relation between $(n/\alpha)^{1/3}$ and hardness with use of values of α calculated in the same way as hardness.[12a] In fact the correlation is so good that calculated values for the d- and f-block elements could be used to determine optimal values of n (and hence electronegativities) for these elements. Further insight into the relationships between electronegativity, hardness, size, and polarizability should emerge from this type of approach.

Since hardness is generally considered to be related to the inverse of radius,[13c] it is of interest to determine what relationship exists between polarizabilities and calculated orbital radii. Figure 4 shows an excellent correlation between polarizability radius ($[10^{30}\alpha/4\pi\epsilon_0]^{1/3}$ in units of Å per atom) and the calculated maximum density in the outermost ground state orbital radii with use of an SCF approach that includes relativistic effects.[39]

Table III provides a summary of various atomic quantities that can be derived from polarizability, the units given following previous suggestions.[13c] Although hardness, η_a, has the units of electrons per farad, these values multiplied by the electron charge e yield valence potentials, μ_a, in volts. Or, if hardness is to be related to the gap between the highest occupied and lowest unoccupied orbitals in the one-electron approach to atomic and molecular electronic structure, then μ_a multiplied by Faraday's constant F yields values in the SI units kJ per mol of atoms. Table II lists values of the various properties defined in Table III for elements of atomic number 1-102.

In conclusion, the use of atomic polarizability values provides a simple and reliable way of calculating Pauling electronegativities for every element based on a measurable atomic property. Since this approach is so simple and is closely related to existing concepts, it should play an important role in discussions of electronegativity at the introductory level. The excellent agreement between the values determined here and the recently published[25b] and publicized[40] values based on multiplet-averaged ionization energies (Figure 5) is encouraging and should provide theoreticians with a guide to further explore the role played by electronegativity in chemical bonding and reactivity. An extension of this work to molecular bond distances[41] and molecular[13c,42] and excited-state[43] polarizabilities is in progress.

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(41) The excellent correlations noted above between $(n/\alpha_v)^{1/3}$ and electronegativities based on atomic covalent radii derived from molecular bond distances (refs 1c,d,e,h,i,23b,c,26) suggest correlations between polarizabilities and such radii should exist also.
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Ab Initio IGLO Studies of the Conformational Dependencies of α-, β-, and γ-Substituent Effects in the ¹³C NMR Spectra of Aliphatic and Alicyclic Hydrocarbons

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Abstract: Ab initio IGLO (individual gauge for localized molecular orbital) methods of SCF-MO theory are used to study and analyze the mathematical form of the angular dependence of α-, β-, and γ-substituent effects in the ¹³C NMR spectra of aliphatic and alicyclic hydrocarbons. The conformational dependencies of the isotropic ¹³C shielding are investigated for all of the carbons in the series of aliphatic hydrocarbons: ethane, propane, n-butane, 2-methylbutane, and 2,2-dimethylbutane. The last three of these serve as model compounds for α-, β-, and γ-effects. In contrast to variation in the absolute ¹³C shielding data, the shifts due to changes in dihedral angles are not sensitive to the size of the MO basis sets. In addition to providing a trigonometric form for the orientational dependence of the γ-effects, from these results it can be concluded that α- *and β-effects are strongly dependent on conformation* even for the usual situation in which the groups are trans and gauche. Each of these substituent effects is analyzed in terms of the variations in the IGLO C–H and C–C bond paramagnetic contributions. In contrast to a steric compression model for ¹³C γ-substituent effects, *the torsional dependence of the calculated C1 shielding in n-butane is dominated by the changes in the paramagnetic contributions for the C1–C2 bond and for the C1–H bond which is directed away from the C4 methyl group.* The calculated shielding data for 2-methyl- and 2,2-dimethylbutanes results are quite consistent with additivity of the trigonometric forms for the γ-substituent effect in n-butane. To investigate α-, β-, and γ-substituent effects in cyclic molecules, shielding calculations at the double-ζ level were performed for methyl-substituted cyclohexanes and bicyclo[2.2.1]heptanes. Except for the carbons directly bonded to the methyl groups, these results are in reasonable agreement with the experimental data.

