# Low-Temperature $^{13}$C Magnetic Resonance. 9.[1] Steric Effects for Methyl Chemical Shift Tensors in Methylcyclohexanes

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**Abstract:** The solid-state low-temperature $^{13}$C NMR spectra of 1-(methyl-$^{13}$C)-1-methylcyclohexane, *cis*-1-(methyl-$^{13}$C)-3,5-dimethylcyclohexane, and *trans*-1-(methyl-$^{13}$C)-3,5-dimethylcyclohexane have been measured and the principal values of the $^{13}$C chemical shift tensors are reported for the labeled methyl carbons. The orientation of the principal axes of the chemical shift tensor has been estimated using *ab initio* calculations of the tensors. The calculated shift tensors for the axial and equatorial isomers of methylcyclohexane, which are also presented in this paper, are almost identical to those from the 3,5-dimethyl-substituted compound. This indicates that chemical shift tensors for a methyl group are primarily determined by local electronic and steric factors. Changes in steric effects and $\beta$-substituent effects between axial and equatorial methyls on the cyclohexane ring are discussed in terms of their effect upon chemical shift tensors in these paraffin hydrocarbons.

## Introduction

Carbon-13 NMR at cryogenic temperatures is a convenient technique to measure the principal values of the $^{13}$C chemical shift tensors in molecules that are liquid or gases at ambient temperatures. In this work low-temperature NMR techniques have been applied to the study of steric interactions in the $^{13}$C chemical shift tensors found in methylcyclohexanes. The systematic study of many structural features of $^{13}$C chemical shifts in hydrocarbons has been reported in earlier papers in this series[1] and elsewhere.[2,3] Further, the steric interactions in methylcyclohexanes have been the subject of a large number of NMR publications,[4–9] but these studies have been restricted to a consideration of isotropic chemical shifts. It is well-documented that a full shift tensor, or in its absence the tensor's principal values, can provide a better understanding of the relationship between chemical shielding and electronic structure.[10] This paper presents the principal values of the $^{13}$C shift tensors of methyl carbons in 1-(methyl-$^{13}$C)-1-methylcyclohexane (**I**), *trans*-1-(methyl-$^{13}$C)-3,5-dimethylcyclohexane (**II**), and *cis*-1-(methyl-$^{13}$C)-3,5-dimethylcyclohexane (**III**). Specific isotopic labeling of the methyl carbons was necessary to avoid overlapping bands from the remaining carbons. The experimental principal values were assigned to specific directions in the molecular frame using *ab initio* GIAO calculations of the $^{13}$C shift tensors.[11,12] For comparison, theoretical calculations of the methyl shift tensors were also done for both the axial (IV) and equatorial (V) conformers of methylcyclohexane because of their importance in understanding systematic changes in the shift tensors due to conformational variations.

## Theoretical Calculations

All chemical shift calculations for each of the methylcyclohexanes were performed using optimized geometries. These geometries were obtained with the Gaussian program[13] and the D95 basis set[14] at the Hartree–Fock level of approximation. Calculations of the chemical shifts were done using the GIAO method[11] implemented in the TEXAS program[12] with the D95** basis set.[14] The D95** basis set includes polarization functions for both carbon and hydrogen atoms and has proven to be reliable for this type of calculation. The calculated shielding values were transformed to the TMS scale by reversing sign and subtracting the absolute shielding of 199 ppm, calculated for methane with the D95** basis set. While shortcomings in the referencing method are acknowledged, an excellent correlation between the calculated and experimental chemical shift values is obtained.

Calculations of steric forces, associated with the local van der Waals repulsions, were performed using the Gaussian optimized geometry and the MM2 parameters[6] for each of the methylcyclohexanes. The Gaussian optimized geometries were modified by reducing the carbon–hydrogen bond lengths by a factor of 0.915 to compensate in part for the manner in which the center of charge of the hydrogen atom is selected in the MM2 method.[6] Tables giving the Gaussian geometry used in the chemical shift tensor calculations of each molecule are included as supporting information. Figure 1 schematically illustrates the general orientation of the methyl carbons in the five compounds for which calculations were performed.

## Experimental Section

The experimental $^{13}$C cross-polarization spectra were obtained on a home-built spectrometer operating at 1.9 T with frequencies of 80.0

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[†] Professor W. James Horton, after a productive and illustrative academic career, passed away at 81 years of age on December 17, 1994. We will miss greatly his enthusiasm for science and his unique contributions that continued until recent months in our laboratory. In keeping with this admiration we dedicate this work to his memory.

