Organic Magnetic Resonance 1971, Vol. 3, pp. 679 to 687. Heyden & Son Limited. Printed in Northern Ireland

CARBON-13 CHEMICAL SHIFTS OF MONOSUBSTITUTED CYCLOHEXANES

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(*Received* 5 *July* 1971; *accepted* 23 *August* 1971)

Abstract—The carbon-13 chemical shifts of monosubstituted cyclohexane derivatives are compared with those of aliphatic compounds. The polar substituents exert a similar influence on the α-, β- and γ-carbons in both series of compounds. The δ-effect is shown to be characteristic mainly to the cyclic compounds, however. The appearance of a δ-effect is discussed as a possible consequence of electron delocalization in alicyclic molecules. A correlation of these δ-effects with inductive parameters of the substituents is presented.

INTRODUCTION

AS A RESULT of the complexity of proton spectra of monosubstituted cyclohexanes the PMR studies of these compounds have been limited mainly to the determination of methine proton resonances.[1] This somewhat traditional approach was first applied to CMR spectroscopy by Buchanan, Stothers and Ross,[2,3] who investigated conformational effects in substituted cyclohexanes, using only methine carbon shifts for this purpose. It was shown in several subsequent reports that all carbon atoms of the cyclohexyl ring are influenced by substituents[4,5,6] and useful information could be obtained from all these chemical shifts. Therefore the influence of substituents on all ring carbons must be investigated. The ^{13}C chemical shifts of the more common monosubstituted cyclohexanes are reported in Table 1 and the chemical shifts of the compounds investigated are briefly discussed in terms of the effects on various carbon atoms. For practical purposes these effects are calculated in relation to the unsubstituted cyclohexane shift, although simpler correlations between the ^{13}C shifts of polar derivatives and unsubstituted hydrocarbons result if the reference compound is formed by replacement of the heteroatoms by carbons.[6,7,8] Unfortunately, this procedure is rather clumsy since different and numerous reference compounds would have to be used. These reference compounds tend to be rather rare and are usually not available.

DISCUSSION

Resonances of the substituted carbon atoms are shifted downfields with one single exception (**36**). There is only a very rough correlation between the substituent electronegativities and measured chemical shifts, as is also the case with other alkyl derivatives.[11] In addition to inductive effects the screening of these carbon atoms is influenced by steric factors and in some cases by other specific interactions (in the case of 33 by magnetic anisotropy of the C≡N bond and in the case of heavier halogens by specific interactions, resulting in high field shifts, etc.).

Another possible way to interpret the chemical shifts of these carbon atoms is comparison with other similarly substituted compounds. Isopropyl derivatives have a similar structure and appear to be quite suitable for this purpose. The carbon chemical shifts of some isopropyl derivatives are given in Table 2 and the methine carbon chemical shifts are plotted against those of C-1 in cyclohexyl derivatives in Fig. 1.