The α-, β-, and γ-substituent effects[1] in the ¹³C NMR spectra of aliphatic and alicyclic compounds are of major importance in the application of NMR techniques to structural and conformational studies.[2] In these applications extensive use has been made of *empirical additivity relationships*. It was noted in ref 1 that ¹³C chemical shifts for aliphatic and alicyclic hydrocarbons could

be described by an empirical equation of which a typical form is[3,4]

$$\delta_C = n_\alpha A_\alpha + n_\beta B_\beta + n_\gamma C_\gamma + n_\delta D_\delta + S \qquad (1)$$

where n_α, n_β, n_γ, and n_δ denote the number of α-, β-, γ-, and δ-substituents having additivity increments A_α, B_β, C_γ, and D_δ,

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respectively, and S is a steric factor. The α- and β-substituent terms are assumed to be independent of conformation. Nominal values for the empirical parameters for hydrocarbons are as follows:[4] $A_\alpha = 9.1$ ppm, $B_\beta = 9.4$ ppm, $C_\gamma = -2.5$ ppm for free rotation (–6.5 ppm for the eclipsed arrangement, and $C_\gamma = -0.4$ ppm for the anti arrangement), and $D_\delta = 0.3$ ppm. This equation is generally not applicable for strained multicyclic hydrocarbons, but consideration of these types has also played an important role in the ^{13}C NMR of polymers.[5]
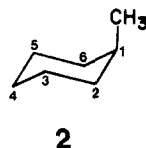
The *conformational dependencies* of the α- and β-substituent effects have not been investigated theoretically although such effects are clear in cyclic hydrocarbons even for the cases in which the dihedral angles are essentially fixed at the trans and gauche values. However, from the experimental data a cos ϕ dependence on dihedral angle ϕ has been inferred[6] for β-substituent effects.

The several values for C_γ in eq 1 are assumed to arise from the angularly dependent γ-substituent effects on ^{13}C chemical shifts, which occur at the C1 carbon. The most commonly observed situation is that in which the C4 methyl is gauche to C1 as in 1. The shift of C1 to lower frequency (higher field on some CW NMR spectrometers) has been extensively used in stereochemical studies and ^{13}C chemical shift assignments.


1
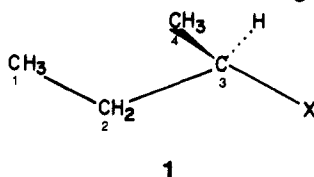
The origin of the angularly dependent γ-effects has been a subject of considerable interest and has widely been interpreted in terms of a model which emphasizes the steric interactions between the hydrogen atoms on the C1 and C4 carbon atoms in 1.[7,8] This[1,7,8] and other[9-11] interpretations of the experimental data, semiempirical MO results,[12] and an empirical relationship to steric van der Waals energy[13] have not yielded a single explanation of the origins of γ-substituent effects. It seems likely from the results presented here that the origins of the γ-effect are sufficiently complex, such that most of the models have some degree of validity. It was not possible to discern[11] a unique mathematical form for the angular dependence of the γ-effect from the experimental data. For convenience, the data are divided into the following three categories:[14] gauche-, anti-, and eclipsed-substituent effects.

1. The γ-Gauche Effect. The most widely observed situation is that in which two 1,4-situated methyl groups are in a gauche (dihedral angle $\phi = 60°$ or 300°) orientation as in 1. If the methyl group of methylcyclohexane (2) is in the axial position, an experimental situation which can be measured at low temperatures, the resonances of the C3 and C5 carbons are 6.5 ppm to low frequency ($\Delta\delta_{C3} = -6.5$ ppm) of cyclohexane.

2

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2. The γ-Axial Effect. There is a relatively small [13]C γ-related shift in those situations in which the 1,4-situated methyl groups are in a trans ($\phi = 180°$) or anti arrangement 3. For example, where the methyl group is equatorial, the C3 and C5 carbons of methylcyclohexane 4 are 0.4 ppm to low frequency of cyclohexane ($\Delta\delta_{C3} = -0.4$ ppm) from the low-temperature measurement. In the NMR spectrum of methylcyclohexane *at room temperature* $\Delta\delta_{C3} = -2.5$ ppm, corresponding to equilibration between the axial and equatorial **5** forms.

