

¹³C NMR DETERMINATION OF THE CONFORMATIONAL EQUILIBRIA IN THE ACETATES,
 BENZOATES AND N-PHENYLCARBAMATES OF 1-METHYLCYCLOHEXANOL AND CYCLOHEXANOL.

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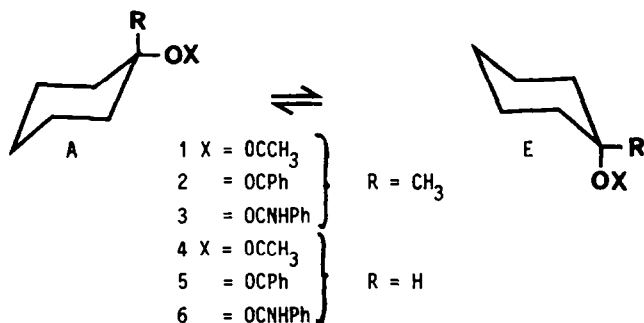
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Abstract - Thermodynamic parameters for the conformational equilibria in the acetates, benzoates and N-phenylcarbamates of 1-methylcyclohexanol and cyclohexanol have been determined using low temperature natural abundance ¹³C nmr, from which -ΔG° values at room temperature and above are obtained. Good agreement between these values and those determined at the higher temperatures using Eliel's method is found, providing care is exercised in correcting the chemical shifts of the model compounds used to find the shifts of pure conformers of the 1,1-disubstituted cyclohexanes. Calculated values for -ΔG° agree reasonably with experimental values with the exception of that for the 1-methylcyclohexyl N-phenylcarbamate. The effect of non polar solvent changes is minimal, but greater for CD₃OD.

INTRODUCTION

Our studies on alkene elimination from esters⁽¹⁾ led us to look for values of the conformational free energy differences (-ΔG°) at elevated temperature for the A ⇌ E equilibria of the 1-methylcyclohexyl esters of acetic, benzoic and N-phenylcarbamic acids (1-3)



The available data was sparse, the only report of a direct determination being for 1 in which Schneider⁽²⁾ found -ΔG° = 3.28 kJ mol⁻¹ at 190 K in CFC1₃. An estimate of -ΔG° = 4.34 kJ mol⁻¹ at 300 K can be made from the -ΔG° values for 1-methylcyclohexane (7.28 kJ mol⁻¹ in CFC1₃) and for cyclohexyl acetate (2.68 kJ mol⁻¹ in CS₂) reported by Booth⁽³⁾ and by Jensen⁽⁴⁾ respectively; likewise -ΔG° for 2 at 190 K is calculated to be 5.10 kJ mol⁻¹ from the reported values for 1-methylcyclohexane of 7.19⁽³⁾ and for cyclohexyl benzoate of 2.09⁽²⁾ kJ mol⁻¹, but this latter value, which is considerably lower than that for cyclohexyl acetate is the only datum available for cyclohexyl derivatives of benzoic acid. There are no data for N-phenylcarbamates. Therefore we have obtained high and low temperature conformational equilibrium constants of the esters 1-3 as well as those for the monosubstituted cyclohexyl esters of acetic, benzoic and N-phenylcarbamic acids (4-6) at low temperatures only.

Of the methods available for these determinations direct measurement of the equilibrium constant,

K from low temperature ^{13}C nmr spectra is probably the most reliable, since it involves measurement of peak areas of the two signals from equivalent carbons in each of the conformers^(2,5,6). However the experimental data is obtainable over a very limited range of low temperatures and extrapolation to room temperature or above may not give reliable values of $-\Delta G^\circ$. Although Booth⁽³⁾ has used this method successfully to determine the conformational thermodynamic parameters of alkylcyclohexanes using ^{13}C enriched samples from which $-\Delta G^\circ$'s at higher temperatures may be calculated, there are few reports of attempts to determine ΔH° and ΔS° values using natural abundance low temperature ^{13}C nmr.

