for 7% of the signal. At this time the tube was opened and fractionated in the vacuum line. The white crystals that passed through −35° and stopped at −60° had an mp of 80° and a vapor pressure of 25 mm at 25° and 8 mm at 0° (estimated bp 120°). The mass spectrum showed strong peaks at m/e 356 and 358 corresponding

to the expected isotopes of $(CF_3)_2CBrI^+$, m/e 229 and 231 corresponding to $(CF_3)_2CBr^+$, and weaker peaks at 337 and 339 corresponding to $C_3F_5BrI^+$. Infrared absorption in the gas phase is very strong at 1258 and 1222 cm^{-1} and strong at 926, 892, 822, 735, and 695 cm^{-1}.

Carbon-13 Magnetic Resonance. XXI.[1] Steric Interactions in the Methylcyclohexanes

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Abstract: Carbon-13 magnetic resonance (cmr) data have been obtained for the four trimethylcyclohexanes having cis-1,2-substituted methyl groups. Assignments of resonance lines are made using previously developed parameters and empirical arguments. A factor analysis was undertaken to determine accurate parameters describing the ^{13}C chemical shift effects associated with geometric features not found in previous data. A successful factor analysis was also executed on methyl chemical shifts, producing an accurate set of parameters for predicting them. The wide variation of chemical shifts associated with γ gauche interactions is discussed. The cmr data for 1,1,4-trimethylcyclohexane are included to complete the data set for the trimethylcyclohexanes.

Introduction

In a previous paper in this series[2] the conformational dependence of the carbon-13 chemical shifts in the methylcyclohexanes was presented, and a method for estimating the energy differences between conformers was proposed. It has been noted that the boat form of the cyclohexane ring is 5.3 kcal/mol[3,4] less stable than the chair forms, so that at room temperature methylcyclohexanes are conformationally inverting at rates which are rapid relative to the chemical-shift difference experienced by any particular carbon in its two environments. Thus, only average ^{13}C chemical shifts are obtained at room temperature. Of course, the chemical shifts to be averaged are weighted by the relative populations of the respective conformers, so that only compounds having conformational isomers of equal or comparable energies will exhibit cmr spectra which differ significantly from those which would be produced by the lower energy conformer alone.

The addition of a methyl group into the cyclohexane ring also introduces steric interactions of the type found in *n*-butane. An equatorial (e) methyl group exhibits conformations which are like those of *trans*-butane, which has minimal steric strain energy, while an axial (a) methyl creates two significant steric interactions of the type found in *gauche*-butane. An additional gauche interaction occurs if methyls are substituted cis-1,2 (ea) or trans-1,2 (ee) to each other. The increment of energy gained due to a gauche interaction is estimated to be from 0.7 to 1.2 kcal/mol;[5–10]

the value used in this study to estimate the magnitude of such steric interactions is 0.9 kcal/mol. An additional 3.7 kcal/mol[11] of strain energy is attributed to the 1,3-diaxial or skew pentane conformation of cis-1,3 methyl groups. In ref 2 proton-decoupled, carbon-13 magnetic resonance data were presented for cyclohexane, methylcyclohexane, all seven configurational isomers of dimethylcyclohexane, and seven of the twelve possible trimethylcyclohexane isomers. Using approximate parameters derived from those chemical shifts which were unequivocably assignable, all carbon-13 resonance lines were associated with specific carbons in these compounds. A factor analysis executed on the chemical-shift data of the ring carbons was used to determine a more accurate set of additive parameters which described the detailed positional and configurational features found in this class of compounds.

Aside from the fact that there is no way to select a unique set of parameters, a further difficulty was encountered in determining the parameters describing the effects of two methyl groups in a vicinal ea configuration, since this interaction appeared in only two compounds studied in ref 2, 1,1,2-trimethylcyclohexane, which was somewhat anomalous, and cis-1,2-dimethylcyclohexane. Since the latter is rapidly interconverting between conformations of equal energy, only an average parameter could be elucidated to describe the effects of vicinal ea methyl groups on ^{13}C chemical shifts. Proton-decoupled, carbon-13 chemical-shift data have now been obtained for four unreported trimethylcyclohexanes, depicted in Table I, each of which has vicinal ea methyls. The number of *gauche*-butane (G) and skew-pentane (AA) interactions is listed beneath each conformer, as well as an approximate en-

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(2) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).
(3) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).
(4) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940)
(5) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2488 (1947).
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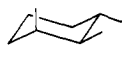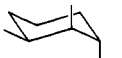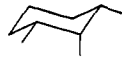(7) D. H. R. Barton, O. Hassel, K. S. Pitzer, and V. Prelog, *Science*, **119**, 49 (1953).
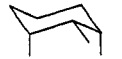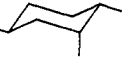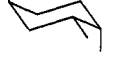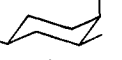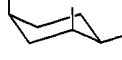(8) R. B. Turner, *J. Amer. Chem. Soc.*, **74**, 2118 (1952).

