Conformational Preferences of some Substituted Methyl Groups in Cyclohexanes as Studied by Carbon-13 Nuclear Magnetic Resonance

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Low temperature ^{13}C NMR spectra of 80:20 mixtures of *cis* and *trans*-4-CH_3-$C_6H_{10}CH_2X$, where $-C_6H_{10}-$ is 1,4-disubstituted cyclohexyl and X=Br, CN, OH, OCH_3, $Si(CH_3)_3$, $Sn(CH_3)_3$, $Pb(CH_3)_3$ and $HgOCOCH_3$ have been recorded. The signals of the *trans* (e, e) components were assigned from the ambient temperature spectra of $C_6H_{11}CH_2X$ and the established substituent effects of an equatorial methyl group in cyclohexane. Conformational equilibria of the *cis* (e, a $\rightleftarrows$ a, e) components were then computed from the intensities of the (remaining) signals ($\sim$180 K) of the two conformational isomers. From these equilibria A values of CH_2X were calculated, assuming additivity of conformational energies of CH_3 and CH_2X (the counter-poise approach). In general, these values are very similar to the value of CH_3, although some trends do emerge. This study provides α, β, γ and δ effects for a wide range of axial and equatorial $-CH_2X$ groups.

INTRODUCTION

For some time we have been concerned with the substituent effects exerted by substituted methyl groups when attached to aromatic systems, and the conformations facilitating this interaction.[1-6] As an extension of this work, and our other interests in conformational preferences of metallo-containing groups,[7-9] it was considered worthwhile to determine (by NMR spectroscopy) the conformational A values of various substituted methyl groups. Information already available[10] indicated that these A values would be comparable with that for CH_3 (1.74 kcal mol^{-1} appears to be the best value),[12] but the selection of the CH_2X groups was limited and did not contain any metal functions.

As determination of A values in excess of 1.7 kcal mol^{-1} by direct low temperature NMR observation is not feasible, or at least highly inaccurate (unless ^{13}C enriched samples are examined[12]), we chose the alternative counter-poise method.[13] In this approach, the conformational preference of the group to be studied (CH_2X) is balanced against that of another group, usually methyl, and if the A value of CH_2X is greater than 1.74 kcal mol^{-1}, then **B** would predominate, and *vice versa*.
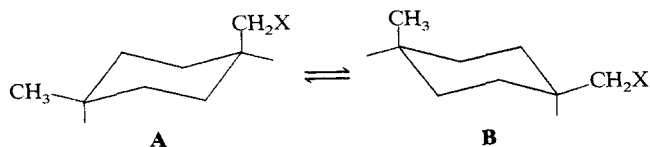
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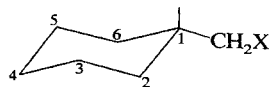
RESULTS

The parent (unsubstituted) cyclohexylmethyl compounds were obtained in a straightforward manner from either cyclohexanecarboxylic acid (ethyl ester) or cyclohexylmethyl bromide. Reduction of *p*-toluic acid provided an 80:20 *cis*:*trans* mixture of 4-methylcyclohexanecarboxylic acid which was esterified (see Experimental). No attempt to separate these isomers was made; the presence of the *trans* isomer ($\sim$20%) was not a problem in the interpretation of the ^{13}C spectra as its signals were essentially temperature invariant. Standard manipulation of the ester function provided the compounds examined.

The ^{13}C chemical shifts and, where appropriate, metal—^{13}C couplings are listed below (Table 1) for the parent system, $C_6H_{11}CH_2X$. Spectral assignments were made on the basis of chemical shifts, signal intensities and substituent effects. In the cases where X = magnetically active nuclei ($I = \frac{1}{2}$), e.g. ^{199}Hg, ^{119}Sn, ^{207}Pb, definite assignment was possible on the basis of these couplings, and these agreed with conclusions based on the other criteria.

The substituent effects listed in Table 1 must be regarded as approximate, as at $\sim$300 K a significant population ($\sim$5%) of the axial $-CH_2X$ conformer will exist. Nevertheless, these values are an adequate basis for calculating the chemical shifts of the *trans*-4-methylcyclohexyl derivatives.