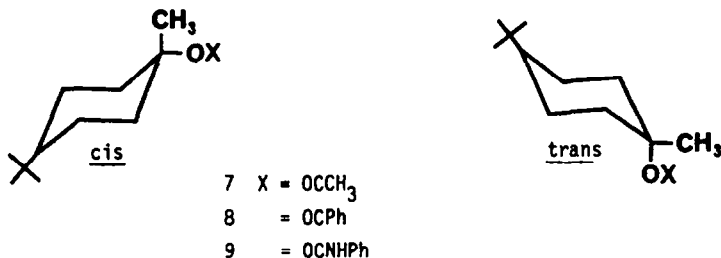
^{13}C nmr may also be used to find $-\Delta G^\circ$ values at higher temperatures by employing the averaging method developed by Eliel⁽⁷⁾, in which the chemical shift of an atom in an equilibrium mixture is considered to be the weighted average of the chemical shifts of the comparable atoms in each of the pure conformers. An inherent weakness of the method lies in the assumptions necessarily made in estimating the chemical shifts of the pure conformers from model conformationally pure compounds, but, with care, errors can be minimised.

Using the above methods $-\Delta G^\circ$ values at higher temperatures have been derived and are shown to be self-consistent. Finally we have calculated $-\Delta G^\circ$ values from the sum of the values for the appropriate monosubstituted cyclohexanes to assess the applicability of the additivity rule to these particular disubstituted compounds.

RESULTS AND DISCUSSION

To determine the low temperature conformational equilibrium constants and the enthalpy and entropy differences by the direct method, a series of 25 MHz ^{13}C nmr spectra of each of the esters 1-6 in $\text{CDCl}_3\text{-CFCl}_3$ solution were recorded at temperatures in the range 300-180 K. All esters, except 2 and 3 gave spectra in which the signals from the carbons in each of the two conformers were separate and distinct at temperatures below 200 K; for 2 the separation did not occur above 183 K and for 3 the poor solubility at the low temperatures resulted in the ester precipitating out of solution and a consequently inferior spectrum. In CD_3OD solution, however, the spectra of the two different conformations of 3 were quite distinct at temperatures below 200 K.

For conformational free energy determinations at higher temperatures 25 MHz spectra of cis/trans mixtures (approximately 50:50) of 1-methyl,4-*t*-butylcyclohexyl-acetate(7), benzoate(8) and *N*-phenyl-carbamate(9) were also recorded in $\text{CDCl}_3\text{-CFCl}_3$ solution at 300 and 184 K.



In the spectra of the 1-methyl substituted esters there is considerable crowding in the 20-26 ppm range, particularly at the low temperatures, making precise identification difficult. Signal assignments were therefore made from 100MHz spectra run in CD_2Cl_2 at 182 and at ca 300 K by comparison with published spectra^(2,6,8). The assignments for the signals from the minor conformers were verified by off-resonance decoupling and the position of the axial methyl carbon signal, which is about 5 ppm upfield from that of its equatorial counterpart was confirmed by a selective transfer experiment⁽⁹⁾. It was found that 3 did not precipitate out if the CD_2Cl_2 solution was cooled rapidly in a pre-cooled nmr tube instead of being allowed to cool slowly in the spectrometer, when its spectrum at 182 K also showed the separate signals for the two conformers. 100 MHz spectra at 182 and 315 K of 3 in CD_3OD were also recorded.

The conformational equilibrium constants for 1-6 at the low temperatures were determined directly from the ratio of the peak areas of the two signals from pairs of equivalent carbons. Peak areas were found by integration and, in some cases, by "cutting and weighing". In the 25 MHz spectra

only the C-1 and C-2 resonances were sufficiently free from crowding to permit accurate integration, but all the ring carbons could be used in the 100MHz spectra, except for 3 where the C-3 signal from the minor conformer (CH_3 axial) overlaps that from the 1- CH_3 in the major conformer and vice-versa. Table 1 gives the average values of K determined from relative peak areas of all the usable signals, and $-\Delta G^\circ$ values at 182 K shown in table 2, confirm that our values for 1 and 5 are the same as those of Schneider⁽²⁾.