(9) A. W. Weitkamp, *Advan. Catal.*, **18**, 1 (1968).
(10) W. S. Johnson, *J. Amer. Chem. Soc.*, **75**, 1498 (1953); *Experientia*, **8**, 315 (1951).
(11) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **83**, 3145 (1961).

Table I. Trimethylcyclohexanes with Vicinal ea Methyl Groups

Compd	Favored form	Unfavored form	kcal/mol
1-Trans-2-trans-3[a]	4G	5G	~0.9
1-Cis-2-cis-3	4G	4G + AA	~3.7
1-Cis-2-trans-4	3G	5G	~1.8
1-Cis-2-cis-4	3G, G = 0.9 kcal/mol	3G + AA, AA = 3.7 kcal/mol	~3.7

[a] Due to an ambiguity in the systematic nomenclature, 1-cis, 2-trans-3-trimethylcyclohexane is an equally appropriate name for this compound, when numbering is begun at the axial substituent of the conformer represented on the left. Perhaps a more appropriate name is 1,2-trans-3-TMC.

ergy difference for each pair of conformational isomers. Analogous to previous work,[2] it is expected that only 1-trans,2-trans-3-trimethylcyclohexane (1-trans-2-trans-3-TMC) has an unfavored form which will contribute significantly to its cmr spectrum. In the other three compounds the lower energy isomer should be highly favored at normal temperatures, and the cmr spectra will not be significantly affected by other than the dominant conformers.

The cmr data on the above four compounds made possible a significant reassessment of substituent parameters for the ring carbons. Furthermore, systematic trends were found for the chemical shifts of methyl groups which made it possible to elucidate the important structural features in the methyl shifts.

In a recent article[12] it was claimed that a new set of ^{13}C chemical shift substituent parameters have been developed for various alkanes, including the methylcyclohexanes. In this approach the experimental data are adjusted first with calculated local diamagnetic screening corrections which result when an α carbon is substituted for hydrogen. The diamagnetic corrections in parts per million are 295.3 for methane and 323.5, 351.4, 379.5, and 407.3, respectively, for ethane, propane, isobutane, and neopentane. The resulting incremental differences are 28.2, 27.9, 28.1, and 27.8 ppm, respectively. It is apparent from these numbers that the correction is linear and for all practical purposes is directly proportional to the number of attached α carbon atoms. A linear regression analysis in the number of α, β, γ, and ϵ carbon atoms was then conducted[12] in the manner designated first by Grant and Paul[13] and then expanded by Dalling and Grant.[2] The only real difference in these regressional fits is the

large difference in the α parameter which is required to compensate for the approximately +28-ppm diamagnetic correction estimated from theoretical considerations. There is no significant improvement in the standard error of the estimate for this limited parameter set over previous work[2,13] and the apparent improvement in the correlation between predicted and experimental values results from the artificial way in which primary, secondary, tertiary, and quaternary carbons are spread over an additional 100-ppm range by making the diamagnetic corrections. The diamagnetic estimates should more appropriately be applied to the theoretical predictions and then used to predict values to be compared with the experimental results. Although no new significance can be attached to the regression analysis, the basic proposal of Mason,[12] that a diamagnetic term comparable in magnitude to the paramagnetic terms is contributing to the α carbon chemical shifts, is indeed very important as this would explain why the α and β substituent shifts are about equal in magnitude. If this reasonable proposal of Mason is correct, one then would observe the expected decrease in the paramagnetic term with chain length as one moves from the α through the β to the γ carbon atoms. In this context it is thus not the β shift which is anomalous, as suspected by workers in the field, but instead it is a small α shift that is the unusual feature.

Experimental Section

A. Instrumentation. The carbon-13 magnetic resonance data were obtained using a Varian AFS-60 spectrometer, operating near 15.1 MHz. Simultaneous proton decoupling was accomplished by irradiating the sample at 60.0 MHz with a Hewlett-Packard 5102A frequency synthesizer, utilizing a Boonton Radio Co. 230A power amplifier for amplification. The 10-mm sample tubes were spun in a Varian V-4331A dual irradiation probe. When necessary, spectra were accumulated in a Varian C1024 time averaging computer. Proton spectra were obtained using a Varian A-56/60 spectrometer.