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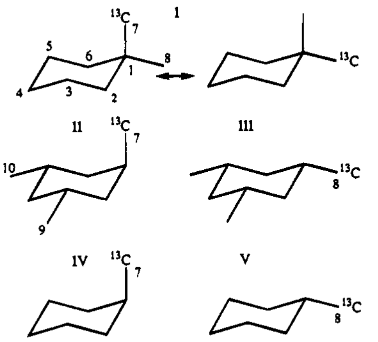
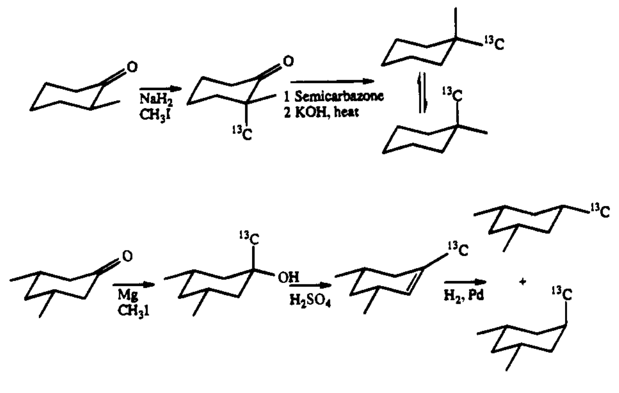


**Figure 1.** Structures showing each of the labeled methyl carbons for which calculations were performed. The numbering of the carbon atoms corresponds to that used in Table 1. For consistency a labeled axial methyl carbon is numbered C7 and a labeled equatorial methyl carbon is number C8.

## Scheme 1



MHz for $^{1}H$ and 20.12 MHz for $^{13}C$. The home-built high-power double-tuned probe and the cryogenic apparatus used respectively to obtain spectra and to maintain the samples at a temperature of 20–25 K have been described previously.[15,16] To minimize probe ring-down, a spin–echo sequence is used to delay the acquisition of the FID data. The experimental spectra were referenced to an external sample of TMS, as explained elsewhere.[16] A recycle delay of 10 s between successive acquisitions is used with sufficient transients to provide adequate signal to noise. The experimental spectra were fit using the POWDER software,[17] and the reported principal values have an estimated error of approximately 2–3 ppm. To aid in fitting spectra with more than one $^{13}C$ resonance band, the overall intensity of the band was locked to the relative intensities of the corresponding peaks in a liquid spectrum. The liquid isotropic shifts for the axial and equatorial methyls of the $^{13}C$-labeled 1,1-dimethylcyclohexane were measured at −85 °C in deuterated methylene chloride with a Varian XL-400.

**Materials and Synthesis.** The $^{13}C$-labeled 1,1-dimethylcyclohexane and 1,3,5-trimethylcyclohexanes synthesized for this study included methyl groups which have either axial or equatorial conformations relative to the cyclohexane ring. They were prepared in accordance with Scheme 1 as follows:

**2-(Methyl-$^{13}$C)-2-methylcyclohexanone.**[18] A 4.25-mL (3.93 g) sample of 2-methylcyclohexanone, dissolved in 25 mL of ether, was added dropwise to a suspension of 2.78 g of $NaNH_2$ in 50 mL of dry ether (held below −6 °C). The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was then refluxed for 2 h, and then cooled, and 5.0 g of methyl iodide (99% $^{13}C$, Cambridge Isotope Labs) in ether was rapidly added. The mixture was then refluxed an additional 2 h and allowed to cool. The resulting mixture was added to 70 mL of ice water, acidified with 20 mL of 6 N HCl (pH ~2), and extracted with ether. The ether solution was washed twice with $Na_2S_2O_3$ solution and once with water and then dried. Distillation gave 3.96 g (88.9%) of yellow liquid boiling at 90–97 °C (78 mm). Purity was checked by $^{13}C$ NMR which showed the presence of the $^{13}C$-labeled 2,2-dimethylcyclohexanone along with small amounts of *cis*-2,6-dimethylcyclohexanone and 2,2,6-trimethylcyclohexanone.

**2-(Methyl-$^{13}$C)-2-methylcyclohexanone Semicarbazone.** The above 3.96 g of labeled ketone mixture was converted to the semicarbazone[19] (73.3%). Recrystallization from a 1:1 ethanol–water solution gave 3.07 g (53.6%) of snow-white crystals melting at 190–193.5 °C, lit.[20] mp 194–195 °C. Purity was confirmed by $^{13}C$ NMR.