TABLE 1. CARBON-13 CHEMICAL SHIFTS OF MONO-SUBSTITUTED CYCLOHEXANES

		^{13}C chemical shifts δ TMS[a]											
Compound No.	Substituent	Cyclohexane ring				Side chain			Substituent effects on the ring carbons				Inductive constant[1] σ^*
		C-1	C-2,6	C-3,5	C-4	CO	CH_2	CH_3	α-	β-	γ-	δ-	
(1)	—H	27·6	27·6	27·6	27·6				0	0	0	0	0·49
(2)	—CH_3	33·4	36·0	27·1	27·0			23·2	5·8	8·4	−0·5	−0·6	0
(3)	—C_2H_5	40·2	33·7	27·1	27·4		30·7	11·5	12·6	6·1	−0·5	−0·2	−0·10
(4)	—n-C_4H_9	38·4	34·1	27·1	27·3			14·5	10·8	6·5	−0·5	−0·3	−0·13
(5)	—t-C_4H_9[b]	48·8	28·1	27·7	27·1				21·2	0·5	0·1	−0·5	−0·30
(6)	—C_6H_{11}	44·3	30·8	27·4	27·4				16·7	3·2	−0·2	−0·2	−0·15
(7)	—$\Delta^{1,2}C_6H_9$[c]	46·7	32·6	27·4	27·1				19·1	5·0	−0·2	−0·5	
(8)	—$\Delta^{2,3}C_6H_9$[c]	43·5	30·8[d]	27·4	27·4				15·9	3·1	−0·2	−0·2	−0·12
(9)	—C_6H_5	45·1	34·9	27·4	26·7				17·5	7·3	−0·2	−0·9	
(10)	—o-C_6H_4OH	38·0	34·0	27·9	27·3				10·4	6·4	0·3	−0·3	
(11)	—p-C_6H_4OH	44·9	35·9	27·9	27·2				17·3	8·3	0·3	−0·4	
(12)	—p-$C_6H_4OCH_3$	44·6	35·6	27·8	27·0				17·0	8·0	0·2	−0·6	
(13)	—F[e]	90·5	33·1	23·5	26·0				62·9	5·5	−4·1	−1·6	3·06
(14)	—Cl	59·8	37·2	25·2	25·6				32·2	9·6	−2·4	−2·0	2·92
(15)	—Br	52·6	37·9	26·1	25·6				25·0	10·3	−1·5	−2·0	2·78
(16)	—I	31·8	39·8	27·4	25·5				4·2	12·2	−0·2	−2·1	2·36
(17)	—CH_2Cl	40·9	31·2	26·4	26·8		50·7		13·3	3·6	−1·2	−0·8	1·05
(18)	—OH	70·0	36·0	25·0	26·4				42·4	8·4	−2·6	−1·2	1·55
(19)	—$OOCCH_3$	72·3	32·2	24·4	26·1	169·2		21·0	44·7	4·6	−3·2	−1·5	2·54
(20)	—OCH_3	78·6	32·3	24·3	26·7			55·1	51·0	4·7	−3·3	−0·9	1·45
(21)	—$OCH_2OC_6H_{11}$	74·4	33·2	24·6	26·5		91·1		46·8	5·6	−3·0	−1·1	
(22)	—$C_2O_6C_6H_{11}$[f]	80·3	31·9	23·9	25·8	152·9			52·7	4·3	−3·7	−1·8	
(23)	—CH_2OH	41·3	30·5	26·7	27·4		68·1		13·7	2·9	−0·9	−0·2	0·56
(24)	—SH	38·5	38·5	26·8	25·9				10·9	10·9	−0·8	−1·7	1·52
(25)	—NH_2	51·1	37·7	25·8	26·5				23·5	10·1	−1·8	−1·1	0·72

TABLE—1(*continued*)

Compound No.	Substituent	^{13}C chemical shifts δ TMS[a]							Substituent effects on the ring carbons				Inductive constant[l]
		Cyclohexane ring				Side chain							
		C-1	C-2,6	C-3,5	C-4	CO	CH_2	CH_3	α-	β-	γ-	δ-	σ^*
(26)	—$NH_2 \cdot HCl$[g]	51·5	33·4	25·6	26·0				23·9	5·8	−2·0	−1·6	4·1
(27)	—$NHCONHC_6H_{11}$[h]	49·7	34·3	25·3	26·5				22·1	6·7	−2·3	−1·1	
(28)	—NO_2	84·6	31·4	24·7	25·5				57·0	3·8	−2·9	−2·1	3·9
(29)	—COOH	43·7	29·6	26·2	26·6	182·1			16·1	2·0	−1·4	−1·0	2·1
(30)	—COO^-[i]	47·2	30·9	26·9	26·9	185·4			19·6	3·3	−0·7	−0·7	0·43
(31)	—COCl	55·4	29·7	25·5	25·9	176·3			27·8	2·1	−2·1	−1·7	
(32)	—$COOCH_3$	43·4	29·6	26·0	26·4	175·3		51·0	15·8	2·0	−1·6	−1·2	
(33)	—CN	28·3	30·1	24·6	25·8	122·4[j]			0·7	2·5	−3·0	−1·8	
(34)	—$COCH_3$	51·5	29·0	26·6	26·3	209·4		27·6	23·9	1·4	−1·0	−1·3	
(35)	—$SiCl_3$	33·9	27·1	25·9	26·4				6·3	−0·5	−1·7	−1·2	
(36)	—$Sn(C_6H_{11})_3$[k]	27·1	33·3	30·0	27·9				−0·5	5·7	2·4	0·3	

[a] From external tetramethylsilane, in 70 to 80% ether solution.