B. Spectral Techniques. All samples were run as liquids with about 10% TMS added. The sample tubes were simply stopped, as degassing was found to be unnecessary. Carbon-13 resonance line frequencies were determined relative to the tetramethylsilane internal standard (except as noted in the table of data, Table III). The chemical shifts were converted to the benzene scale by adding 128.82 ppm to the value calculated from TMS. The value of 128.82 ppm for the chemical shift of TMS relative to neat benzene was determined by measuring the average resonance value of 10% TMS in solution with methylcyclohexane, the chemical-shift values of which were determined for the neat liquid by use of the Γ method.[2] This procedure effectively references the ^{13}C chemical shifts to the ^{1}H chemical shift of TMS.

The previously described[1] selective decoupling technique was used to distinguish methyl carbons from ring carbons in all compounds but 1-cis-2-trans-4-trimethylcyclohexane. The latter compound was investigated as a minor component in solution with 1-cis-2-cis-4-TMC, from which it is very difficult to separate. In this case it was necessary to accumulate on the time averaging computer while decoupling all protons with a random noise decoupler.[14]

C. Compound Preparation. The sample of 1-trans-2-trans-3-TMC was obtained from the American Petroleum Institute. The remaining compounds were synthesized from the corresponding methylbenzenes by hydrogenation. The isomers obtained and their relative amounts are tabulated in Table II. The material to be hydrogenated (50 g) was dissolved in 250 ml of cyclohexane and the solution was put in a stainless steel lined, high-pressure bomb of 3-l. capacity. The catalyst used was 5% ruthenium on charcoal, as this material gives a high percentage of cis addition products.[9]

(12) J. Mason, J. Chem. Soc. A, 1038 (1971).
(13) D. M. Grant and E. G. Paul, J. Amer. Chem. Soc., 86, 2984 (1964).

(14) N. F. Chamberlain, Anal. Chem., 31, 56 (1959).

Table II. Products Resulting from the Hydrogenation of Two Trimethylbenzenes in the Presence of Ru/C Catalyst

Compd hydrogenated	Catalyst	Initial psi	Temp,[a] °C	% yield[b]	Products, %[b]
1,2,3-Trimethylbenzene	Ru/C[c]	1800	200	99	1-*cis*-2-*cis*-3-TMC,[d] 90
					Undetermined, 10
1,2,4-Trimethylbenzene	Ru/C	1400	230	95	1-*cis*-2-*cis*-4-TMC, 70
					1-*cis*-2-*trans*-4-TMC, 20
					1-*trans*-2-*trans*-4-TMC, 10

[a] The reactions were begun at room temperature, but were held at the listed temperature for 12–36 hr. [b] As determined by gas–liquid chromatography. [c] Obtained from Engelhard Industries, Inc. [d] TMC = trimethylcyclohexane.

Table III. Carbon-13 Chemical-Shift Data for Trimethylcyclohexanes Having Cis 1,2 Methyl Groups

Item	Compd	Carbon position[a,b]	$\delta_{^{13}C}$, exptl Ppm from TMS	Ppm from benzene	$\delta_{^{13}C}$, predicted from Tables IV and V[c]
1	1-Trans-2-trans-3[d]	2	41.88	86.94	86.66
2		6	35.19	93.63	92.68
3		3⎫	33.97	94.85	94.65
4		4⎭	33.67	95.15	94.89
5		1	33.04	95.78	96.33
6		5	21.29	107.53	108.24
7		CH₃(1)	20.51	108.31	108.52
8		CH₃(2)	17.42	111.40	111.34
9		(CH₃(3)	13.81	115.01	116.77
10	1-Cis-2-cis-3	2	39.81	89.01	89.10
11		1,3	37.51	91.31	91.63
12		4,6	28.48	100.34	100.06
13		5	27.19	101.63	101.67
14		CH₃(1,3)	20.41	108.41	108.52
15		CH₃(2)	5.33	123.49	123.54
16	1-Cis-2-trans-4[e]	3	43.15	85.67	85.65
17		5⎫	35.84	92.98	92.69
18		1⎭	35.25	93.57	93.57
19		2	33.91	94.91	94.65
20		6	29.15	99.67	99.79
21		4	26.29	102.53	102.33
22		CH₃(4)	22.78	106.04	105.70
23		CH₃(1)	19.71	109.11	108.52
24		CH₃(2)	12.76	116.06	116.77
25	1-Cis-2-cis-4	3	38.04	90.78	90.81
26		2	35.50	93.32	93.81
27		6⎫	34.06	94.76	94.68
28		1⎭	33.70	95.12	94.93
29		4	32.93	95.89	95.76
30		5	29.32	99.50	99.26
31		CH₃(4)	22.96	105.86	105.70
32		CH₃(2)	20.34	108.48	108.52
33		CH₃(1)	11.68	117.14	116.77
34	1,1,4[f]	2,6	39.50	89.32	88.48
35		CH₃(e)	32.90	95.92	95.27
36		4	32.81	96.01	96.02
37		3,5	31.38	97.44	96.97
38		1	29.79	99.03	98.36
39		CH₃(a)	24.56	104.26	103.52
40		CH₃(4)	22.39	106.43	105.70