The signals for the *trans*-4-methyl series could be selected in the ambient spectra on the basis of their intensities ($\sim$20%) and agreement with the calculated shifts. These signals also exhibited very little response to lower temperature as expected,[14] whereas the *cis*

Table 1. Carbon-13 chemical shifts[a] of cyclohexylmethyl compounds

X	1	2,6	Carbon[b-d] 3,5	4	CH_2	Other carbons
Br[e]	40.05	31.74	25.97	26.27	40.51	
	(+12.95)	(+4.64)	(−1.13)	(−0.83)		
CN	34.40	32.02	25.34	26.56	24.27	118.42
	(7.30)	(4.90)	(−1.80)	(−0.54)		
OH	40.35	29.55	25.78	26.53	68.32	
	(13.25)	(2.45)	(−1.32)	(−0.57)		
OCH_3	37.91	29.94	25.78	26.51	78.7	58.5
	(10.81)	(2.84)	(−1.32)	(−0.59)		
$Sn(CH_3)_3$[e]	36.36(18.32)	37.25(42.12)	26.67	26.30	21.2(362.55)	−9.41(313.11)
	(9.26)	(10.15)	(−0.43)	(−0.80)		
$Si(CH_3)_3$	34.45	36.94	26.66	26.31	25.78	−0.54
	(7.35)	(9.84)	(−0.44)	(−0.79)		
$Pb(CH_3)_3$	38.15(34.43)	37.22(70.3)	26.54	26.28	29.23(331.2)	−3.94(192.7)
	(11.05)	(10.12)	(−0.56)	(−0.82)		
$HgOCOCH_3$	37.62(82)	38.26(156.9)	26.22(~14)	25.78	35.99(1507.6)	177.28; 23.88
	(10.52)	(11.16)	(−0.88)	(−1.32)		

[a] Chemical shifts for $CDCl_3$ solutions (298 K) referenced to internal TMS.
[b] Substituent effects of $-CH_2X$ in parentheses below chemical shift. A chemical shift of 27.1 ppm has been used for cyclohexane to calculate the substituent chemical shifts.
[c] Metal—[13]C coupling constants in parentheses following chemical shift.
[d] α, β, γ and δ effects of e-CH_3 are: +6.4, +8.5, −0.4 and −0.1 ppm, respectively. Corresponding values for a-CH_3 are +1.1, +5.2, −5.9 and +0.2 ppm.
[e] Data for X = Br and $Sn(CH_3)_3$ obtained at 67.89 MHz, others at 25 MHz.

isomers exhibited marked broadening and essential separation into two sets of signals corresponding to **A** and **B**. The observed and calculated ^{13}C chemical shifts of trans-4-methylcyclohexyl-CH_2X are located in Table 2, and values at ~180 K are also listed. The agreements between observed and calculated shifts are very good.

With the signals for the trans isomers assigned, it was possible then to assign the remaining signals in the low temperature ('frozen') spectra to the two conformations of the cis isomers (Table 3). The CH_3 and CH_2X signals were straightforwardly assigned, as there is a large difference between axial (~17 ppm) and equatorial (~23 ppm) methyl group chemical shifts, as well as in the α and γ effects such groups exert. Additional assistance is provided by easy observations of metal—[13]C couplings (e.g. [207]Pb, [199]Hg) which lead to unambiguous assignment of certain signals, and significant population differences between the cis conformers was also useful. Spectral observations at intermediate temperatures also indicated the relationship between signals at low and higher temperatures.

With the assignments for the cis conformers **A** and **B** determined, the substituent chemical shifts of equatorial and axial $-CH_2X$ groups were calculated (knowing the α, β, γ and δ effects of equatorial and axial CH_3 groups) and are listed in Table 4.

DISCUSSION

The chief features to emerge from the data in Tables 1–4 concern: substituent chemical shifts of

CH_2X groups in equatorial and axial orientations; metal—[13]C spin coupling and the information it might provide on preferred conformations within the CH_2X group relative to the ring; and the conformational preferences of the various CH_2X groups.