Subtraction of each of the values for 4-6 from the published value of 7.19 kJ mol^{-1} for methylcyclohexane in CFCl_3 gives the calculated values for 1-3 also shown in table 2. These are all a little higher than the experimental values, but the agreement is reasonable, the largest discrepancy being for the 1-methylcyclohexyl benzoate where the difference between experimental and calculated values is about 30%. Other workers⁽⁶⁾ have found calculated and experimental values for 1-methyl, 1-halogenocyclohexanes to be identical, and those for 1-ethynylcyclohexyl acetate to differ by 16%. Large differences between calculated and experimental $-\Delta G^\circ$ values have been found for 1-methylcyclohexanol^(2,5,10,11) and have been attributed to differences in H-bonding in the tertiary and secondary alcohols⁽⁶⁾; in contrast, 1-ethynylcyclohexanol shows good agreement⁽¹⁰⁾.

Conformational enthalpy and entropy differences for 1 and 4-6 in CDCl_3 - CFCl_3 and for 3 in CD_3OD were obtained from the linear least squares plots of $\ln K$ versus T^{-1} and are shown in table 2. Since there is some scatter in the graphs (corr:coefs:=0.99-0.95) and the number of points obtainable is necessarily limited, the accuracy of $-\Delta G^\circ$ values found by extrapolation of these lines was open to question. However the $-\Delta G^\circ$ value of 2.94 kJ mol^{-1} calculated in this way for 4 accords with the reported value of 2.78 kJ mol^{-1} in CS_2 ⁽¹²⁾.

To confirm the accuracy of our other extrapolated results we have also determined experimentally the conformational equilibrium constants at ca 300 K using the Eliel equation $K = \delta A - \delta / \delta - \delta E$, where δA and δE are the chemical shifts of the pure A and E conformers and δ that of the time-averaged signal from the equilibrium mixture. Use of this method requires an estimate to be made of δA and δE . Customarily this is done by comparing the chemical shifts, δ_{cis} and δ_{trans} , of the conformationally pure 4-t-butyl derivatives of the cyclohexanes under investigation and correcting for the shielding effect, $\delta\delta$, of the 4-substituent. The small differences between δA , and δE make calculation of K extremely sensitive to errors in the estimated values of δA and δE and it is essential to determine the shielding effect of the 4-t-butyl group in the model compounds for each carbon of each isomer, a fact which is still not always appreciated^(5,13). Schneider⁽²⁾ has shown that substituents in cyclohexanes shield the carbons in the two conformations differently, and has attributed this to distortions of the ring, particularly by axial alkyl groups.

The shielding effect of the 4-t-butyl group in each of the esters 7-9 was determined by comparing the spectra of cis and trans mixtures of these compounds at low temperatures with those of 1-3 recorded under the same conditions.

Though mixtures of the two isomers of the 4-t-butyl, 1-methylcyclohexyl esters were used to ensure identical conditions for the nmr spectra, the assignments were verified using samples of the pure compounds. The $\delta\delta$ values, which are all less than 0.6 ppm (table 3) show some variation from ester to ester in the ring carbons, but are similar at the more remote 1- CH_3 carbons. In all cases the carbons of the cis and trans isomers are shielded differently. Solvent however appears to have little effect on the chemical shift changes induced by the 4-substituent, consistent with their steric origin⁽²⁾.

Values for δA and δE at the higher temperatures were found by addition of the appropriate $\delta\delta$ value to the chemical shifts δ_{cis} and δ_{trans} of the esters 7-9 at the higher temperatures, the assumption being made that $\delta\delta$ is temperature independent. A similar approach has been used by Jensen⁽⁴⁾. The 1- CH_3 carbons show the largest differences in δA and δE values (about 5 ppm) so that calculations of K from this data are least likely to be affected by imprecision in chemical shift determination. K has also been calculated from the data for the C-1 carbons, where δA and δE differ by about 2 ppm, but for all other carbons the difference in the chemical shifts of the two conformers was usually too small to give reliable results. The average K and $-\Delta G^\circ$ values are given in table 4

alongside the values derived from the ΔH° and ΔS° values from table 2. We have also calculated $-\Delta G^\circ$ for 1-3 using our derived $-\Delta G^\circ$ values for 4-6 and Booth's for methylcyclohexane⁽³⁾.