[a] Number in parentheses indicates the carbon to which a methyl is attached or its orientation. [b] The brackets indicate proximate chemical shifts where a degree of uncertainty remains in the specified assignments. Labeling techniques may be necessary to make unequivocal assignments in these cases. [c] Only the lower energy conformer is considered. [d] Numbering was initiated at the carbon having the outside equatorial methyl. See the left-hand figure for this compound in Table I. [e] This compound was studied as an inseparable minor component in solution with 1-*cis*-2-*cis*-4-TMC. The CH₃(4) line of the latter compound was used as the internal standard; TMS was used as internal standard for all other compounds. [f] This compound was acquired (from Chemical Samples Co., Columbus, Ohio) at a very late stage in the preparation of this paper and is included for the sake of completing the trimethylcyclohexane data. Although the predicted values differ from the experimental ones somewhat more than anticipated (probably as result of noticeable contributions from the higher energy conformer), we did not feel that there was any advantage to be gained in redoing the regression analysis with this compound included.

The percentage yields expressed in Table II were determined by gas–liquid chromatography, and because of considerable peak overlap, the yields given have an accuracy of only about ±3%. The compounds were identified on the basis of their cmr spectra. For example, the possible hydrogenation products of hemimellitene

are 1-*trans*-2-*cis*-3-, 1-*trans*-2-*trans*-3-,[15] and 1-*cis*-2-*cis*-3-trimethylcyclohexane. The proton-decoupled cmr spectra of these com-

(15) See footnote a, Table I.

pounds will give six, nine, and six lines, respectively, the reduction in the number of lines being due to the existence of a plane of symmetry in the first and third molecules. The product from hydrogenation of hemimellitene with Ru/C produced a six-line cmr spectrum only, which was not that of the previously measured 1-trans-2-cis-3 compound.[2] Thus, the hydrogenation product is 1-*cis*-2-*cis*-3-TMC, which is the product which would be expected to result from all cis addition of hydrogen to the 1,2,3-trimethylbenzene ring.

The 1-trans-2-trans-3 molecule[15] gave a nine-line cmr spectrum as anticipated.

Complete cis addition of hydrogen to pseudocumene (1,2,4-trimethylbenzene) would produce 1-*cis*-2-*cis*-4-trimethylcyclohexane. The principal hydrogenation product of pseudocumene in the presence of Ru/C catalyst was shown to be 1-*cis*-2-*cis*-4-TMC by means of the factor analysis to be discussed later. This conclusion was confirmed in part by examination of the carbon-13 spectrum of the hydrogenation product, which was unlike that of the two known isomers,[2] 1-*trans*-2-*trans*-4- and 1-*trans*-2-*cis*-4-trimethylcyclohexane. A minor product of the hydrogenation of 1,2,4-trimethylbenzene produced a fourth carbon-13 spectrum that was uniquely different from any of the other three. This compound was subsequently shown to be 1-*cis*-2-*trans*-4-TMC. The latter compound was run as a mixture with the 1-cis-2-cis-4 isomer, because they form an inseparable solution; it has been estimated that these two compounds boil within 0.08° of one another.[16]

Spectral Assignments.

The carbon-13 chemical-shift data for the trimethylcyclohexanes having cis-1,2 configurations are contained in Table III. The shifts are reported with respect to both benzene and TMS. While present uncertainty regarding referencing standards suggests the advisability of reporting the data in both scales, the discussion of the values will continue to use the benzene scale in light of its previous use in cyclic paraffin hydrocarbons.[2] Use of the selective decoupling technique[13] made it possible to distinguish the signals arising from methyl carbons from those due to ring carbons,[17] and assignment of the two types of carbons can be done independently. Items 7-9, 14, 15, 22-24, 31-33, 35, 39, and 40 of Table III were determined to be methyl resonances.

A. Assignment of the Methyl Carbons. Items 14 and 15 of 1-*cis*-2-*cis*-3-trimethylcyclohexane may be assigned unambiguously to $CH_3(1,3)$ and $CH_3(2)$, respectively, on the basis of line intensities. By considering Table V of ref 2 we conclude that items 22, 31, and 40 result from isolated, equatorial methyls in their respective compounds.