[b] From Ref. 6.

[c] Cyclohexenyl group.

[d] Two unequal shifts, 30·8 ppm and 30·6 ppm.

[e] $J(CF) = 171$ Hz, $J(CCF) = 19$ Hz, $J(CCCF) = 5$ Hz.

[f] Dicyclohexyl percarbonate, saturated solution in CCl_4 with internal C_6H_{12}.

[g] Solution in methanol-ether mixture.

[h] Dicyclohexyl urea melt, measured from external C_6H_{12}.

[i] Solution in water-ether mixture.

[j] Cyano group.

[k] Tetracyclohexyl tin.

[l] From Refs. 23 and 24; for **19** and **26** the σ^* values are calculated from the respective σ_I values using the proportionality relationship $\sigma^* = 6{\cdot}2\,\sigma_I$.

TABLE 2. CARBON-13 CHEMICAL SHIFTS IN SOME ISOPROPYL DERIVATIVES

Substituent	^{13}C chemical shifts[a] δ TMS CH	^{13}C chemical shifts[a] δ TMS $-CH_3$	Substituent	^{13}C chemical shifts[a] δ TMS CH	^{13}C chemical shifts[a] δ TMS $-CH_3$
—H[b]	16·6	16·1	$-C_6H_5$	34·6	24·3
$-CH_3$[b]	25·7	24·8	$-o\text{-}C_6H_4OH$	27·8	23·5
$-C_2H_5$[b]	30·4	22·5	$-CH_2Cl$	31·7	20·3
—Cl	53·6	27·6	$-CH_2OH$	31·6	19·6
—Br	44·8	28·8	$-NH_2$	43·1	25·9
—I	20·7	31·4	$-NH_2{\cdot}HCl$	45·7	21·3
—OH	64·0	25·6	$-OCOCH_3$	67·2	22·1
$-NO_2$	79·0	20·5	—COOH	34·7	19·3

[a] Measured from internal ethyl ether methyl signal (δ = 15·6 ppm).
[b] From Ref. 25 taking $\delta_{C_6H_6}$ = 129·2 ppm.

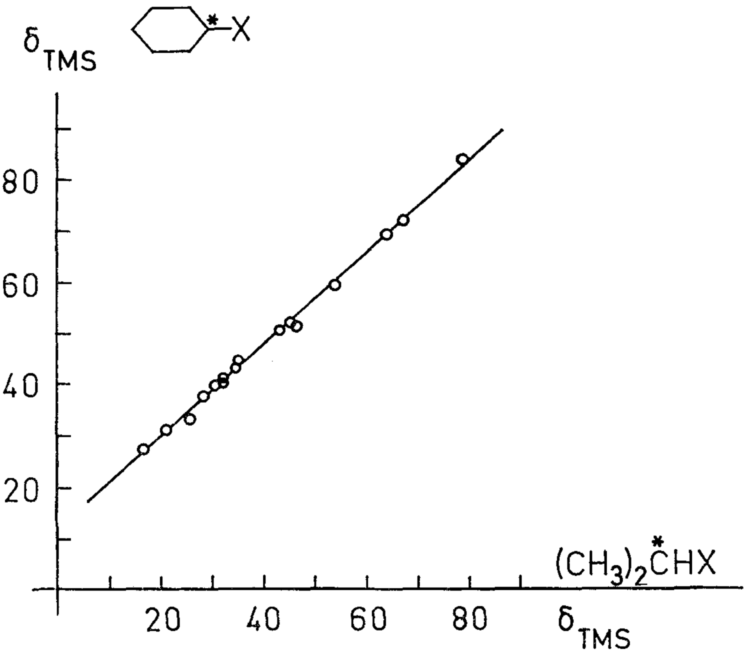

FIG. 1. Comparison of carbon ^{13}C chemical shifts of the substituted atoms in cyclohexyl and isopropyl derivatives.