The two sets of results (experimental and derived) are in excellent agreement and confirm that the use of natural abundance ^{13}C nmr to obtain thermodynamic data for conformational equilibria leads to valid results. The $-\Delta G^\circ$ values found using the additivity rule, which are again higher than the experimental values, are in reasonable agreement for 1 and 2 but show a large discrepancy for 3. Indeed the experimental values for 3 at the higher temperatures in the halocarbon solvents are considerably lower than would be expected from a comparison of the other results. However the determinations in the two halo solvents are self-consistent so that we are confident that they represent the true values under these conditions. The value of K at 373 K was obtained from the 25 MHz spectra of 3 and of 9 in a deuteriated toluene-diphenyl ether mixture, recorded at 373 K, by correcting the chemical shifts for the 1-CH_3 carbons of 9 with the corrections for 9 in CD_2Cl_2 . As these values differ only marginally from those in CD_3OD we believe the error introduced by the change in solvent to be negligible.

In general, solvent appears to have little effect on conformational equilibria of substituted cyclohexanes if the polarity change is not too large, or if the substituents are non-polar. For example Buchanan⁽¹⁴⁾ found that the equilibrium constant of vinyl cyclohexane was the same in $\text{CD}_2\text{Cl}_2\text{-CS}_2$ as in C_7D_8 , and Chiurdoglu et al⁽¹⁵⁾ have found little effect of non polar solvents in a variety of cyclohexanes. It is to be expected therefore that our results in the different non polar solvent systems would be consistent and this is precisely the case. A rough estimate of $-\Delta G^\circ = 2.48 \text{ kJ mol}^{-1}$ for 3 in CD_2Cl_2 at 373 K can be made by extrapolation of the data for 182 and 315 K, which agrees well with the experimental value of 2.78 kJ mol^{-1} in $\text{C}_7\text{D}_8\text{-Ph}_2\text{O}$. The somewhat larger equilibrium constant in CD_3OD at 315 K is due to solvation of the carbamate group which reduces 1,3 diaxial interactions⁽⁵⁾. The hydrogen at N in 3 does not exchange with deuterium under the conditions of the experiment so that conversion to the deuterio-form need not be considered.

The order of magnitude of K for the monosubstituted esters is acetate > carbamate > benzoate, indicating an increasingly stable axial conformer as K decreases, which is reflected qualitatively in the order of magnitude of K for the disubstituted esters at low temperatures, benzoate > carbamate > acetate, since here the major conformers have the carboxylate group in the axial position. Schneider has attributed the increased stabilisation of the axial position of 5 compared with 4 to the lower electron density on the alkyl lone-pairs, which lowers the 1,3 repulsions. This would lead one to expect the axial form of 6 to be even more stable, since OOCNHPh is more electron withdrawing than OOCPh ⁽¹⁶⁾. That this is not so, and in fact at higher temperatures the axial position of the carboxylate is apparently less stable in 3 than in 1, may result from additional interactions of the lone-pair or the H on the N atom. Equally, distortion of the ring leading to increased interactions between the OOCNHPh group and the ring hydrogens in the disubstituted compared with the monosubstituted compound can provide an explanation for the lower equilibrium constant of 3 at the higher temperatures. Some evidence of this is provided by our studies on thermal elimination of alkenes from these esters⁽¹⁶⁾ in which we find that the ratio of exo:endo alkenes from the carbamate is higher than that found for the acetates and we attribute this to a flattening of the ring which allows the transition state in the thermal decomposition of 3 yielding the exo alkene to attain greater planarity than is possible for 1. A distortion of the ring in 3 also accounts for the large difference between the experimental and calculated values of $-\Delta G^\circ$ for this compound, not found in 1 or 2.

EXPERIMENTAL

Commercial samples of cyclohexanol, 1-methylcyclohexanol and cyclohexyl acetate were used.

1-Methyl,4-t-butylcyclohexanol prepared by a Grignard reaction (10% excess CH_3I) and recrystallised from petroleum ether (b.p. $40\text{--}60^\circ$) had a cis:trans ratio estimated by glc to be 1:3. The isomers were separated as described by dePuy and King.¹⁷

Acetates 1 and 7 and benzoates 2, 5 and 8, prepared by esterification of the alcohols with acetyl or benzoyl chloride in N,N dimethylaniline and purified by vacuum distillation yielded: 1 b.p.