3   **4**

5
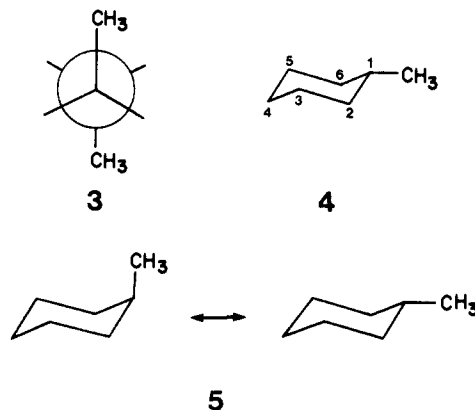
3. The γ-Eclipsed Effect. When the 1,4-situated methyl groups are eclipsed 6, such as in 2(*exo*),3(*exo*)-7 ($\Delta\delta_{C3} = -6.6$ ppm) and 2(*endo*),3(*endo*)-dimethylbicyclo[2.2.1]heptanes (8) ($\Delta\delta_{C3} = -5.6$ ppm), the observed shifts relative to corresponding methylbicyclo[2.2.1]heptanes are substantial.

6

7   **8**
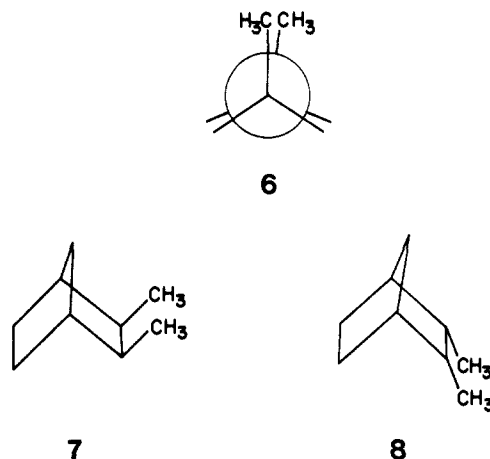
Computational Details. All calculations in this study were based on the IGLO (individual gauge for localized orbitals) formulation of Kutzelnigg and Schindler.[15-17] Problems associated with origin dependence usually found in coupled Hartree–Fock (CHF) shielding computations, arising from a common origin and an incomplete basis set,[18] are reduced in the IGLO method. In this method the usual MO's are converted to localized MO's, which can be associated with inner shells, bonding orbitals, and lone pairs in the molecule. Each of these localized MO's has a unique origin for the calculation of diamagnetic and paramagnetic terms. For the compounds of this study it is only necessary to consider inner shell and localized bonds contributions.

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Ab Initio IGLO Studies

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Table I. Basis Sets Used in the IGLO Calculations

basis	atom	contraction	polarization functions	exponents
1	C	[4111,21]		
	H	[21]		
II	C	[51111,311]	d	1.0
			d	0.5
	H	[311]		
III	C	[51111,311]	d	1.0
	H	[311]	p	0.7
IV	C	[41111111,211111]	d	2.0
			d	0.5
	H	[21111]	p	1.2
			p	0.3

The improvement of the IGLO method over CHF methods has been attributed to the damping of basis set errors associated with longer range contributions to chemical shielding.[15] The IGLO method has been used for a large number of NMR shielding calculations for first- and second-row elements. Schindler and Kutzelnigg[16] investigated the basis set dependence of the IGLO method and concluded that the results were adequate to predict major trends with basis sets of double-ζ quality, and that the results were satisfactory for carbon with triple-ζ plus polarization functions. More recently, the random phase approximation (RPA) has been used in the related context of a localized-orbital local-origins (LORG) method,[19,20] and comparisons have been made[21] between the shielding results of the LORG and IGLO methods. An earlier method for avoiding the problem of origin dependence of the shielding made use of the so-called gauge invariant atomic orbitals (GIAO).[22-24] Results from the latter method are comparable to those from the IGLO method if basis sets of similar quality are used.[23] The GIAO method has also been used in a number of semiempirical MO descriptions of chemical shifts.[12,24]

All calculations were performed with the FORTRAN computer program of Kutzelnigg and Schindler[15,16] which has been modified at the University of Utah and the University of Arizona for use on Digital Equipment Corp. VAX computers.