Substituent chemical shifts of CH_2X

In Table 4 are listed α, β, γ and δ effects of equatorial and axial CH_2X. Two sets of values for the equatorial groups are presented—the first for the parent system $C_6H_{11}CH_2X$ and the second based on trans-4-methylcyclohexyl-CH_2X (after correction for the effects of equatorial CH_3). The first set is approximate, as at ~300 K a significant population of axial CH_2X conformer will exist and influence, in particular, the α and γ effects. This is fairly clear when the two sets of values are compared and the second set of γ values are generally significantly more positive because of the 'factoring' out of the slight axial contribution in the first set of values. One set of values for axial-CH_2X is available from the cis-conformer **A**. The differences between the values for CH_3 and CH_2X are quite
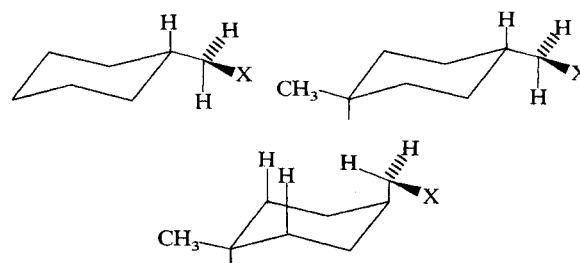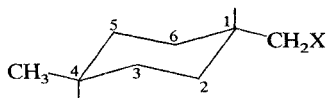
Table 2. Carbon–13 chemical shifts[a] of trans-4-methylcyclohexylmethyl compounds

X	1	2,6	3,5	4	CH₃	CH₂	Other carbons
Br(300 K)	40.38	32.10	35.08	32.91	22.52	41.11	
(Calc.)[b]	39.75	31.74	34.87	31.87	~23.	~41.	
(193 K)	39.89	31.63	34.56	32.60	22.71	42.09	
CN(300 K)	35.01	32.77	34.90	32.50	22.53	24.90	119.71
(Calc.)	34.1	32.00	34.20	32.04	~23	~24	~118
(183 K)	34.57	32.26	34.38	32.15	22.75	24.93	120.42
OH(300 K)	40.76	29.95	35.13	33.30	22.84	68.91	
(Calc)	40.05	29.55	34.68	32.13	~23	~68	
(185 K)	40.01	29.57	34.63	33.05	23.06	67.97	
OCH₃(300 K)	38.21	30.40	35.18	33.32	22.88	79.16	58.8
(Calc.)	37.61	29.94	34.68	32.11	~23	~78	~58
(183 K)	37.70	29.94	34.54	32.95	23.05	78.88	58.98
Si(CH₃)₃(300 K)	34.63	37.34	36.06	32.85	22.56	25.62	−0.48
(Calc.)	34.15	36.94	35.56	31.91	~23	~25.	~−0.5
(173 K)	34.05	36.70	35.43	32.45	23.09	25.20	−0.43
Sn(CH₃)₃(300 K)[c]	36.66	37.76 (~39)	36.06	32.90	22.77	21.27	−9.47
(Calc.)	36.06	37.25	35.57	31.90	~23	~21	~−9
(193 K)	36.08 (~20)	37.23(42)	35.53	32.51	22.98	21.60(362)	−9.47(313)
Pb(CH₃)₃(300 K)[c]	38.26 (34.48)	37.53 (71.4)	35.82 (7.19)	32.80	22.74	29.23 (346.62)	−3.94 (192.35)
(Calc.)	37.85	37.21	35.44	31.88	~23	~29	−3 to −4
(193 K)	37.75 (33.96)	37.08 (72.0)	35.37	31.96	22.93	29.02(330)	−3.98(191.4)
HgOCOCH₃[c](300 K)	37.81	38.64 (158)	35.50 (~15)	32.60	22.63	35.92	177.3; 24.07
(Calc.)	37.32	38.26	35.12	31.38	~23	~36	~177; 23–24
(173 K)	37.36	37.91	34.89	32.24	22.98	36.47 (1510)	177.48; 24.6

[a] Spectra recorded at 67.89 MHz for CD₂Cl₂ solvent relative to internal TMS.
[b] Assuming additivity of substituent chemical shifts and values for e-CH₂X from Table 1.
[c] Values in parentheses are metal—¹³C couplings.

substantial and, of course, reflect the substituent chemical shifts of the X groups themselves, operating presumably from the favoured conformations drawn below. For example, the reduced β effect of CH₂OH and CH₂OCH₃ [3.19 and 3.24 ppm, respectively, compared with CH₃ (5.2 ppm)] is associated with the shielding 'γ-anti' effect of OH and OCH₃.[15] Similarly, the greater β effects of CH₂M(CH₃)₃ and CH₂HgOAc reflect the positive γ effects[16,17] of M(CH₃)₃ and HgOAc and so on. The γ effects of axial-CH₂X are all larger than that of axial-CH₃ (−5.9 ppm) although the differences are not large, except for –OH and –OCH₃.[18] This would be reasonable if the conformation above for the axial-CH₂X was highly predominant, as would be expected on statistical and energetic grounds.