**1-(Methyl-$^{13}$C)-1-methylcyclohexane (99% $^{13}$C).**[21] The above 3.07 g of semicarbazone was added to 3.09 g of KOH that had been dissolved in 50 mL of diethylene glycol by heating (~100 °C). The temperature was slowly raised over 15 h until reflux began. The solution was refluxed for 7.5 h and allowed to cool. The product was distilled, and the fraction boiling between 32 and 110 °C was collected and extracted once with pentane. The pentane solution was washed with 1 N HCl, 8% $NaHCO_3$, and saturated NaCl. Distillation of the fluorescent green liquid gave 1.17 g (62.0%) of a clear liquid. Purity and identity were confirmed by $^{13}C$ NMR.

***cis*-3,5-Dimethylcyclohexanone.** Mixed isomers of 3,5-dimethylcyclohexanol were oxidized to the corresponding ketone isomers with $CrO_3$ (88.1%), bp 73–78 °C (23 mmHg).[22] The mixed ketone isomers were converted to the (*p*-nitrophenyl)hydrazone and recrystallized (95% ethanol) to give the *cis*-hydrazone isomer (61.7% from the mixed ketone), orange crystals mp 170–173 °C. The addition of 6.73 g of the above hydrazone to 295 g of levulinic acid and 34 mL of water was followed by heating for 20 min in a boiling water bath, cooling with ice water, addition of 375 mL of water, and extraction with ether. The ether solution was washed three times with 10% $Na_2CO_3$ and once with saturated NaCl and then dried. Distillation gave 2.85 g (87.6%) of light yellow liquid, bp 60–66 °C (13 mm). Purity was confirmed by $^{13}C$ NMR.

**1-(Methyl-$^{13}$C)-3,5-dimethylcyclohexene.** The Grignard reagent was prepared by adding 5.0 g of $^{13}CH_3I$ (99.2% $^{13}C$, Isotec Inc.) to 0.75 g of Mg turnings in 5 mL of dry ether chilled in an ice bath followed by stirring at room temperature for 15 min. The resulting solution was chilled and 4.55 g of the above *cis*-3,5-dimethylcyclohexanone in 20 mL of dry ether was added dropwise. The solution was allowed to stir over 2 days and then chilled and an $NH_4Cl$ solution (64.5 g of $NH_4Cl$ in 175 mL of water) was added. The aqueous portion was extracted with ether and the combined ether solution was washed with water and saturated NaCl and the ether removed by distillation. The alcohol was added to 15 mL of 10% $H_2SO_4$ and 20 mL of water, refluxed 7.5 h, and allowed to cool. The resulting solution was added to 50 mL of water and extracted with ether. The ether solution was washed with 8% $Na_2CO_3$ and water and then dried. Distillation gave 2.27 g (55.9%) of clear product, bp 133–136 °C, at atmospheric pressure. The purity was confirmed by $^{13}C$ NMR.

**1-(Methyl-$^{13}$C)-3,5-dimethylcyclohexane mixture (99% $^{13}$C).** The above 2.27 g of 1-(methyl-$^{13}C$)-3,5-dimethylcyclohexene was hydrogenated over 0.5 g of 5% $Pd^0$ on charcoal in 65 mL of dry pentane by shaking under hydrogen atmosphere. Distillation gave 1.43 g (62.0%) of clear liquid, bp 125–127 °C. Purity and relative amounts of isomers were checked by $^{13}C$ NMR.

## Results and Discussion

The experimental powder spectra, the "best fit" composite simulation, and the unbroadened individual $^{13}C$ shift tensors for the labeled 1-(methyl-$^{13}C$)-1-methylcyclohexane (**I**) are given in Figure 2, and the corresponding data for *trans*-1-(methyl-$^{13}C$)-3,5-dimethylcyclohexane (**II**) and *cis*-1-(methyl-$^{13}C$)-3,5-dimethylcyclohexane (**III**) are shown in Figure 3. In fitting the principal values of $^{13}C$ chemical shift tensors, the determi-

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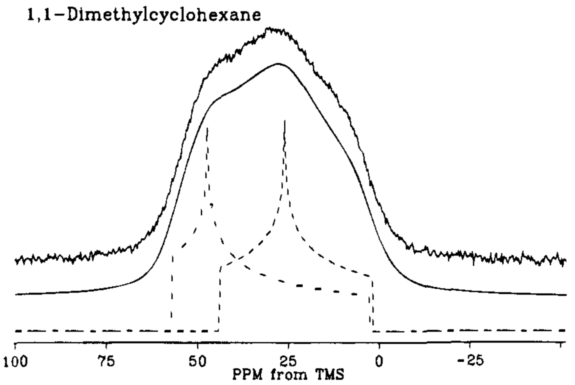

**Figure 2.** Carbon-13 powder spectrum of the labeled 1,1-dimethylcyclohexane showing the experimental spectrum, the "best fit" simulation of the experimental spectrum, and the two unbroadened individual chemical shift patterns determined from the fit (top to bottom, respectively). The relative intensity of the two patterns is approximately 1 to 1.