Consideration of the equatorial methyls in the 1-cis-2-cis-3 compound (item 14) and in *trans*-1,2-dimethylcyclohexane (108.3 ppm) demonstrates that equatorial methyls involved in a single, vicinal interaction have resonances occurring at about 108.5 ppm, irrespective of the conformation of the adjacent methyl. Items 7, 23, and 32 may be assigned on that basis, leaving items 24 and 33 to be assigned by default. Since items 24 and 33 result from axial methyls having a vicinal, equatorial neighbor, item 9 may be assigned by analogy allowing item 8 to be assigned by default. Items 35 and 39 were assigned analogous to the geminal methyls of 1,1,3-trimethylcyclohexane.

A detailed factor analysis of these recurring spectral features, to be given later, substantiates the methyl assignments made above in every instance. Many of

(16) B. H. Mahmoud, Ph.D. Thesis, Ohio State University, 1962.
(17) Selective decoupling was not used with 1-*cis*-2-*trans*-4-TMC, but the methyl chemical shifts are conformationally relatable to those of the 1-cis-2-cis-4 compound and are assigned on that basis.

the spectral features noted here were not accessible from the data of ref 2 because of the small number of vicinal methyl pairs occurring in those compounds.

B. Assignment of the Ring Carbons. No ring carbons may be assigned on the basis of intensity alone. The assignments for the compounds listed in Table III were made originally by comparison of the experimental values with the values predicted by use of Table IX of ref 2. A new factor analysis was then undertaken on the ring data for all methylcyclohexanes (except the three which have higher energy conformers which contribute significantly to their carbon-13 spectra, i.e., the 1,1,2-, 1-*trans*-2-*cis*-4-, and 1-*trans*-2-*trans*-3-trimethylcyclohexanes), adding new parameters which characterize the geometric features resulting from vicinal ea methyls which were not accessible from the previous data. The regression was done several times, changing the tentative assignments as necessary until self-consistent results were obtained. The resulting parameters were used to calculate the predicted chemical shifts listed in Table III.

It will be noted that the poorest agreement between experimental and predicted values in Table III occurs for 1-*trans*-2-*trans*-3-trimethylcyclohexane. This most probably is a result of the unfavored conformer making a noticeable contribution to the cmr spectrum. In those cases where the uncertainty in the predicted shifts approaches the separation of closely placed peaks, the assignments are felt to be tentative at best, which is indicated with a bracket. In the three cases where the assignments are not unequivocal, the two peaks lie within 0.6 ppm from one another, and no great significance can be attributed to the difference in any case.

Discussion

A. Factor Analysis of the Carbon-13 Shifts of the Ring Atoms. A least-squares analysis of all ring carbon data was undertaken to determine more precise values for the parameters describing the positional and geometrical factors influencing chemical shifts in these molecules. Sixty-four chemical shifts derived from 13 compounds of ref 2 and three compounds of Table III were included in the analysis, omitting those chemical shifts from the three previously mentioned compounds where unfavored forms seem to influence the carbon-13 spectra significantly (i.e., the 1,1,2-, 1-*trans*-2-*cis*-4-, and 1-*trans*-2-*trans*-3-trimethylcyclohexanes).

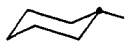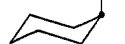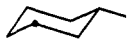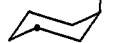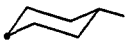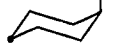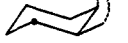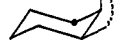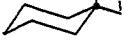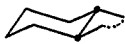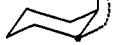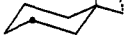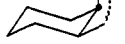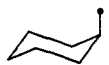Table IV contains the results of the factor analysis. The standard deviation of the fit and multiple correlation coefficient squared are also listed. It is noted that this statistical information indicates a satisfactory fit of the data. Within the error of the fit the constant term corresponds to the chemical shift of the cyclohexane parent.

In addition to five significant (α_e, α_a, β_e, β_a, γ_a) and three negligible (γ_e, δ_e, δ_a) positional parameters eight additional parameters of significant magnitude were found to be necessary to achieve a highly accurate fit of the data. Five of the parameters ($\alpha_e\beta_e$, $\alpha_e\beta_a$, $\alpha_a\beta_e$, $\beta_e\gamma_a$, $\beta_a\gamma_e$) relate to vicinal effects while the remaining three (G_α, G_β, G_γ) result from geminal substitution. It may be noted that 11 of the parameters are similar to those published in ref 2, and that their respective values are comparable. The average of $\alpha_e\beta_a$ and $\alpha_a\beta_e$
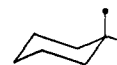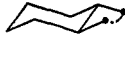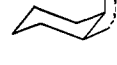
Table IV. Carbon-13 Chemical-Shift Parameters[a] Indicating the Effects of Methyl Substitution on Cyclohexane, as Determined by Least-Squares Analysis of 64 Chemical Shifts[b]