A very high correlation coefficient (r = 0·998) and a standard error, equal to only 1·0 ppm are indicative of the existence of a good correlation. On the comparison of carbon chemical shifts of various other pairs of similarly substituted compounds a good correlation was found between the phenyl and vinyl derivatives[12] with a standard deviation of 3·4 ppm. In other cases standard deviations of up to 15 ppm were not unusual.

High correlation in our case shows that the influence of polar substituents is very similar in isopropyl and cyclohexyl derivatives. This is surprising, because the ^{13}C shifts in substituted cyclohexanes are statistical mean values for the axially and equatorially substituted carbons. Different substituents lead to various populations of equatorially and axially substituted carbon atoms between which the difference of shifts is about 5 to 6 ppm.[2,6,13]

The close similarity of methine carbon shifts in isopropyl and cyclohexyl derivatives may be used for the prediction of methine carbon shifts in these series of compounds.

The β- and γ-carbon shifts are also strongly influenced by steric factors. Nevertheless, there is a satisfactory correlation between the methyl shifts of isopropyl derivatives and the shifts of C-2,6 carbons in substituted cyclohexanes ($r = 0{\cdot}976$, standard error of the predicted C-2,6 chemical shifts 0·8 ppm). The most interesting fact about the C-2,6 carbon shifts is their non-equivalence in **8** and at the same time equality in **7** and **10**.*

Resonances of the carbon atoms in the γ-position from the substituent (C-3,5) are as a rule shifted to high field owing to the 1,4-interactions with the substituent. These diamagnetic shifts are for the most part caused by the axially oriented substituents. Nevertheless, it seems that equatorial substituents also lead to some diamagnetic shifts in the γ-position, at least in the case of alcohols. It can be seen from the data of Roberts *et al.*,[6] if one compares the shifts of *t*-butylcyclohexane with those of *cis*- and *trans*-4-*t*-butylcyclohexanols. Such diamagnetic shifts were found on C-6 in the case of *exo*-2-hydroxy derivatives of norbornane.[10] Of course, these shifts were much smaller than those caused on C-6 by the *endo*-2-hydroxy group.

It is usually assumed that in cyclohexane derivatives the non-bonded interactions play a greater role than in *n*-alkyl derivatives due to the forced proximity of interacting atoms in the first case. Yet if one compares the γ-effects in some *n*-amyl derivatives (Table 3) with those in cyclohexyl derivatives one must arrive at the opposite conclusion. A shift correlation exists between these two series with $r = 0{\cdot}933$ and a standard deviation of the predicted γ-effects in the $C_6H_{11}X$ series (from those in the $C_5H_{11}X$ series) equal to 0·4 ppm. In fact, the comparison of γ-effects in cyclic compounds with those in aliphatic compounds, having the substituent connected to a methine carbon, would be more correct. It follows from the chemical shifts of some isomeric octanols and chloro- and bromo-octanes[14] that in the case of two γ-interactions with the same substituent the γ-effects on carbon atoms are both only about 1·6 times smaller than in the case of 1-substituted compounds. The smaller value of γ-effects in the case of CHX-groups does not invalidate the conclusion about the generally larger γ-effects in aliphatic compounds. Yet on this basis one might expect by analogy that any δ-effect due to steric interactions is also stronger in the case of aliphatic compounds. In 1-substituted *n*-pentanes, however, the δ-carbons are practically not influenced by the substituent and have a chemical shift equal to $23{\cdot}3 \pm 0{\cdot}2$ ppm in all cases where the substituent does not contain heavy atoms from higher than the second period. In all substituted cyclohexanes a high-field δ-effect is operative with the exception of a tin derivative (**36**). In fact, there must be differences between the mechanisms, which determine the carbon chemical shifts in cyclic and aliphatic compounds, because in the calculation of ^{13}C chemical shifts on the basis of additive parameters, some extra terms are needed in the case of cyclic carbon compounds,[9,15] just as in the case of fluorine chemical shifts.[16]

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* Note added in proof—This effect may be caused by molecular asymmetry as described by J. D. Roberts *et al.*, *J. Am. Chem. Soc.* **91**, 5927 (1969).