Metal—¹³C spin coupling

In the case of X = ¹¹⁹,¹¹⁷Sn, ²⁰⁷Pb and ¹⁹⁹Hg, the observation of satellite signals in the ¹³C spectra was generally possible and, as mentioned previously,

greatly facilitated assignment of certain signals. The generalization is that $^1J > {}^3J > {}^2J$ and, additionally, ^3J (vicinal coupling) is largely regulated by the dihedral angle (Karplus-type dependence).[8,19,20] The observed ^3J values are summarized below.

X	1	2	3	4
¹¹⁹Sn	42.1	42.0	44	42
²⁰⁷Pb	70.3	70.1	73.2	74.9
¹⁹⁹Hg	156.9	158	165±2	140±2

Utilizing the angular dependences for ^3J already established in other systems for these nuclei,[8,19,20] it is quite clear that the conformations previously drawn

Table 3. Carbon-13 chemical shifts[a] of cis-4-methylcyclohexylmethyl compounds
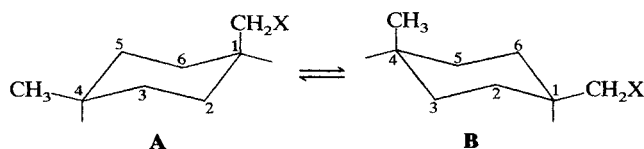

X	1	2,6	3,5	4	CH_3	CH_2	Other carbons
Br(300 K)	38.64	27.60	30.83	30.10	19.96	39.37	
A	34.64	29.33	28.80	33.21	23.12	38.08	
B	40.69	25.76	31.24	26.94	17.31	42.27	
B(Calc.)[b]	39.95	26.34	31.17	27.37	~17	~41–42	
CN(300 K)	33.29	28.14	30.57	29.78	19.94	22.61	119.71
A	30.08	31.06	28.96	32.86	23.10	19.62	121.15
B	35.28	26.51	29.12	26.81	17.27	25.15	120.42
B(Calc.)	34.3	26.62	30.54	27.54	~17	~24	~118
OH(300 K)	38.69	25.62	31.08	30.46	20.23	66.46	
A	34.72	29.89	26.82	33.20	23.32	62.44	
B	40.85	23.66	31.18	27.41	17.42	67.97	
B(Calc.)	40.25	24.15	30.98	27.63	~17	~68	
OCH_3(300 K)	35.80	26.07	31.13	30.58	20.36	76.61	58.80
A	33.16	29.94	27.26	32.42	23.31	73.42	58.98
B	38.56	24.03	31.13	27.34	17.41	78.88	58.98
B(Calc.)	37.81	24.54	30.98	27.61	~17	~78	~58
$Si(CH_3)_3$(300 K)	30.68	31.03	32.45	31.11	20.62	22.87	−0.65
A	28.56	32.78	29.10	33.35	23.42	18.01	−0.78
B	34.99	30.75	31.98	26.81	17.45	25.57	−0.46
B(Calc.)	34.35	31.54	31.86	27.41	~17	~25	~−0.5
$Sn(CH_3)_3$(300 K)[c]	34.41(~17)	32.80(40)	31.18	30.34	20.25	18.64(~340)	−9.69
A	30.46(~22)	33.44(42)	29.03	33.56	23.35	14.18(330)	−9.85(313)
B	36.98(~20)	31.32(44)	32.09	26.84	17.49	21.05(366)	−9.47(313)
B(Calc.)	36.26	31.85	31.87	27.40	~17	~21	~−9
$Pb(CH_3)_3$(300 K)[c]	36.04	32.68	31.03	30.19	20.19	26.80	−4.16(192.36)
	(34.38)	(71.47)	(14.00)			(336.56)	
A	32.07(~35)	33.51(74.9)	29.02	32.50	23.33	22.68(336)	−4.36(191.3)
B	38.64(~28)	31.18(73.2)	31.96	26.78	17.47	28.61(~330)	−3.98(191.4)
B(Calc.)	38.05	31.81	31.74	27.38	~17	~29.30	~−3 to −4
$HgOCOCH_3$(300 K)[c]	36.4(75)	33.28(165)	31.22	29.16	19.37	34.35(1495)	23.95; 177.30
A	31.64	33.96(~140)	28.97	33.48	23.28	31.34	24.63; 177.52
B	38.21(~75)	31.98(~165)	31.55	26.58	17.41	36.47(1510)	24.63; 177.52
B(Calc.)	37.52	32.86	31.42	26.88	~17	~36	~24; ~177