Parameter		Value	No. of occurrences	Parameter		Value	No. of occurrences
α_e	(structure)	-5.96 ± 0.12	23	α_a	(structure)	-1.40 ± 0.23	9
β_e	(structure)	-9.03 ± 0.08	35	β_a	(structure)	-5.41 ± 0.19	14
γ_e	(structure)	-0.05 ± 0.07^c	22	γ_a	(structure)	$+6.37 \pm 0.15$	14
δ_e	(structure)	$+0.22 \pm 0.09^c$	22	δ_a	(structure)	$+0.06 \pm 0.13^b$	9
$\beta_e\alpha_a$	(structure)	$+0.80 \pm 0.22$	4	$\beta_a\alpha_e$	(structure)	-1.57 ± 0.22	4
G_α	(structure)	$+3.80 \pm 0.31$	2	$\alpha_e\beta_e$	(structure)	$+2.45 \pm 0.14$	5
G_β	(structure)	$+1.27 \pm 0.24$	3	$\alpha_e\beta_a$	(structure)	$+2.91 \pm 0.24$	4
G_γ	(structure)	-2.02 ± 0.22	3	$\alpha_a\beta_e$	(structure)	$+3.43 \pm 0.21$	4

[a] In parts per million $\pm$ standard error. [b] ^{13}C chemical shifts not contained in Table I are listed in ref 2. Standard error of the fit = 0.29 ppm; constant term = 101.70 ppm; multiple correlation coefficient squared = 0.9985. [c] This parameter is negligible, but it was retained in the factor analysis so that its lack of significance would be demonstrated.

Table V. Carbon-13 Chemical-Shift Parameters for Methyl Groups Attached to Cyclohexane Rings as Determined by Least-Squares Analysis of 27 Chemical Shifts

Parameter		Value[a]	No. of occurrences	Parameter		Value[a]	No. of occurrences
Axial	(structure)	4.30 ± 0.40	10	β	(structure)	-10.43 ± 0.28	3
γ_g	or (structures)	2.82 ± 0.15	12	Buttress	or (structures)	3.95 ± 0.43	6

[a] In parts per million $\pm$ standard error. Standard error of fit = 0.39 ppm; multiple correlation coefficient squared = 0.9957; constant term (corresponds to unperturbed, equatorial methyl) = 105.70 ppm.

parameters (3.17 ppm) corresponds to the former V_{ea} parameter (3.07 ppm),[2] and it is seen that the latter values also compare favorably. The G_γ, $\beta_e\gamma_a$, and $\beta_a\gamma_e$ parameters were not included in the previous set.
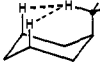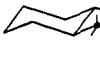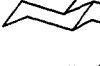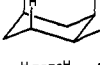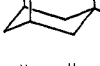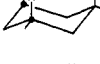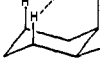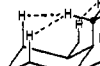
B. Factor Analysis of Methyl Carbon Chemical Shifts. A least-squares regression analysis was executed on the 27 methyl carbon chemical shifts of 16 methylcyclohexanes from ref 2 and the present work which have carbon-13 spectra which are not significantly affected by unfavored conformers (i.e., excluding the chemical shifts of the three previously mentioned compounds as before). It was found that a good fit of the data could be achieved using only four parameters, which are listed in Table V, together with the standard deviation, multiple correlation coefficient squared, and the resulting constant term. The constant term corresponds to the chemical shift of a sterically unperturbed, equatorial methyl; its value (105.70 ppm) is seen to compare well with the average value found for

the isolated, equatorial methyls in Table V of ref 2 (105.65 ppm).

The parameter set derived for methyl groups is consistent with the previous parametric trends noted for ring carbons in Table IX of ref 2 and Table IV of t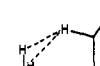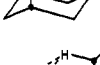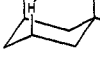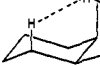he present work, in that a large negative chemical shift is associated with β substitution, while upfield chemical shifts result from interactions which involve close approach of hydrogens. Methyl groups are not as constrained as the methylenes are in the ring, and as a result the methyls should have relatively greater freedom to bend and rotate about the carbon–carbon bonds. The bending freedom complicates chemical-shift analysis, since, following the approach taken in ref 2, methyl resonances should be shifted upfield different amounts depending on the proximity which they attain to other hydrogens. The resulting wide variety of values associated with γ-gauche interactions is treated in the following section.

C. The Variation of Chemical Shifts Associated with γ-Gauche Interactions.

A number of upfield chemical shifts which were determined from the experimental values associated with carbons involved in γ gauche interactions are collected for comparison in Table VI, including some from compounds other than methylcyclohexanes.