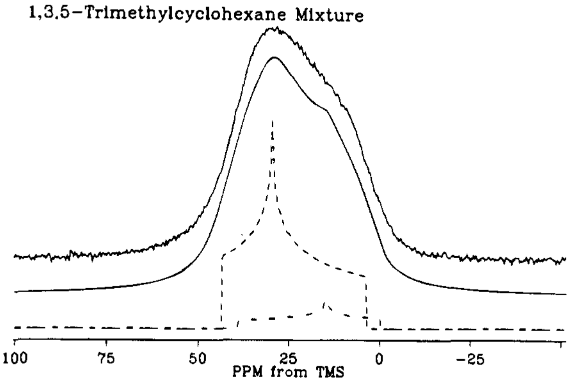

**Figure 3.** Carbon-13 powder spectrum of the mixture of *cis*- and *trans*-1,3,5-trimethylcyclohexane isomers showing the experimental spectrum, the best fit simulation of the experimental spectrum, and the two unbroadened individual chemical shift patterns determined from the fit (top to bottom, respectively). The relative intensity of the two patterns is approximately 1 to 7.

nation of isolated or well-separated components is relatively accurate whenever the principal values differ by 5 ppm or more. When two components fall within 5 ppm of one another, they introduce statistical correlations between the two proximate shift values which may increase the spectral broadening functions used in simulating the powder patterns. For example, the upfield $\delta_{33}$ components for the two methyls in the spectrum of **I** are within experimental error of each other, and they exhibit a very high correlation factor (i.e., 0.97) even though they arise from two different conformers in the mixture. In the spectra of **II** and **III**, the lack of intensity (12.8%) from the *trans* conformer also reduces the accuracy of the *trans* shift data. However, the combined spectral simulation with two tensors significantly improves the agreement between the simulated and experimental data.

In Table 1 the experimentally determined chemical shift principal values are presented along with their theoretical estimates and their isotropic values measured in liquids. The isotropic values were taken from the literature[23,24] except for compound **I** which was measured here at −85 °C. At this temperature the conformations of the two methyl groups are frozen, and the NMR signals no longer coalesce from molecular motion into a single average peak.

**Table 1.** Principal Values of Methyl $^{13}C$ Chemical Shift Tensors in Methyl-Substituted Cyclohexanes[a]

| compd | $\delta_{C-H}$ | $\delta_{\perp}$ | $\delta_{C-C}$ | $\alpha^b$ | $\delta_{ave}$ | $\delta_{liq}$ |
|---|---|---|---|---|---|---|
| Axial | | | | | | |
| **I** | 44 (43) | 26 (26) | 2 (1) | 5.7° | 24 (23) | 24.0[c] |
| **II** | 39 (39) | 15 (16) | 0 (0) | 12.3° | 18 (18) | 19.5[d] |
| **IV** | (38) | (13) | (0) | 12.3° | (17) | 19.0[e] |
| Equatorial | | | | | | |
| **I** | 48 (44) | 57 (50) | 3 (1) | 0.7° | 36 (32) | 33.6[c] |
| **III** | 44 (37) | 30 (30) | 4 (−1) | 7.4° | 26 (22) | 23.4[d] |
| **V** | (38) | (30) | (-1) | 7.0° | (22) | 23.3[d] |
| Isobutane[f] | | | | | | |
| | 42 (36) | 33 (29) | 6 (-1) | 7.3° | 27 (21) | 24.3 |
| Neopentane[f] | | | | | | |
| | 50 (45) | 50 (45) | 5 (1) | 0° | 35 (30) | 33.0 |

[a] Components are labeled according to their orientation in the molecular frame. All values are reported in ppm. Experimental values were referenced to external TMS and calculated values were referenced to methane as explained in the text. Labeling of the principal components follows from the calculations (see Figure 5). [b] A positive value for the calculated angle between $\delta_{C-C}$ and the methyl bond axis designates a rotation of this shift direction away from the proton in the CCH symmetry plane. [c] Measured in $CD_2Cl_2$ at −85 °C. The measured room temperature value of 29.0 ppm is the average value for both conformers. [d] Literature values are taken from ref 23. [e] Calculated from the value for methylcyclohexane using the substituent parameter of ref 24. [f] Values from ref 10.