[a] Spectra recorded at 67.89 MHz for CD_2Cl_2 solvent.
[b] Calculated assuming additivity of chemical shifts, and using substituent chemical shifts (SCS values) for axial-CH_3 and equatorial $-CH_2X$ (Table 1).
[c] Values in parentheses are metal—^{13}C couplings.

for equatorial and axial CH_2X are consistent with these ^3J values, and that populations of (presumed) higher energy forms (below) are relatively low. For example, in the favoured conformations for axial and equatorial CH_2X, the average ^3J would be derived from $^3J_{180°}$ and $^3J_{60°}$. The calculated values are ~40 Hz (^{119}Sn), ~80 Hz (^{207}Pb) and 170 Hz (^{199}Hg), all in reasonable agreement with the ^3J observed. (The $^3J_{180°}$ and $^3J_{60°}$ values employed[8,19,20] were: ^{199}Hg, 270 and 70 Hz; ^{119}Sn, 65 and 10 Hz and ^{207}Pb, 120 and 20 Hz.)
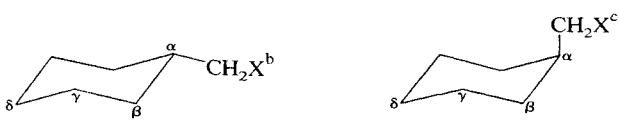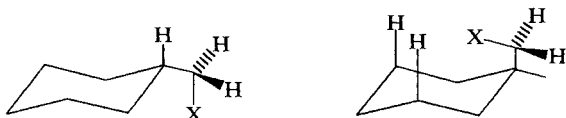

Significant populations of the presumed less stable conformers above would reduce $^3J_{AV}$, as the dihedral angle to each of the two vicinal carbons is 60°. The

one and two bond couplings reported here are unexceptional, but nevertheless greatly assist in assignments.

Conformational preferences of CH_2X

Assuming additivity of conformational free energies, it is possible to determine A values for CH_2X in several ways. Previously we have shown that in cis-4-methylcyclohexyltin compounds, the 'ambient' (~300 K) chemical shift of the $C-CH_3$ signal could be used, along with standard values for axial and equatorial $C—CH_3$, to calculate relative populations of **A** and **B** type cis-conformers, and hence an A value for $Sn(CH_3)_3$, in excellent agreement with that based on direct observation of the system at ~180 K where chair–chair reversal is sufficiently slow.[21] We have employed this procedure in the present cases, and A values based on this procedure are entered in Table 5.

Table 4. Substituent chemical shifts[a] of substituted methyl groups (–CH₂X)

X	α	β	γ	δ	α	β	γ	δ
Br	12.95	4.64	−1.13	−0.83	7.64	2.64	−6.80	−0.29
	13.38	5.40	−0.52	−0.59				
CN	7.30	4.90	−1.80	−0.54	3.08	4.36	−6.64	−0.64
	8.01	6.07	−0.70	−1.00				
OH	13.25	2.45	−1.32	−0.57	7.72	3.19	−8.78	−0.30
	13.76	3.25	−0.47	−0.20				
OCH₃	10.81	2.84	−1.32	−0.59	6.16	3.24	−8.34	−1.08
	11.21	3.70	−0.42	−0.18				
Si(CH₃)₃	7.35	9.84	−0.44	−0.79	1.56	6.08	−6.50	−0.15
	7.63	10.64	+0.46	−0.65				
Sn(CH₃)₃	9.26	10.15	−0.43	−0.80	3.46	6.74	−6.57	+0.06
	9.66	11.06	+0.46	−0.60				
Pb(CH₃)₃	11.05	10.12	−0.56	−0.82	5.07	6.81	−6.58	−1.00
	11.26	10.83	+0.22	0.70				
HgOCOCH₃	10.52	11.16	−0.88	−1.32	4.64	7.26	−6.63	−0.02
	10.81	11.94	−0.10	−0.90				
H[d]	6.4	8.5	−0.40	−0.1	1.1	5.2	−5.9	+0.2

[a] Using a value of 27.1 ppm for cyclohexane relative to TMS.

[b] For e-CH₂X, the first set of values based on the parent C₆H₁₁CH₂X system, and the second on the trans-4-methyl system, with correction for the e-CH₃ effects, on the spectra obtained under ambient conditions.

[c] The SCS values for a-CH₂X were derived from conformer A (table 3) (with correction for e-CH₃ effects), necessarily from the low temperature spectra.