Basis sets (Table I) are at least of double-ζ (DZ) quality: in most cases a (7,3/3) set in the contraction (4111;21/21). Some of the calculations were performed with a (9,5/5) Huzinaga set,[25] contracted to a triple-ζ (51111;311/311) set with d- and p-type polarization functions on C and H. Since calculations for n-butane with this set initially posed some problems, it was found that a triple-ζ set with two sets of d-polarization functions on carbon gave comparable results. Chesnut and Foley[23] claimed good results for GIAO calculations with basis sets of this quality. Data for the isotropic shielding are referred to the bare nucleus unless noted otherwise.

It was the intent of this study to investigate only those features associated with changes in the torsional angles as distinct from internal angles and bond lengths. Therefore, all calculations were based on a standard geometrical model[26] with r(C–C) = 1.54 Å, r(C–H) = 1.09 Å, and tetrahedral bond angles. Exceptions are geometries for the bicyclo[2.2.1]heptane compounds.

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Table II. Calculated Energies and Shieldings of CH_4 for the Four Basis Sets in Table I

basis	σ^d(1s); ppm	σ^d(C–H),[a] ppm	σ^p(C–H),[a] ppm	σ, ppm	energy, au
I	200.80	12.57	−7.99	219.10	−40.1402
II	200.86	12.72	−8.74	216.81	−40.2031
III	200.86	12.78	−9.27	214.91	−40.2089
IV	200.88	12.90	−14.41	194.84	−40.2146

[a] Contribution per bond.

Table III. Comparison of IGLO Chemical Shift Results for a Representative Series of Hydrocarbons with Solution NMR Data Referenced to Methane[a]

compound		I	II	III	IV	expt[b]
ethane		5.6	12.9	12.0	13.5	9.6
propane	C1	14.6	21.2	20.0		17.7
	C2	9.3	23.0	20.6		18.2
isobutane	C1	22.5	27.6			26.6
	C2	11.0	29.5			27.3
n-butane	C1	14.0	20.0			15.4
	C2	17.7	31.3			27.2
neopentane	C1	29.5				23.7
	C2	10.3				33.7
C(4)H₃-C(3)H₂-C(2)H(C(5)H₃)-C(1)H₃						
	C1	21.2[c,d]				24.2
	C2	17.5[c]				32.0
	C3	23.9[c]				34.0
	C4	12.5[c]				13.7
C(4)H₃-C(3)H₂-C(2)(C(5,6)H₃)₂-C(1)H₃						
	C1	30.0				31.0
	C2	12.6				32.5
	C3	27.4				38.8
	C4	9.0				10.8

[a] All values in ppm referenced to CH_4. [b] Solution experimental values from the compilation of the following: Breitmaier, E.; Haas, G.; Voelter, W. *Atlas of Carbon-13 NMR Data*; Plenum: New York, 1975. [c] Values based on conformations (ϕ = 79.4° and 160.6°) which were calculated to have the lowest total energy. [d] Average value for the C1 and C5 methyl in the lowest energy ϕ = 150° conformation of 2-methylbutane.

Results and Discussion

A. Calculated Chemical Shifts in Representative Cyclic and Alicyclic Hydrocarbons. 1. Chemical Shifts of Aliphatic Hydrocarbons. For investigation of the basis set dependence of the calculated shielding effects, IGLO computations were performed for a series of hydrocarbons. The calculated isotropic shielding data and total energies of CH_4 are given in Table II for each of the basis sets listed in Table I. The results in Table II are very close to those of Kutzelnigg and Schindler.[16] The several ppm difference, which is noted for basis set III, is attributable to our use of a standard geometrical model[26] rather than the experimental one of 1.094 Å for CH_4. Also included in Table II are the diamagnetic contributions from the inner shell (1s) orbitals, diamagnetic σ^d(C–H), and paramagnetic σ^p(C–H) bond contributions. It can be noted from the data in Table II that the approximate 25-ppm decrease in the total calculated shielding in proceeding from basis set I to basis set IV is almost entirely attributable to the 6.5 ppm decrease in the individual bond paramagnetic contributions. Since the calculated diamagnetic bond contributions vary by no more than 0.1–0.2 ppm as the dihedral angles are varied over the whole range of angles for the hydrocarbons studied here, it will be sufficient to consider only the local paramagnetic bond contributions (PBC) in analyzing those features leading to the observed results.