TABLE 3. CARBON-13 CHEMICAL SHIFTS IN SOME *n*-AMYL DERIVATIVES[a]

Substituent	^{13}C chemical shifts[a] δ TMS					Substituent effects on the hydrocarbon chain	
	C-1	C-2	C-3	C-4	C-5	γ-	δ-
—H[b]	14·2	23·1	35·0	23·1	14·2	0	0
—CH_3	23·5	32·5	32·5	23·5	14·4	—2·5	0·4
—C_2H_5[b]	32·9	30·0	32·9	23·5	14·4	—2·1	0·4
—*n*-C_3H_7[b]	30·2	30·2	32·9	23·5	14·5	—2·1	0·4
—OH	62·5	33·2	29·0	23·4	14·4	—6·0	0·3
—CH_2OH	33·5	26·4	32·6	23·5	14·7	—2·4	0·4
—Cl	44·8	33·1	29·7	22·6	14·1	—5·3	—0·5
—CH_2Cl	33·1	27·0	31·6	22·9	14·1	—3·4	—0·2
—Br	33·5	33·2	30·9	22·4	14·2	—4·1	—0·7
—CH_2Br	33·6	28·6	31·7	23·2	14·3	—3·3	0·1
—I	6·8	33·6	32·9	22·0	14·1	—2·1	—1·1
—CH_2I	33·7	30·4	30·8	22·6	14·2	—4·2	—0·5
—F[c]	84·3	31·1	28·3	23·2	14·2	—6·7	0·1
—NH_2	43·9	34·3	30·0	23·2	14·4	—5·0	0·1
—COOH	34·7	25·4	32·3	23·3	14·5	—2·7	0·2
—CH_2COOH	29·8	25·6	32·5	23·5	14·5	—2·5	0·4
—$COOCH_3$	34·3	25·4	32·2	23·2	14·2	—2·8	0·2
—$OCOCH_3$	64·5	28·9	29·2	23·1	14·2	—5·8	0

[a] Measured from internal ethyl ether methyl signal (δ = 15·6 ppm).
[b] From Ref. 25 taking $\delta_{C_6H_6}$ = 129·2 ppm.
[c] J(CF) = 170 Hz, J(CCF) = 19 Hz, J(CCCF) = 5 Hz.

Upfield shift of the δ-carbon resonance depends on the orientation of the substituent as can be seen from the investigation of ^{13}C chemical shifts in alicyclic alcohols,[6] methylcyclohexanes[4] and substituted norbornanes.[10] In all these cases the equatorial substituents (in the case of norbornane derivatives the *exo*-compounds) lead to more pronounced high-field δ-effects. That is, with less pronounced steric interactions to larger δ-effects. Under these circumstances it is natural to try to connect these δ-effects with the 'through-the-bonds' effects and polar properties of substituents. It is immediately clear that the more electronegative substituents give larger δ-effects and that a correlation exists between the σ^* constants of the substituents and the δ-effects (Fig. 2) (r = 0·93, standard error of the predicted δ-effects 0·3 ppm). In the case of halogens, corrected cyclohexyl δ-effects were used, which were obtained by substracting from the measured shift differences the 'abnormal' δ-effects in *n*-amyl derivatives. In this way the halogens, between themselves, gave a good fit with the σ^* constants (r = 0·991, mean deviation of the δ-effects from a linear relationship being less than the experimental uncertainity). The inductive constants are simply connected with the δ-effects, being about 1·4 units higher than the δ-effects. Considering the differences of the populations of axial and equatorial conformers in various compounds,[17] and the different axial and equatorial δ-effects,[4,6] these correlations can be regarded as quite satisfactory. Regularities in the effects caused by the structurally related substituents also show that the more electronegative substituents lead to the largest δ-effects (*cf.* **6**, **7**, **8**, **9**; **18**, **19**, **20**; etc.). In the cases of **25** and **26** the δ-effect is larger in the protonated form as should be the case on the grounds of the enhanced electronegativity