[d] From ref. 11.

In the low temperature spectra, where the populations of the two cis-conformers are comparable, several measures of relative concentrations are possible, but the signals for C—CH₃ and CH₂X are assignable unambiguously and are used in the calculations in Table 5. We have also conducted calculations based on the intensities of other signals, and these values are

Table 5. Conformational free energies $(-\Delta G^0)$ of CH₂X

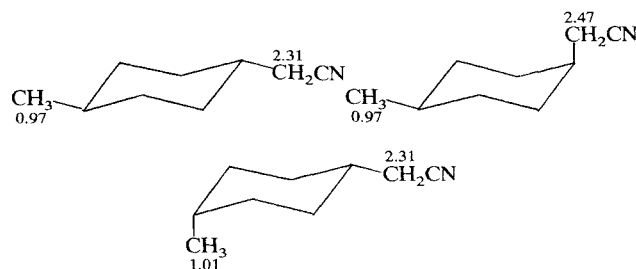|	A values (kcal mol⁻¹)			
	Method			
X	C—CH₃ Chemical shift[a]	C—CH₃ Intensity[b]	CH₂X Intensity[b]	Average
Br	1.84	1.73	1.79	1.79
CN[c]	1.84	1.69	1.78	1.77
OH	1.79	1.73	Signal overlap	1.76
OCH₃	1.74	1.69	1.74	1.72
Si(CH₃)₃	1.67	1.67	1.61	1.65
Sn(CH₃)₃	1.81	1.71	1.84	1.79
Pb(CH₃)₃	1.87	1.79	1.76	1.81
HgOCOCH₃	2.16	2.08	1.91	2.05

[a] Utilizing values for axial and equatorial C—CH₃ from low temperature spectra but these were 17.3±0.1 ppm and 23.3±0.2 ppm for all systems.

[b] Based on spectra (CD₂Cl₂ solvent) recorded for the temperature range 173–193 K.

[c] Low temperature ¹H examination of cis-4-methylcyclohexylmethyl cyanide provided an A value of 1.78 kcal mol⁻¹ based on intensities of the CH₂CN doublets. See text.

not seriously different. Integral comparisons of carbons bearing the same number of hydrogen atoms for spectra at 180 K are expected to introduce insignificant errors with the pulse repetition times employed.

This is supported by our examination of the ¹H spectra (at various temperatures) of the cis, trans-4-methylcyclohexylmethyl cyanide system. At ambient temperature, the trans isomer exhibits signals (doublets, $J \sim 6.5$ Hz) for C—CH₃ at δ 0.87 and CH₂CN at δ 2.23, with corresponding signals for the cis isomer at δ 0.93 and δ 2.31. At 189±3 K, with ring reversal suitably slowed, the following chemical shifts are observed (all relative to internal TMS for CD₂Cl₂ solvent). Utilizing the integrals for the CH₂CN signals, and correcting for the presence of the (c. 20%) trans isomer, an A value of 1.78±0.07 kcal mol⁻¹ is obtained. This is in excellent agreement (Table 5) with the value based on ¹³C signal intensities.

The clear and perhaps not surprising result is that A values for CH₂X are barely distinguishable from the accurately determined¹² value (1.74 kcal mol⁻¹) for CH₃ itself. This is again consistent with the presumed

highly preferred conformations for axial and equatorial CH$_2$X below, as in these arrangements
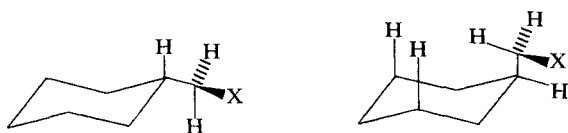
little change to the torsional energy difference between the conformers would result. The interesting result concerns -CH$_2$HgOAc and that the larger A value (2.05 kcal mol^{-1}) (compared with CH$_3$) is real is quite obvious from the low temperature spectrum. The factor involved here is not apparent, but it is worthwhile noting that -HgOAc prefers the axial orientation in cyclohexylHgOAc.[7]

Previously, Stothers[10] had reported A values for CH$_2$OH and CH$_2$OCH$_3$ of c. 1.40 kcal mol^{-1} (^{13}C method) and 1.70 kcal mol^{-1} (^{1}H method), values close to those reported here. Eliel[22] has provided a value of 1.65 kcal mol^{-1} for -CH$_2$OH, based on the equilibration method. Although not presented in detail, our methods provide A values for -COOCH$_2$CH$_3$ of 1.29 kcal mol^{-1} (C—CH$_3$ chemical shift) and 1.24 kcal mol^{-1} (C—CH$_3$ intensities in low temperature spectra), values in good agreement with the literature[23] ($\sim$1.1 kcal mol^{-1}), and providing confidence in the methods used here. The main conclusion to be drawn is that from the viewpoint of general conformational analysis, substituted methyl groups, with both electro-negative and -positive substituents, differ only marginally from the methyl group itself. This situation may not obtain, however, if other polar functionality were installed at appropriate positions in the ring, so that energy-lowering interactions could emanate from axially disposed polar CH$_2$X groups.