66-67°/15mm (lit: 68/14mm)¹⁸; 7 b.p. 70°/0.6mm as a 45:55 cis:trans mixture; trans-7 was bulb-distilled (lit: b.p. 106-107°/14mm)¹⁷; cis-7, after bulb-distillation, solidified, m.p. 47.5-48.5° (lit: 48°)¹⁷; 2 b.p. 80°/0.07mm (lit: 110°/0.6mm)¹⁷; 5 b.p. 110-12/1mm (lit: 192-3/61mm)²⁰; 8 b.p. 134-136°/0.2mm. After further purification on an alumina column, 8 gave an analysis C, 78.76; H, 9.53. C₁₈H₂₆O₂ requires C, 78.77; H, 9.52. The cis:trans ratio was 55:45.

Carbamates 3,6 and 9 were prepared by heating the alcohols with N-phenyl isocyanate in toluene using stannous 2-ethyl hexanoate catalyst²¹. Recrystallisation from petroleum ether (b.p. 60-80° yielded: 3 m.p. 105°; 6 m.p. 81-82°, cis-9 m.p. 100-101°; trans-9 m.p. 145°. Analysis of the solids gave: 3-C, 72.06; H, 8.17; N, 5.92, C₁₄H₁₉O₂N requires C, 72.06; H, 8.22; N, 6.00; 6 C, 71.25; H, 7.75; N 6.30, C₁₃H₁₇O₂N requires C, 71.23; H, 7.76; N, 6.39; cis-9 C, 74.88; H, 9.16; N, 4.90, C₁₈H₂₇O₂N requires C, 74.68; H, 9.42; N, 4.84; trans-9 C, 74.95; H, 9.21; N, 4.98.

¹³C nmr spectra were run in 20% solutions on a 25 MHz Jeol FX100 and on a 100.6 MHz Bruker WM400 spectrometer. For 3 in CD₂Cl₂ a saturated solution was used. The position of the axial signal in 1 was confirmed by selective transfer of a 180° pulse at the equatorial signal.

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TABLE 1

EQUILIBRIUM CONSTANTS FOR THE CHAIR-CHAIR CONVERSIONS OF 1-METHYLCYCLOHEXYL AND CYCLOHEXYL ESTERS AT LOW TEMPERATURE.

Equilibrium 1A ⇌ 1E in CDCl₃-CFC1₃.

T/K	198.0	194.0	190.5	188.0	184.0
K	6.42	6.80	7.21	7.32	7.38

$$\ln k = (3.57 \times 10^2 \pm 5.36 \times 10)T^{-1} + 0.072 \pm 0.28 \quad \text{cc 0.96}$$

Equilibrium 3A ⇌ 3E in CD₃OD.

T/K	198.0	193.0	188.0
K	7.9	8.3	8.7

$$\ln k = (3.59 \times 10^2 \pm 8.9)T^{-1} + 0.26 \pm 0.04 \quad \text{cc 0.99}$$

Equilibrium 4A ⇌ 4E in CDCl₃-CFC1₃.

T/K	203.0	198.0	193.0	183.0
K	8.31	8.45	9.20	11.10

$$\ln k = (5.65 \times 10^2 \pm 7.5 \times 10)T^{-1} - 0.69 \pm 0.39 \quad \text{cc 0.98}$$

Equilibrium 5A ⇌ 5E in CDCl₃-CFC1₃.

T/K	223.0 ^a	198.0	193.0	188.0
K	3.40	3.91	3.94	4.00

$$\ln k = (2.02 \times 10^2 \pm 2.43 \times 10)T^{-1} + 0.32 \pm 0.12 \quad \text{cc 0.98}$$

Equilibrium 6A ⇌ 6E in CDCl₃-CFC1₃.

T/K	203.0	198.0	193.0	188.0	183.0
K	5.41	6.69	7.37	7.44	8.57

$$\ln k = (5.12 \times 10^2 \pm 7.4 \times 10)T^{-1} - 0.67 \pm 0.38 \quad \text{cc 0.97}$$

a. Obtained by averaging method assuming $\delta A, \delta E$ values for 198K.