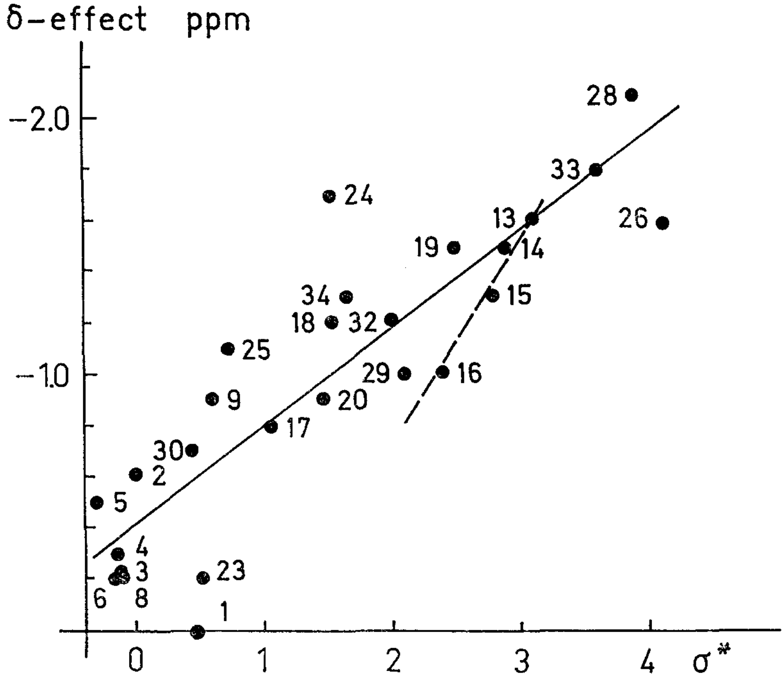

FIG. 2. Correlation between the δ-effects and inductive σ* constants in cyclohexane derivatives. Numbering is according to Table 1.

of **26**. In the cases of **29** and **30** the less pronounced electronegativity of the carboxylate anion is poorly reflected on carbon chemical shifts, just as in aliphatic compounds.[8,18] The paramagnetic δ-shift in **36** may be caused by the electronegativity of tin—it is the only substituent having the Pauling electronegativity lower than hydrogen. (The $SiCl_3$ group probably has a much higher electronegativity than Si.)

Although the correlation between the electronegativities and the δ-effects is obvious in a qualitative manner, there remains the problem as to how the electronegative substituents cause these high-field shifts. The simplest approach would be to connect the carbon chemical shifts with charges on the carbon atoms. Therefore, as a first step one must assume that more favourable conditions for charge delocalisation must exist in cyclohexyl derivatives than in aliphatic compounds. This assumption seems promising on the basis of various specific properties of alicyclic molecules, as compared with those of aliphatic compounds. The next step would be to compare the measured effects with those calculated from electron densities. For saturated molecules with many atoms the EHT calculations[19] are the most widely used. If one compares the calculated charges on carbon atoms in cyclohexane and methylcyclohexane,[19] the alternation of charges becomes evident, although the effect on δ-carbon is zero. The same alternation of charges appears in the EHT calculation of 1-chloroadamantane, as compared with that of adamantane.[20] The alternation of charges is also noted in EHT calculations of aliphatic compounds with polar substituents.[21] In the report of Pople and Gordon,[22] it is shown that alternation of charges is operative in both saturated and unsaturated compounds. Yet there remains one difficulty in connection with charge alternation in saturated molecules. That is the conclusion about the alternating charges on all atoms. According to these results the electron density effects on δ-carbons in the case of —F and —NO_2, or —OH and —CH_2OH groups should have opposite signs. This is not the case in carbon spectra. So in the light of alternating charges the high field δ-effects could be explained, if one would assume that up to the ring connection the substituents behave according to the classical concept of the inductive effect (monotonous change of charges along the chain), followed by some superimposed charge alternation in the cycle.