Before investigating the *conformational dependencies* of the shielding in model aliphatic compounds, the applicability of the IGLO method in predicting isotropic ^{13}C *chemical shifts* is presented for representative aliphatic and alicyclic molecules *in solution*. Experimental gas-phase NMR data are the obvious

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choice for comparison with calculations for isolated molecules. Comparisons of the calculated chemical shift and experimental gas-phase ^{13}C chemical shift data for representative simple organic molecules have been presented by Kutzelnigg and Co-workers.[16] However, NMR studies of conformational effects are invariably measured in solution. It is important to know how well the calculated chemical shift data agree with the solution NMR data. Calculated ^{13}C chemical shifts for representative hydrocarbons are entered in Table III. These correspond to the lowest energy conformations of the representative aliphatic hydrocarbons ethane, propane, isobutane, n-butane, 2-methylbutane, neopentane, and 2,2-dimethylbutane. An exception is 2-methylbutane for which the lowest energy conformations correspond to the all trans situations. In all cases the calculated chemical shifts δ in Table III are taken relative to the calculated methane shielding values for the same basis set from Table II. The experimental ^{13}C isotropic shift values in Table III are taken from the solution NMR data with methane as the reference value also. The ab initio SCF total energies for these molecules are included as references for the quality of the basis sets used in the shielding calculations.

Shielding values and chemical shifts in Table III for ethane, propane, isobutane, and n-butane were obtained with basis sets of at least triple-ζ with polarization functions (basis set II). Calculations for neopentane, 2-methylbutane, and 2,2-dimethylbutane were made with a double-ζ set (basis set I). Results for several of these molecules were given by Schindler and Kutzelnigg.[16] It was noted that chemical shifts due to substituents in the α-position were not reproduced at the double-ζ level. Therefore, all of the results for basis set I tend to be substantially smaller in magnitude than the experimental values. However, any of the basis sets with polarization functions on carbon gives a much better description of the shielding. In general, best agreement is with the largest basis sets in Table III.

Even though the absolute values of the shieldings for basis sets II and III are about 20 ppm too large, the chemical shifts in Table III differ from the solution values by only a few ppm, a result which is no worse than the gas-phase data with the smaller basis sets. The data indicate that gas-to-solution shifts are relatively small for ^{13}C.

The ^{13}C chemical shifts for carbons C1–C5 correspond to the conformations of 2-methylbutane having equal values of the lowest energy at $\phi = 79.4°$ and $160.6°$ as inferred from the linear regression data. Since the C1 and C5 methyl carbons are nonequivalent in these arrangements, the data in Table III is the average of the calculated values for these conformations. Also given in Table III are the calculated chemical shifts for 2,2-dimethylbutane with basis set I. The shifts are in generally poor agreement with the experimental data because the basis set used does not provide an adequate representation of α-substituent effects.[16]

For aliphatic molecules of the type investigated here, the experimental ^{13}C shieldings are average values of $\sigma(\phi)$ over the barrier $E(\phi)$ which hinders internal rotation about ϕ

$$\langle \sigma \rangle = \int \sigma(\phi) e^{-E(\phi)} d\phi / \int e^{-E(\phi)} d\phi \qquad (2)$$

The rotationally averaged ^{13}C shielding data could very easily be obtained from eq 2 with the calculated shielding $\sigma(\phi)$ and energy data $E(\phi)$ obtained in this study. However, the resulting correction of the calculated data by a few tenths ppm is negligible when compared with the differences between results among the several basis sets and the expected disparities between data for isolated molecules and experimental isotropic shift values from solution NMR data. A completely rigorous calculation would include an average over *all* internal degrees of freedom.