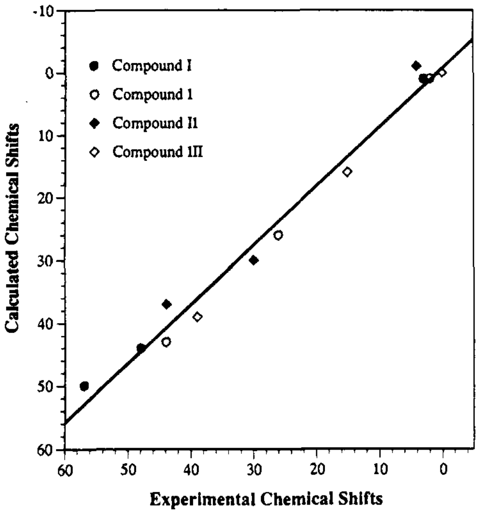

**Figure 4.** Calculated versus experimental chemical shifts for methyl carbons in 1-(methyl-$^{13}C$)-1-dimethylcyclohexane (**I**), *cis*-1(methyl-$^{13}C$)-3,5-dimethylcyclohexane (**II**), and *trans*-1-(methyl-$^{13}C$)-3,5-trimethylcyclohexane (**III**) show an excellent linear correlation between theory and experiment. Values for axial methyl carbons are represented by open symbols while values for equatorial methyl carbons are represented by solid symbols. All values are in ppm, referenced as explained in the text.

In Figure 4 we present a correlation plot between the experimental principal shift components measured here and the corresponding calculated values using optimized geometries as described in the Theoretical Calculations section. This correlation exhibits a rms in the scatter equal to 2.7 ppm and a correlation slope of 0.94 with the reference intercept equal to 0.6 ppm. The success of the correlation is reduced somewhat (i.e., rms = 3.27 ppm, slope = 0.85, and intercept = 5.1 ppm) when idealized geometries, based on standard bond distances and tetrahedral angles, are used in the shielding calculations.

The 2−3-ppm discrepancies observed between the liquid isotropic values and the averaged principal shifts roughly reflect

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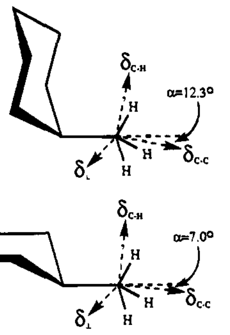

**Figure 5.** Orientation and labeling of the methyl $^{13}$C chemical shift tensor is shown for the axial and equatorial conformers of methylcyclohexane. Calculations place $\delta_{C-C}$ and $\delta_{C-H}$ in the molecular symmetry plane which includes the methyl carbons and one of the methyl protons (the CCH plane of the methyl group) and $\delta_\perp$ perpendicular to the molecular symmetry plane. The $\delta_{C-C}$ axis is always in a direction that is nearly along the methyl bond axis.

the precision of the powder methods and/or the inadequacies introduced by our external referencing procedures. These differences are in line with similar deviations observed in previous studies of the chemical shift tensors of $^{13}CH_3$ groups.[10] The improved correlation obtained in recent years between experimental and calculated principal values increases confidence in using the quantum mechanical calculations to assign the principal values and to determine the direction in the molecular frame of the principal shift components, information which is generally unavailable from experiments on powder samples without using dipolar spectroscopy.[25]

The orientation and labeling of the principal axes of the $^{13}$C chemical shift tensors is displayed in Figure 5. The axis labels, shown in Figure 5, are based on the calculated orientations of the principal axes relative to the local symmetry elements of the methyl carbon. Each of the molecules has a symmetry CCH plane that includes the C−C bond containing the $^{13}$C-labeled methyl carbon and one of the methyl protons. Therefore, from symmetry considerations one of the principal shift components has to be perpendicular to this plane. This component is labeled $\delta_\perp$. The other two components lie in the symmetry plane and are designated as $\delta_{C-C}$ and $\delta_{C-H}$. These terms reflect the corresponding bonds closest to the direction of these components. The calculations provide the information necessary to orient these components in the symmetry plane. The orientational angle α describes the rotation within the symmetry plane of the $\delta_{C-C}$ component from the methyl C−C bond direction. As shown in Figure 5, a positive value for α corresponds to a rotation away from the methyl proton in the CCH symmetry plane. In Table 1 the calculated and experimental principal components have been arranged according to this convention. The in-plane components lie very near the methyl bond axis[10] with α angles ranging from 0.7° to 12.3°, as indicated in Table 1.

It is apparent from Table 1 that $\delta_{C-C}$, which lies closest to the $C_3$ axis of the methyl group, is relatively insensitive to proximate molecular groups. However, there are significant differences in both $\delta_\perp$ and $\delta_{C-H}$ including an exchange in their relative order. This scrambling occurs in compound **I**, where the highest shift component corresponds to $\delta_\perp$ for the equatorial methyl and to $\delta_{C-H}$ for the axial methyl. The value $\delta_{C-H}$ has the highest shift value for the other methyls in the remaining two compounds. By far the largest variations in the methyl shielding are observed in the $\delta_\perp$ principal component which is associated with the direction perpendicular to the CCH symmetry plane. These large changes in $\delta_\perp$ almost totally dominate the variations found in the isotropic methyl shifts.