From the data given above it is clear that the substituents exert an influence on the screening of all cyclohexyl ring carbons. One of the most important substituents for the purpose of conformational analysis is the *t*-butyl group. It seems that it also has an influence on the δ-carbon shift, which must not be ignored in the determination of conformational equilibria and free energies from the α-carbon shifts of substituted cyclohexanes and the corresponding *cis*-*trans*-*t*-butyl-cyclohexyl derivatives. In this respect we propose an alternative method for the estimation of conformational free energies of polar groups on the basis of ^{13}C chemical shifts of monosubstituted and 1,4-disubstituted compounds, the generally well-established additivity of carbon chemical shifts, and an additional assumption about the relative insignificance of the less stable conformer of *trans*-1,4-derivatives. It is simple to show that the fraction X of the more stable conformer of a monosubstituted compound is equal to

$$x = \frac{\alpha + \delta - 2c + t}{2(t - c)}$$

where α is the ^{13}C chemical shift (from cyclohexane) of C-1 in the monosubstituted compound, δ is the ^{13}C chemical shift (from cyclohexane) of C-4 in the monosubstituted compound, t is the ^{13}C chemical shift (from cyclohexane) of C-1,4 in the 1,4-*trans* derivative and c is the ^{13}C chemical shift (from cyclohexane) of C-1,4 in the 1,4-*cis* derivative.

Applying this formula to the data for methylcyclohexane and 1,4-dimethylcyclohexanes,[4] one gets $x = 0{\cdot}96$ and $-\Delta G = 1{\cdot}9$ kcal/mole (Ref. 17 values $1{\cdot}5 + 2{\cdot}1$ kcal/mole). From the chemical shifts of cyclohexanol[2] and quinitols (measured from TMS using a mixture of isomers; *trans* isomer C-1,4 = 70·3 ppm, C-2,3,5,6 = 37·2 ppm; *cis* isomer C-1,4 = 68·3 ppm, C-2,3,5,6 = 31·3 ppm), one obtains $x = 0{\cdot}63$ and $-\Delta G = 0{\cdot}31$ kcal/mole (literature values $0{\cdot}25 + 1{\cdot}25$ kcal/mole). In this case the diaxial form of *trans*-quinitol may probably be of some significance for the chemical shifts of this compound. On the basis of trends observed in the case of the methyl groups,[4] it may be concluded that the true $-\Delta G$ value in this case might in fact be somewhat higher.

From the data for the 1,4-di-*t*-butylcyclohexanes and *t*-butylcyclohexane[6] one obtains $x = 1{\cdot}02$, showing that the *t*-butyl group in *t*-butylcyclohexane is purely equatorial.

The dependence of the chemical shifts of all carbon atoms in the cyclohexane ring on the molecular conformation and the ease of the determination of all these ^{13}C shifts opens up new possibilities for the investigation of conformational effects in cyclic compounds. It also shows that the 'through-the-bonds' inductive effects of polar substituents may be of a somewhat different nature in aliphatic and alicyclic compounds.

EXPERIMENTAL

The details of experimental conditions are given in earlier reports.[9,10] Some diethyl ether (20 to 30 per cent) was added to the samples as solvent and internal reference (shift of the methyl group $\delta = 15{\cdot}6$ ppm). The measured chemical shifts (Tables 1, 2 and 3) are not substantially dependent on the sample dilution, as was determined by the dilution of cyclohexane and cyclohexanol solutions in ethyl ether from 90 to 10 per cent concentration. The ether methyl group carbon shielding is not affected by the solutes either, as was shown by comparison of the chemical shifts of methylcyclohexane, cyclohexanol and cyclohexyl chloride in a mixture of cyclohexane and ethyl ether. The chemical shifts are reported from tetramethyl silane ($\delta_{CS_2} = 193{\cdot}1$ ppm) and are reproducible to ± 0·1 ppm. Most substances were commercial products. Some of them (**13, 15, 16, 19, 20, 24, 26, 30, 31, 32, 33, 34** in Table 1) were prepared by standard methods from the appropriate derivatives of cyclohexane.

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