2. Axial and Equatorial Methylcyclohexane: Bicyclo[2.2.1]-heptane and the Methylbicyclo[2.2.1]heptanes. The calculated IGLO ^{13}C isotropic shielding data, (basis set I) for cyclohexane, and the methylcyclohexanes with axial 2 and equatorial 4 arrangements of the methyl are given in Table IV. The differences $\Delta\delta$ between the calculated isotropic shielding data for the methyl-substituted compounds and cyclohexane are given in the table along with the experimentally determined differences for these

compounds based on the low-temperature NMR data. The calculated IGLO shielding results and experimental chemical shift data for several methyl-substituted bicyclo[2.2.1]heptanes are also entered in Table IV. The chemical shifts are based on the values for the parent compounds. Entries for the methyl groups of the dimethylbicyclo[2.2.1]heptanes in Table IV are taken as the differences between the methyl group shielding for the compound with a single methyl and the value for the compound listed. These calculations were also based on the double-ζ set I, but the bicyclo[2.2.1]heptane geometry was based on electron diffraction data.[27] Except for the C1 carbons, for which the α-substituent effects are not adequately described, the calculated chemical shifts are quite reasonable: the average deviation of the $\Delta\delta$ in Table IV is 1.3 ppm for the 29 carbons which are not directly bonded to a methyl group. Any of the larger basis sets in Table I would be expected to give substantially better agreement with the experimental data, but the computations could not easily be performed. For example, some improvement in the calculated values for the cyclohexanes was found with a double-ζ set which included one set of d-orbitals on carbon [for **2** $\Delta\delta = -1.4$, 3.1, -5.2, and 0.4 ppm, for carbons C1–C4, respectively, and for **4** $\Delta\delta = 2.3$, 5.2, -0.2, and -0.1 ppm, respectively]. These results did not seem to justify extensive calculations with this slightly larger basis. As shielding calculations become routine with the larger basis sets, it will be appropriate to use experimental geometries rather than the standard geometrical model. For example, it appears that the cyclohexane ring is flatter than the one used here.[28]

The calculated chemical shift data in Table IV are clear examples of the salient features of the γ-substituent effects noted in the previous section; in axial (equatorial) methylcyclohexane a calculated γ-gauche shift of -5.9 ppm (γ-anti shift of -0.1 ppm) for the C3 carbon compares favorably with the experimental value of -6.5 ppm (-0.4 ppm). In the dimethylbicyclo[2.2.1]heptanes **7** and **8** the calculated γ-substituent effects are -4.9 and -3.9 ppm. In comparison, the solution NMR values are -6.6 and -5.6 ppm, respectively. The experimental data for axial and equatorial methylcyclohexanes in Table IV clearly show the dependence of the α- and β-substituent effects on conformation. For the C1 carbon with an α-methyl group, $\Delta\delta$ are 0.4 ppm and 5.9 ppm for the methyl group axial and equatorial, respectively. For the C2 carbon in which the methyl is in the β-position, the values are 4.8 ppm and 8.3 ppm for the axial and equatorial forms. These values will be shown to be consistent with the calculated conformational dependencies of the shielding in the model aliphatic compounds investigated in the next section.

The trends in the calculated ^{13}C shielding data noted here for a series of cyclic molecules are consistent with those recently reported by Bouman and Hansen[29] for ^{13}C isotropic shielding data in 2-oxobicyclo[2.2.1]hept-5-ene also using a double-ζ basis set but with the LORG algorithm;[19] the authors also concluded that the method was adequate to distinguish all but the C3 and C4 assignments and that errors in the calculated shielding values were comparable for those groups having comparable chemical environments.

B. Conformational Dependencies of the Shielding in Aliphatic Compounds. The presentation of all of the conformation dependent data obtained in this study would require an inordinate number of tables. However, it was noted that both the ^{13}C isotropic shielding data and the total computed energies could be represented to very high precision by means of Fourier series expansions of the forms

$$\sigma(\phi) = \sum_{n=1}^{6} A_n \cos n\phi + B \qquad (3)$$

$$E(\phi) = \sum_{n=1}^{6} A_n' \cos n\phi + B' \qquad (4)$$

(27) Chiang, J. F.; Wilcox, C. F., Jr.; Bauer, S. H. *J. Am. Chem. Soc.* **1968**, *90*, 3149. Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356.