Since the 3,5-dimethyl equatorial substitutions in compounds **II** and **III** lock the labeled methyl into either the axial or equatorial conformation, calculations for compounds II and **III** were compared with calculations of compounds **IV** and **V** to determine the effect of the equatorial 3,5-dimethyl substitution on the indicated tensors. While experimental data are unavailable for compounds **IV** and **V**, the calculations indicate that the equatorial 3,5-dimethyl groups have little effect on the $^{13}$C chemical shift tensors of either axial or equatorial methyl groups at $C_1$ since the calculated principal values for compound **IV** and **V** are almost identical to those calculated for **II** and **III**, respectively. Further evidence that the equatorial 3,5-dimethyl substitution does not affect significantly the $^{13}$C chemical shift tensors of methyl groups at $C_1$ is reflected in the nearly identical angle, α, of $\delta_{C-C}$ with the methyl bond axis for the respective axial or equatorial methyl groups of compounds **II**−**V**. It is therefore concluded that the differences observed between the $^{13}CH_3$ tensors in **I**−**III** originate from β-substituent effects and short-range γ-steric effects.

The β-substituent effect may be estimated by comparing the tensors of compounds **I**−**III** with those obtained for isobutane and neopentane[10] which also have a similar CCH symmetry plane through their methyl groups. Thus, these literature values for isobutane and neopentane are presented also in Table 1 for the convenience of the reader. The changes in the principal values of the $^{13}$C methyl shielding tensor between isobutane and neopentane are 8, 17, and −1 ppm, for $\delta_{C-H}$, $\delta_\perp$, and $\delta_{C-C}$, to be compared with the corresponding shift changes of 5, 11, and 2 ppm for the axial methyl shifts and 4, 27, and −1 ppm for equatorial methyl shifts of methylcyclohexanes. For both axial and equatorial methyl groups the $\delta_{C-C}$ component is relatively insensitive to the substituent effect as seen also for isobutane and neopentane. The $\delta_{C-H}$ component of axial and equatorial methyls shows a larger sensitivity than does the $\delta_{C-C}$ component, but these values are less than the corresponding effect for $\delta_{C-H}$ in isobutane and neopentane. In all cases the $\delta_\perp$ component is the most sensitive for reflecting the steric force vectors that lie in the CCH symmetry plane of the various methyl groups and/or the angular dependence of the β-substituent effect.[26,27]

Since the principal values and the α-angle associated with $\delta_{C-C}$ in compound **III** are similar to those in isobutane,[10] it may be concluded that the equatorial methyl of compound **III** experiences an environment not greatly different from that in isobutane. The agreement for the equatorial methyl of compound **I** with the methyls in neopentane[10] is similar, though not quite as good as observed in the isobutane analogy. Angular distortions, arising presumably from steric interactions between axial methyls and the proximate ring protons located in the axial positions at C-3 and C-5, introduce significant perturbations in the methyl shift tensors.

The steric effect can be estimated by comparing the shift data between axial and equatorial methyl groups in otherwise similar molecular environments. The differences between principal values, $\delta_{C\text{-}H}$, $\delta_\perp$, and $\delta_{C\text{-}C}$, of the shift tensors for an equatorial methyl carbon and an axial methyl carbon in compound **I** are −4, −31, and −1, and those between compounds **II** and **III** are −5, −15, and −4. Again, the largest differences are found in the $\delta_\perp$ principal values.

Figure 6 reflects the proton−proton steric interactions affecting the methyl groups of compound **I**. The upper views

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[25] Zilm, K. W.; Grant, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2913.

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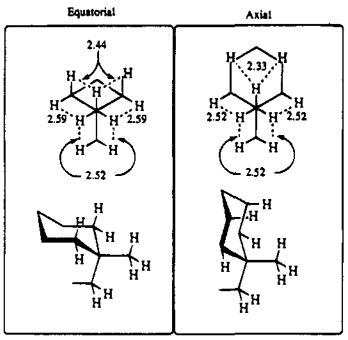

**Figure 6.** Symmetry of the non-bonded proton–proton interactions for both methyl groups of compound **I**. The upper view for each methyl shows the molecule looking down the methyl carbon–ring carbon bond toward the cyclohexane ring and the lower view is a perspective view to show the different protons involved in the steric interactions. In the upper views the proton–proton interactions are shown by dashed lines and the proton–proton distances from the optimized geometry are given. All distances are in Å.

