the dynamic properties of molecules in restricted states of dimers. In a nonrigid dimer or an associated molecule, in addition to the vibrational motion of each molecule, two molecules can undergo restricted motion: namely, hindered rotational motion and restricted back-and-forth translational motion. The dynamics of these types of motion can be analyzed with the limited use of mathematics, and the information obtained from the analysis can be particularly useful in understanding processes which are associated with the formation of hydrogen bonds. One such process is the transfer of vibrational energy in collisions involving hydrogen fluorides at low temperatures where strong hydrogen-bond attraction can act between the molecules.[5]

The current interest in elementary processes taking place in chemical lasers has generated a need for kinetic information concerning energy transfer steps that govern excited state lifetimes.[6] Vibrationally excited deuterated fluoride molecules are known to undergo efficient vibration–vibration energy transfer with other molecules such as CO_2 thus producing, for example, $CO_2(00^\circ1)$ which, as a basis of lasing, converts chemical energy to coherent radiation energy. It is then important to know how vibrationally excited hydrogen fluoride molecules undergo deactivation. Since strong attractive forces act between the molecules, the energy transfer between DF($v = n$) and other DF molecules becomes an important process for the relaxation of such excited species.

In the present paper we shall develop a nonrigid dimer model by deriving the hydrogen-bond interaction energy near the equilibrium configuration. From experimental[7-9] and ab initio[10-13] studies the equilibrium configuration and the strength of the hydrogen bond are known, thus enabling us to determine the interaction energy as a function of pertinent intermolecular coordinates. We shall then discuss the dynamics of the restricted translational motion in the nonrigid structure and the quantum mechanical behavior of the hindered-rotational (small-amplitude oscillatory) motion of each molecule in the dimer. The idea will then be applied to calculate vibration–vibration energy transfer probabilities of DF($v = n$) + DF($v = 0$) $\rightarrow$ DF($v = n - 1$) + DF($v = 1$) + ΔE at low temperatures with the mechanism that the energy mismatch ΔE is transferred to the back-and-forth translational motion. The result will then be compared with that obtained from the complete rotational motion. The dimer model will also be applied to formulate the probability of the self-deactivation of hydrogen fluorides. Since the dimer model has already been introduced in ref 5, we shall briefly outline the derivation of pertinent expressions in the following section, but throughout the paper special emphasis will be given to a complete, rigorous discussion of the model and its application to molecular collisions.

Nonrigid Hydrogen-Bond Interaction

For two hydrogen fluoride molecules (HF or DF) forming a loosely bound nonrigid dimer at low temperatures, we can define the intermolecular coordinates as shown in Figure 1. The intermolecular atom–atom distances are complicated functions of r, θ_1, θ_2, and ϕ, but for the relative separation r significantly greater than the equilibrium bond distance d the atom–atom distances can be obtained in simpler forms. Recent ab initio calculations[10] show that $\theta_{1e} = 344.2°$, $\theta_{2e} = 52.2°$, $r_e = 2.80$ Å (5.29 bohr), and $\phi = 0°$, i.e., a planar configuration. The