TABLE 2

CONFORMATIONAL EQUILIBRIUM CONSTANTS AND FREE ENERGY DIFFERENCES IN 1-METHYLCYCLOHEXYL AND CYCLOHEXYL ESTERS AT 182K, AND CONFORMATIONAL ENTHALPY AND ENTROPY DIFFERENCES.

Ester	Solvent	K	$-\Delta G^\circ/\text{kJ mol}^{-1}$		$-\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1}\text{K}^{-1}$
			Found	Calc		
1	$\text{CDCl}_3\text{-CFCI}_3$	7.65	3.08 ± 0.04	3.67	2.97 ± 0.9	0.6 ± 0.2
	CD_2Cl_2	7.62	3.07 ± 0.02			
2	CD_2Cl_2	10.97	3.62 ± 0.03	5.14	$(3.85)^a$	(-1.3)
3	CD_2Cl_2	8.7	3.27 ± 0.01	4.07	$(4.02)^a$	-4.1
	CD_3OD	8.4	3.22 ± 0.05		2.98 ± 0.15	2.16 ± 0.2
4	$\text{CDCl}_3\text{-CFCI}_3$	11.11	3.64		4.70 ± 1.2	-5.8 ± 3.2
5	$\text{CDCl}_3\text{-CFCI}_3$	3.91	2.06		1.68 ± 0.4	2.66 ± 1.1
6	$\text{CDCl}_3\text{-CFCI}_3$	8.51	3.24		4.25 ± 0.60	-5.62 ± 3.2

a estimated from two values

TABLE 3

SHIELDING EFFECTS^a OF 4-t-BUTYL SUBSTITUENT IN ^{13}C NMR SPECTRA OF 1-METHYL,4-t-BUTYLCYCLOHEXYL-ACETATE (7) BENZOATE (8) AND N-PHENYLCARBAMATE (9).

Ester	C-1	C-2	C-3	1-CH ₃	CO-CH ₃	CO-CH ₃
7 ^b cis ^c	0.23	-0.03	-0.50	0.10	0.05	-0.11
	0.47	-0.28	-0.58	0.54	0.03	0.18
7 ^d cis	0.01	-0.52	-0.44	0.09	-	-
	0.34	-0.29	-	0.49	-	-
8 ^b cis	0.35	0.01	-0.46	0.13		0.62
	0.62	-0.20	-0.52	0.54		0.15
9 ^b cis	0.33	-0.06	-	0.03		-
	0.43	-0.44	-	0.55		-
9 ^e cis	0.23	-0.14	-	0.01		-
	0.45	-0.44	-	0.48		-

a. ppm Upfield from 1-methylcyclohexyl ester signals at 182K;

b. 100MHz spectra in CD_2Cl_2 ;

c. cis = CH₃ axial;

d. 25 MHz spectra in $\text{CDCl}_3\text{-CFCI}_3$;

e. 100 MHz spectra in CD_3OD .

TABLE 4
CONFORMATIONAL EQUILIBRIUM CONSTANTS AND FREE ENERGY DIFFERENCES,
- ΔG° FOR 1-METHYLCYCLOHEXYL ESTERS AT HIGHER TEMPERATURES.

Ester	Solvent	T/K	K	$-\Delta G^\circ(\text{exp})^a$	$-\Delta G^\circ(\text{der})^a$	$-\Delta G^\circ(\text{calc})^a$
Acetate	CD ₂ Cl ₂	303	4.16	3.59	-	
	CDCl ₃	298	4.58	3.77	3.15	4.38
Benzoate	CD ₂ Cl ₂	307	3.89	3.46		4.77
N-Phenyl Carbamate	CD ₂ Cl ₂	315	2.82	2.72		
	CDCl ₃	298	2.90 ^b	2.64		4.70
	CD ₃ OD	315	4.20	3.76	3.66	
	C ₇ D ₈ -Ph ₂ O	373	2.40 ^b	2.78	2.48 ^c	

a. in kJ mol⁻¹, exp = determined experimentally using Eliel equation under conditions shown, der = derived from ΔH° , ΔS° values (table 2), calc = calculated from additivity rule, using ΔG° for 4, 5 or 6 from ΔH° , ΔS° values in table 2; b. 1-CH₃ signal only using t-butyl corrections for CD₂Cl₂; c. see note a Table 2.

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