are projections toward the cyclohexane ring along the methyl C–C bond, while the lower drawings give a perspective view of the proton–proton interactions to avoid possible confusion in the upper drawings. The distances between proximate protons are given also in this figure. It is readily apparent that the shorter 2.33 Å non-bonded proton–proton interactions observed for one of the axial methyl hydrogens introduce more energetic van der Waals repulsions than do the corresponding non-bonded interactions in an equatorial methyl. Similar structural features are seen in the non-bonded proton–proton interactions of compounds **II** and **III**. The angle α, which measures the deviation of the $\delta_{C-C}$ direction from that of the methyl C–C bond direction, exhibits a smaller value in the equatorial methyl of compound **I** versus the axial orientation. This reduction in α is directly attributable to smaller non-bonded proton–proton interactions, and therefore the value of α reflects non-bonded steric interactions in these systems.

Li and Chesnut[6,7] have reported a correlation between the isotropic $^{13}C$ chemical shift of methylcyclohexanes and the van der Waals interactions involving the carbon nucleus and the remaining atoms in the molecule, some of which are separated from the carbon nucleus by three or more bonds. Since variations in the isotropic component are primarily due to changes in the $\delta_\perp$ component, calculations of the force due to the local van der Waals interactions were performed to assess the importance of non-bonded interactions on principal shift values. Previous results[10,28,29] have shown that steric shifts are observed in those tensor components whose directions are perpendicular to the plane in which the interaction forces operate. Since all of the methyls in this study have a symmetry plane through the C–C methyl bond with one of the tensor components directed nearly along this methyl bond axis, a common axis system may be used to estimate the van der Waals forces. In this axis system the methyl bond direction designates the *x*-axis, the direction in the molecular symmetry plane perpendicular to the methyl bond designates the *y*-axis, and the *z*-axis is mutually perpendicular to these first two directions and to the molecular symmetry plane. The results for compounds **I**–**III** are tabulated in Table 2 and the forces along the *x*- and *y*-axes for the methyls of compounds **I**–**III** are depicted in Figure 7.

**Table 2.** Local van der Waals Steric Energies and Forces for Methyl Carbons in Methyl-Substituted Cyclohexanes[a]

| compd | $E_{vdw}$ | $F(x)$ | $F(y)$ | $F(z)$ |
|---|---|---|---|---|
| axial | | | | |
| I | 0.564 | 3.99 | 0.11 | 0.0 |
| II | 0.140 | 2.33 | 1.47 | 0.0 |
| equatorial | | | | |
| I | 0.898 | 4.72 | 0.48 | 0.0 |
| III | 0.308 | 2.59 | 1.44 | 0.0 |

[a] Values were calculated using the equation and values for the van der Waals energy given in ref 6. The values for $E_{vdw}$ are in kcal mol$^{-1}$ (see refs 6 and 7) and the values for the forces are in kcal mol$^{-1}$ Å$^{-1}$.

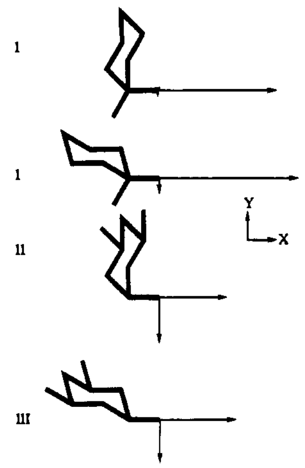

**Figure 7.** Forces, derived from local van der Waals energies, on the methyl carbons in 1,1-dimethylcyclohexane, on the equatorial methyl carbon in *cis*-1,3,5-trimethylcyclohexane, and on the axial methyl carbon in *trans*-1,3,5-trimethylcyclohexane. The forces along the *x*-direction would tend to increase the C–C bond length and the forces along the *y*-direction would tend to flatten the molecule into a planar configuration at the $C_1$ ring position. Force vectors are drawn to scale.

In calculating the steric van der Waals energies, Li and Chesnut[6] used a modified Hill equation in the MM2 method of the following form

$$E_{vdw} = \epsilon[2.9 \times 10^5 \exp(-12.5r/r_0) - 2.25(r_0/r)^6] \quad (1)$$

in which $\epsilon$ is a measure of the energy minimum and $r/r_0$ is a normalized distance parameter. A $r_0$ value of 3.80 Å and an $\epsilon$ value of 0.044 kcal mol$^{-1}$ were used for calculations involving sp$^3$ carbon–carbon interactions, and for sp$^3$ carbon–hydrogen interactions values of 3.34 Å and 0.046 kcal mol$^{-1}$ were used for $r_0$ and $\epsilon$, respectively. The interaction force along the different *x*-, *y*-, and *z*-directions in the specified axis system may be found from the partial derivative of the potential energy functions relative to these directions. The interaction force in the *x*-direction, after appropriate rearrangement of the terms, is given by

$$F(x) = (\epsilon x/r^2)[13.5(r_0/r) - (3.625 \times 10^6)(r/r_0)\exp(-12.5r/r_0)] \quad (2)$$

with corresponding expressions for the *y*- and *z*-directions. The energy and force values from eqs 1 or 2 are given in Table 2 for the atoms included in the calculation.