(28) Altona, C.; Sundaralingam, M. *Tetrahedron* **1970**, *26*, 925.

(29) Bouman, T. D.; Hansen, Aa. E. *Chem. Phys. Lett.* **1988**, *149*, 510.

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Table IV. Calculated ^{13}C Isotropic Shielding (Basis Set I) in Cyclic- and Methyl-Substituted Hydrocarbons—Comparison of Calculated Shifts $\Delta\delta$ with Experimental Values Relative to those of the Parent Hydrocarbon

compound	C1	C2	C3	C4	C5	C6	C7	Me
cyclohexane[a]								
σ	199.7	199.7	199.7	199.7	199.7	199.7		
axial methylcyclohexane[b] (2)								
σ	203.9	194.5	205.6	199.4	205.6	194.5		202.4
$\Delta\delta$, basis I	-4.2	5.2	-5.9	0.3	-5.9	5.2		
$\Delta\delta$, exptl[c]	0.4	4.8	-6.5	0.1	-6.5	4.8		
equatorial methylcyclohexane[d] (4)								
σ	199.4	192.4	199.8	199.7	199.8	192.4		196.6
$\Delta\delta$, basis I	0.3	7.3	-0.1	0.0	-0.1	7.3		
$\Delta\delta$, exptl[c]	5.9	8.3	-0.4	-0.8	-0.4	8.3		
bicyclo[2.2.1]heptane[e]								
σ	188.0	189.0	189.0	188.0	189.0	189.0	179.4	
1-methylbicyclo[2.2.1]heptane[f]								
σ	189.4	185.1	187.7	188.2	187.7	185.1	172.1	198.7
$\Delta\delta$, basis I	-1.4	3.9	1.3	-0.2	1.3	3.9	7.3	
$\Delta\delta$, exptl[g]	6.4	7.1	1.6	1.5	1.6	7.1	6.9	
2-*exo*-methylbicyclo[2.2.1]heptane[h]								
σ	183.4	189.4	180.1	187.6	189.2	189.2	181.7	197.4
$\Delta\delta$, basis I	4.6	-0.4	8.9	0.4	-0.2	-0.2	-2.3	
$\Delta\delta$, exptl[i]	6.7	6.8	10.2	0.6	0.4	-0.9	-3.5	
2-*endo*-methylbicyclo[2.2.1]heptane[j]								
σ	185.8	194.8	179.5	187.3	188.8	195.6	177.4	197.9
$\Delta\delta$, basis I	2.2	-5.8	9.5	0.7	0.2	-6.6	2.0	
$\Delta\delta$, exptl[i]	5.4	4.4	10.6	1.4	0.6	-7.5	0.1	
2-*exo*,3-*exo*-dimethylbicyclo[2.2.1]heptane[k] (7)								
σ	182.7	188.3	188.3	182.7	189.2	189.2	184.2	202.3
$\Delta\delta$, basis I	5.3	0.7	0.7	5.3	-0.2	-0.2	-3.8	-4.9
$\Delta\delta$, exptl[i]	8.2	10.3	10.3	8.2	0.1	0.1	-6.4	-6.6
2-*endo*,3-*endo*-dimethylbicyclo[2.2.1]heptane[l] (8)								
σ	185.3	193.6	193.6	185.3	195.3	195.3	178.5	201.8
$\Delta\delta$, basis I	2.7	-4.6	-4.6	2.7	-6.3	-6.3	0.9	-3.9
$\Delta\delta$, exptl[i]	6.8	5.2	5.2	6.8	-7.8	-7.8	1.4	-5.6