Table VI. Summary of [13]C Chemical Shifts Associated with Gauche Interactions

Item	Interaction	Value[a,b]	Value per H···H interaction[a]
1		+3.97[c]	+1.98
2		+2.05[d]	+2.05
3		+2.58[e]	+2.58
4		+6.20[d]	+3.10
5		+11.44[f]	+3.81
6		+8.37[g]	+4.18
7		+4.22[h]	+4.22
8		+8.51[i]	+4.26
9		+17.79[j]	+4.45
10		+5.10[b]	+5.10
11		+10.75[k]	+5.38
12		+5.48[i]	+5.48
13		+6.32[l]	+6.32

[a] In ppm. [b] Calculated by subtracting the parametric value for an unperturbed methyl (105.70) or ring (101.70) carbon from the empirical value noted. [c] Taken from 1-cis-3-trans-5-TMC. [d] Taken from 1-trans-2-cis-3-TMC. [e] Taken from the trans-1,2-dimethyl compound. [f] Taken from 1-cis-2-cis-4-TMC. [g] Taken from 1,1,3-TMC. A correction was made for the β methyl using the appropriate parameter from Table V. [h] Taken from 1,1-dimethyl compound. [i] Taken from the spectra of methyl-cis-decalins as compared to trans-decalin. Complete spectral information will be published later. [j] Taken from 1-cis-2-cis-3-TMC. [k] Taken from the low-temperature spectrum of spiro[5.5]undecane. The complete spectrum will be published at a later date. [l] Taken from 1-cis-3-trans-5-TMC after correcting for the α methyls.

In previous work[2] it was shown that the differences in γ gauche steric shifts between vicinal ee methyls (items 2, 3, and 4 of Table VI) could be rationalized solely on the basis of rotation of the vicinal methyls about their C–C bonds using eq 1 where θ is the H···

$$\delta^{13}_{C} = +1680 \cos\theta \exp(-2.671r) \qquad (1)$$

H–C angle and r the H···H distance. Consideration of Table VI reveals that the above approach, using eq 1 and reasonable variations in methyl dihedral angles only, is unable to account for many of the results, and that changes in methyl carbon ring bond angles and/or flattening of the cyclohexane ring are also important for relaxation of steric interactions.

Although eq 1 could be modified for use in calculating more complex deformations, two difficulties are encountered. First, the geometries of the various compounds are not well known. Cyclohexane itself varies from tetrahedral geometry,[18,19] and the additional distortions resulting from methyl substitution are not readily determined. Second, it is necessary to scale eq 1 so that zero deformation corresponds to the "true" chemical shift resulting from γ gauche interactions of a "standard" system. However, the results in Table VI indicate that no "standard" system exists, and that the constants in eq 1 must be determined by the somewhat arbitrary selection of a "normal" γ gauche chemical-shift value.

With the above limitations in mind, a rough calculation using eq 1, scaled to make +6.4 ppm (the value of γ_a) the maximum value of the γ ring carbon chemical shift, tetrahedral geometry being assumed initially, demonstrates that the 2.4-ppm range of axial methyl shifts can be explained by rotating the methyl carbon–ring carbon bond axis about 13° (in the symmetry plane) from its ideal position. However, the calculation indicated a concomitant downfield shift of the resonances resulting from the γ gauche ring carbons of almost 5 ppm, which is not observed experimentally. It is possible that the latter downfield shift does not occur in part because of increased eclipsing of the ring protons due to flattening. This premise is supported by the carbon-13 chemical shift of cyclopentane[20] which is upfield 1.3 ppm from that of cyclohexane. The higher field chemical shift of cyclopentane is presumably due to departures from ideal geometry and increased eclipsing of hydrogens.

It might be expected that methyl groups would have greater freedom to bend away from steric interactions than methylenes which are locked in a ring. However, although ring carbons γ gauche to a methyl have higher net upfield shifts than methyls involved in gauche interactions, the range of such shifts (4.2–6.4 ppm) is about the same as that of methyl carbons which experience gauche interactions (2.0–4.4 ppm). This result again indicates that the larger net upfield shift of the ring carbons is the result of factors such as increased hydrogen eclipsing resulting from deformations.

Buttressing of a methyl group or methylene involved in gauche interactions by another methyl (items 4, 5,

(18) M. Davis and O. Hassel, *Acta Chem. Scand.*, 17, 1181 (1963).

(19) E. L. Eliel, N. L. Allinger, S. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 455.

(20) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 86, 1870 (1964).

and 6) or by its presence in another ring (items 8, 10, and 11) results in upfield shifts greater than those of carbons not exhibiting such relationships. For example, the chemical shift of the center methyl of 1-*trans*-2-*cis*-3-TMC (item 4 of Table VI) is 1.0 ppm farther upfield than might be expected from consideration of the methyl shift in *trans*-1,2-dimethylcyclohexane and all of the "other" ring axial methylenes experience greater upfield shifts (per interaction) than lone or singly buttressed methyls.