As exhibited in Figure 7, the force along the *x*-axis tends to increase the C–C bond length while the force along the *y*-axis tends to flatten the molecule into a planar configuration at the $C_1$ ring position. The force along the *z*-axis is zero from molecular symmetry. The forces along the *y*-axis exhibit no

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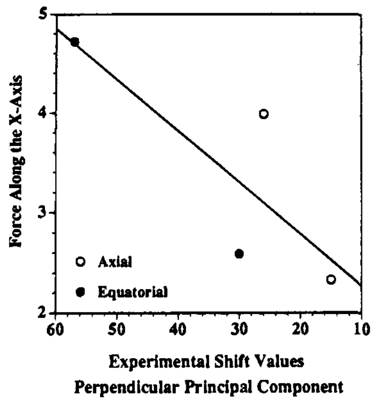

**Figure 8.** Scatter in the data for the van der Waals force along the methyl bond and the experimental $\delta_\perp$ principal value. Chemical shift components in ppm from TMS; forces in kcal mol$^{-1}$ Å$^{-1}$.

consistent pattern due in part to the interaction of the second proximate methyl group in compound **I**. From Figure 6 it is apparent that the force between the two methyl groups in compound **I** should have non-zero values along both the $x$- and $y$-axes for each methyl carbon. In compounds **II**–**IV** the interaction between the methyl carbon and the proton bonded to the same cyclohexane ring carbon at $C_1$ is not included in the Li and Chesnut calculation which excludes interaction between two nuclei separated by only two bonds. It is also observed that the force along the $x$-axis shows variations which support the previous analysis[6,7] wherein the shielding for an axial methyl group of a methylcyclohexane arises from variations in the p-orbitals on the methyl carbon. These changes may be ascribed to attractive and repulsive variations in the van der Waals energy. Figure 8 shows considerable scatter in the data for the force along the $x$-axis and the associated $\delta_\perp$ principal values. It is apparent from this scatter that the van der Waals steric model, while qualitatively correct, is unable to correlate quantitatively the conformational effects on the chemical shift tensor with the same degree of accuracy as the GIAO method calculations using the D95** basis set. This also may be an indication of the importance of the angular dependence of the $\beta$-substituent effect[26,27] that may only reflect an indirect dependence on the steric model. The GIAO quantum mechanical calculations with optimized distances and angles appear to correlate fully the features found in the experimental tensor components.

## Conclusions

There is an excellent correlation between the changes observed between the experimentally measured chemical shift tensors of axial and equatorial methyl groups of methylcyclohexanes and the corresponding *ab initio* calculations using the GIAO method with a basis set which includes polarization functions for both carbon and hydrogen atoms. The 3,5-dimethyl substitution that is required to lock the methyl group at $C_1$ of the ring with an axial or equatorial conformation in 1,3,5-trimethylcyclohexane has been shown to have a negligible effect on the tensor of the axial and equatorial methyl carbon bonded to the ring at $C_1$ thereby allowing these two trimethylcyclohexanes to be used as model systems for discussing axial and equatorial methyl $^{13}C$ shift tensors. The present GIAO results along with the qualitative steric arguments used by Chesnut and Li combine to explain the conformational variations noted in these hydrocarbon shifts. While the correlation between the van der Waals energies and steric shifts has been verified by *ab initio* shielding calculations in other systems,[30] the simplest isotropic argument, commonly used in the early literature[4] of contraction of the p-electron orbitals with the corresponding increases in values for $\langle 1/r^3 \rangle$, is inadequate to predict the $\beta$-substituent effects on the principal values of the shift tensor. These results provide further evidence of the importance of analyzing individual tensor components instead of averaged isotropic values. The highly anisotropic shifts associated with $\beta$-substituents and its angular dependence[26,27] clearly indicate that more intricate mechanisms are in operation. These features are captured to a significant extent in the full GIAO treatment used to predict the variations in the $^{13}C$ chemical shift tensors in this work.

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**Supporting Information Available:** Tables containing the Gaussian optimized geometry used to calculate the chemical shift tensors for each of the reported methylcyclohexanes (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Inernet; see any current masthead page for ordering information and Internet access instructions.

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