Recently, Booth and Everett[33] have demonstrated that in the series methyl, ethyl and isopropyl, $-\Delta H^\circ$ and ΔS° move in opposite senses so that at very low temperatures ($\sim$40 K) methyl has a greater equatorial preference than isopropyl. At higher temperatures, e.g. room temperature, ΔG° is dominated by $T\Delta S^\circ$ so that isopropyl has the greatest equatorial preference. This study[33] confirmed that the 'counter-poise' approach, utilizing a relatively evenly balanced equilibrium, allowed calculation of conformational parameters of good accuracy.

EXPERIMENTAL

Compounds

cis and trans-4-methylcyclohexylmethyl derivatives.
As outlined in the Discussion, examination was conducted on an 80:20 cis:trans mixture of these derivatives, this ratio being established by GLC and ^{1}H, ^{13}C NMR analysis. This predominantly cis mixture results from the hydrogenation of p-toluic acid, as described by Eliel.[23] Thus, this 80:20 cis:trans mixture of 4-methylcyclohexanecarboxylic acid was esterified[24] and reduced (LiAlH$_4$) in the normal way to

provide the same mixture of cis,trans-4-methylcyclohexylmethyl alcohol, with b.p. 85–88° (15 mm). (Lit.[25] 90–91° (12 mm) for cis and 90–91° (15 mm) for trans). ^{1}H NMR: CH$_3$ (d, $J \sim 6$ Hz), δ 0.91 (cis), δ 0.89 (trans); CH$_2$-OH (d, $J \sim 6$ Hz), δ 3.47 (cis) and δ 3.40 (trans). (Cyclohexyl protons resonated in the δ 1.0–2.0 range in all compounds and are not detailed further.) The 4-CH$_3$ and CH$_2$X groups appeared as doublets ($J \sim 6$–7 Hz) in all derivatives and the chemical shifts of the doublets are provided below.

4-Methylcyclohexylmethyl bromide.
This was obtained by treatment of the alcohol with triphenylphosphine/bromine in the standard way.[26] Yield = 70% b.p. 64–65° (5.5 mm). (Lit.[27] 82–83° (13 mm). ^{1}H NMR: CH$_3$ δ 0.91 (cis), 0.88 (trans); CH$_2$Br δ 3.36 (cis), δ 3.28 (trans).

4-Methylcyclohexylmethyl cyanide.
This was prepared from the bromide by treatment with sodium cyanide in DMSO, according to Smiley and Arnold.[28] Yield = 75%; b.p. 90–93° (10 mm). [Lit.[29] 218–219°]. ^{1}H NMR: CH$_3$ δ 0.93 (cis), 0.90 (trans); CH$_2$ δ 2.33 (cis), 2.30 (trans).

4-Methylcyclohexylmethyl methyl ether.
This resulted from treatment of the lithio salt (CH$_3$Li on the alcohol at -78°) with methyl iodide. Yield = 78%; b.p. 47° (6 mm). ^{1}H NMR: C—CH$_3$ δ 0.91 (cis), 0.89 (trans); CH$_2$ δ 3.26 (cis, trans); O—CH$_3$, δ 3.30 (cis, trans).

4-Methylcyclohexylmethyltrimethylstannane.
This was synthesized in the standard way by reaction of trimethyltin chloride (0.95 equivalent) with the Grignard reagent from the above bromide. Yield = 41%; b.p. 93–94° (5 mm). ^{1}H NMR: (CH$_3$)$_3$Sn (cis, trans) δ 0.07 [J(H, Sn) = 52 Hz]; CH$_2$—Sn and C—CH$_3$ overlap at δ 0.90.