The spatial relationship of 1,2-ae methyls is identical with that of 1,2-ee methyls, at least for undistorted molecules, and it is anticipated that there is a similar reciprocal relationship in the chemical shifts of the two cases. This is corroborated by the fact that a single shift parameter can be used to describe the two geometric features (see Table V). Having this idea in mind, we may interpret item 5 of Table VI somewhat differently as the sum of γ gauche interactions of different magnitudes. If we subtract the parametric value for one vicinal interaction from the total shift, 2.8 ppm from 11.4 ppm, the resulting 8.6-ppm chemical shift can be attributed to interaction of the axial methyl with the axial hydrogens at the γ ring carbons. Since the 8.6-ppm value is more than double that found for item 1 of Table VI, it is assumed that the axial methyl is more strongly involved in steric interactions with the axial protons at C-3,5 as a result of the vicinal buttressing.

A similar upfield effect may be observed for an axial methyl buttressed by a geminal, equatorial methyl group (item 6 of Table V). When the effect of a β methyl (-10.4 ppm) is subtracted from the experimental value, a net upfield shift of about 8.4 ppm is again noted. It is concluded that the methyl is again interacting more strongly with the axial protons at C-3,5 than is an unbuttressed axial methyl.

The discussion may be logically expanded to include the effects of double buttressing. The axial methyl associated with item 15 of Table III (1-*cis*-2-*cis*-3-TMC) has a resonance signal found at 123.49 ppm above benzene, which is $+17.79$ ppm from an unperturbed methyl. The average upfield shift for the four γ gauche interactions is 4.4 ppm (item 9 of Table VI). However, if only about $+5.6$ ppm of the total shift is attributable to the vicinal methyls, the remaining 12.2 ppm must result from ring interactions. This is equivalent to a $+6.1$-ppm shift per H$\cdots$H interaction, which is now approaching the $+6.3$-ppm shift normally observed for ring methylenes γ to axial methyls. The close agreement of the two numbers may be coincidental, but it is logical that the chemical shift of a methyl involved in γ gauche configurations should approach that of a ring methylene as the methyl loses its freedom to move away from steric interactions, if in fact, that is the origin of a wide range of chemical shifts associated with such methyls. The other example of a doubly buttressed axial methyl which occurs in the trimethylcyclohexanes is found in the 1,1,2 com-

pound. Even though the results for it are complicated by the probable contribution of boat forms to its carbon-13 spectrum,[2] an average upfield shift of 4.7 ppm per gauche interaction or 5.7 ppm per interaction with C-3,5 axial protons is noted after correction for the β methyl group has been made.

The chemical-shift changes exhibited by γ-gauche methylenes in the two-ring compounds (items 8, 10–12) fall in general between those of the methyls and the one-ring methylenes, which is logical since bending freedom is more restricted and symmetry dictates that the tendency to deform due to steric strain must be equally distributed between the two rings. It may be noted that a second gauche interaction in *cis*-decalin and spiro[5.5]undecane does not cause as great an upfield shift as the first one (item 8 compared to item 12 and item 10 compared to item 11). Also, it is noteworthy that item 11 (5.4 ppm) is almost exactly equal to the 5.3 ppm average of the axial and γ_g parameters of Tables IV and V.

The effects of buttressing on the ring carbons are complex (items 7 and 9), involving both upfield and downfield shifts (*cf.* the γ_a, G_γ, and $\beta_e\gamma_a$ parameters of Table IV). However, it does appear that when a methyl is geminally buttressed, the ring has deformed to decrease the steric effects on the γ-methylenes, since the upfield shift at C-3,5 has decreased to the intermediate value noted for item 7 of Table VI.

It is concluded from this discussion that, although a set of shift parameters may be developed to predict accurately most of the chemical-shift effects resulting from methyl substitution into unstrained ring systems, there is an almost continuous variation over several parts per million of the chemical shifts resulting from γ gauche interactions. To a considerable extent, this variable γ gauche parameter accounts for the rather large set of variables required to fit the experimental data to a high degree of accuracy. It must be realized that uniqueness is not possible in the selection of a parameter set and various other combinations of parameters can be chosen which are linearly independent, a restraint required by the linear regression computer program. In fact, the extraction of the various types of γ gauche interaction contained in Table VI illustrates how parameters may be combined to yield a shift value corresponding to a given structural feature. The process, however, requires that a given model for the shift mechanism be proposed before the separation is possible. Based on the conceptual constructs, which are given in this paper, we are led to conclude that the carbon-13 chemical shift moves in a continuous manner to higher fields as the extent of steric crowding increases. The data contained in Table VI substantiate this conclusion providing reasonable assumptions are made concerning the ease with which various parts of a molecule will deform or distort from idealized geometries under steric stress.