4-Methylcyclohexylmethylmercuric acetate.
The corresponding mercuric bromide (m.p. 76°, 46% yield) was prepared from the Grignard reagent of the bromide above in the manner outlined by Jensen and Gale.[30] Treatment of this mercuric bromide with silver acetate at room temperature (acetone) provided the title compound in 96% yield, m.p. 102–103°. ^{1}H NMR: CH$_3$ δ 0.91; CH$_2$—Hg δ 2.05 [J(H ^{199}Hg) = 204 Hz]; acetate, δ 2.00 (No resolution of cis/trans signals).

4-Methylcyclohexylmethyltrimethylplumbane.
Trimethyllead chloride (0.95 equivalents) was added (as a THF solution) to the Grignard reagent prepared from the bromide described above, until the first signs of darkening of the solution ($\sim$10–15 min). After work-up of the reaction mixture in the normal way, the crude oil was distilled. Yield = 46%; b.p. 96–100° (4 mm). ^{1}H NMR: (CH$_3$)$_3$Pb δ 0.70 [J(H ^{207}Pb) = 56 Hz]; C—CH$_3$ δ 0.93; CH$_2$—Pb, δ 1.65 (?).

4-Methylcyclohexylmethyltrimethylsilane.
This was prepared from the Grignard reagent of the bromide,

Table 6. Physical properties[a] of cyclohexylmethyl derivatives ($C_6H_{11}CH_2X$)

X	Yield (%)	Observed b.p./m.p.	Literature value	^1H NMR[b]
OH	80	86–88 (20 mm)	88–89[31] (22 mm)	CH_2OH δ 3.50
Br	60	60–64 (10 mm)	76–77[31] (26 mm)	CH_2Br δ 3.26
CN	86	78 (10 mm)	208–209[29]	CH_2CN δ 2.28
OCH_3	60	40–42 (10 mm)	154[32]	$CH_2\cdot OCH_3$ δ 3.20; OCH_3 δ 3.38.
$Sn(CH_3)_3$	40	50–51 (2 mm)	—	$Sn(CH_3)_3$ δ 0.07 [J(H, Sn) $\sim$ 52 Hz] CH_2 δ 0.87
HgBr	31	(m.p.) 48°	—	CH_2—Hg δ 2.20 [J(H, Hg) = 192 Hz]
$HgOCOCH_3$	48	(m.p.) 108°	—	CH_2—Hg δ 2.08 [J(H, ^{199}Hg) = 204]; CH_3 δ 2.00
$Pb(CH_3)_3$	36	88 (3 mm)	—	CH_2—Pb δ 1.60(?); $Pb(CH_3)_3$ δ 0.70 [J(H, ^{207}Pb) = 56 Hz]
$Si(CH_3)_3$	29	60–62 (10 mm)	—	CH_2—Si δ 0.50; $Si(CH_3)_3$ δ 0.00.

[a] New compounds provided satisfactory C, H analyses.
[b] Cyclohexyl protons absorbed in the general range δ 0.7–2.2. The CH_2 resonances were all doublets with $J \sim$ 6–7 Hz.

and trimethylchlorosilane, utilizing the *in situ* technique. Vacuum distillation provided the required silane in 30% yield; b.p. 69° (9 mm). ^1H NMR: $(CH_3)_3Si$, δ 0.00 (*cis, trans*); C—CH_3, δ 0.95 (*cis*), δ 0.91 (*trans*), CH_2—Si; δ 0.58 (*cis, trans*).

The elemental analyses of the above compounds were in satisfactory agreement with the assigned molecular structures which are, of course, fully consistent with the ^1H and ^{13}C NMR spectra.

Cyclohexylmethyl derivatives. Several of these were known compounds, and all were prepared in the manner outlined above for the corresponding 4-methyl derivatives. The essential aspects are summarized in Table 6.

NMR spectra

^1H NMR spectra were recorded on JEOL MH-100 or JEOL PS-100 instruments for $CDCl_3$ solutions of the samples. Chemical shifts are relative to internal TMS. ^{13}C spectra of the parent cyclohexylmethyl series were, in the main, obtained on the JEOL FX-100 instrument and chemical shifts are again relative to internal TMS. They were recorded in the Fourier transform mode for solutions *c*. 0.5 M in $CDCl_3$ or CD_2Cl_2 with internal lock to the solvent. Spectral widths of 5 or 2.5 kHz were employed with 16 K/8 K data points. Digital resolution was better than ±0.05 ppm.

Low temperature ^{13}C spectra were obtained (CD_2Cl_2 solutions) on the Bruker spectrometer (67.89 MHz) of the National NMR Center, Canberra.

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