[a] E = -233.8924 au. [b] E = -272.8676 au. [c] Unpublished work cited in ref 14; see, also: Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612. [d] E = -272.8765 au. [e] E = -271.6910 au. [f] E = -310.6776 au. [g] Della, E. W.; Pigou, P. E. *J. Am. Chem. Soc.* **1982**, *104*, 862. Poindexter, J. S.; Kropp, P. J. *J. Org. Chem.* **1976**, *41*, 1215. [h] E = -310.6742 au. [i] Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107. Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893. [j] E = -310.6608 au. [k] E = -349.6426 au. [l] E = -349.6159 au.

where the coefficients A_n, etc., are determined by linear regression analyses of the calculated shielding and energy data. The minimum number of terms n in the regression analysis of the shielding were consistent with $r^2 > 0.999$ unless otherwise specified. Standard deviations in the estimates of the σ values and the coefficients from these expansions in Table V are less than 0.01 ppm. Exceptions are the shielding data for the C1 and C5 carbons of 2-methylbutane for which $r^2 = 0.995$ and the standard deviation in the calculated shielding values is 0.33 ppm. The correlation coefficients for the regression analyses of the energies are at least 0.9999, and the standard deviations in the energy are not more than 1×10^{-5} au. These data are included in the Supplementary Material.

1. Ethane. The conformational dependence of the ^{13}C shielding in ethane has been investigated by the GIAO method and geometry optimization.[30] In this study IGLO results for the isotropic ^{13}C shielding in ethane 9 as a function of the dihedral angle were
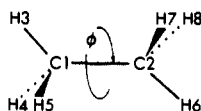
9

obtained with each of the four basis sets I–IV described in Table I. These data are plotted in Figure 1 at 30° intervals of the dihedral angle ϕ.[31,32] The calculated ^{13}C isotropic shielding data
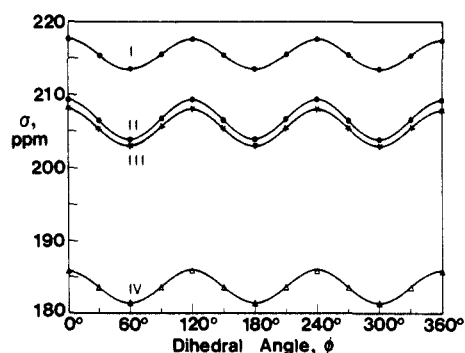
Figure 1. Calculated ^{13}C isotropic shielding data σ for ethane plotted as a function of the dihedral angle ϕ: ($\bullet$), basis set I; (O) basis set II; (*), basis set III; and ($\triangle$), basis set IV. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression from Table V.

were fit in the least-squares sense to trigonometric polynomials with only one term in the summation of eq 3

$$\sigma(\phi) = A_3 \cos 3\phi + B \qquad (5)$$

where the constants A_3 and B are entered in Table V for the four basis sets used for ethane, and ϕ is the dihedral angle measured about the C1–C2 bond in 9. The correlation coefficients r^2 for

(30) Chesnut, D. B.; Wright, D. W.; Macphail, R. A. *Chem. Phys. Lett.* **1988**, *151*, 415.

(31) The IGLO values for the conformational dependencies of the shielding constants and the total energies are given in the Supplementary Material.

(32) In the figure the solid lines through the calculated data at 30° intervals were based on eq 3 with either the shielding coefficients given in Table V or those for the paramagnetic bond contributions in Tables VI and VII. All of the figures were plotted in the range 0° to 360° so that the data for those compounds having periodicities of 180° could be compared with those which do not.

Table V. Coefficients in Shielding Expressions Based on Linear Regression Results for the Calculated IGLO Isotropic Shielding Data for Ethane, Propane, n-Butane, 2-Methylbutane, and 2,2-Dimethylbutane[a]

hydrocarbon		A_1	A_2	A_3	A_4	A_5	A_6	B
ethane								
basis I				1.93				215.39
basis II				2.63				206.47
basis III				2.38				205.27
basis IV				2.23				183.52
propane								
basis I	C1			−0.70			0.04	203.74
	C2			1.96			0.02	211.71
	C3			1.16			0.02	205.62
basis II	C1			−0.62			0.04	194.93
	C2			2.44			0.02	196.20
	C3			1.78			0.07	197.31
basis III	C1			−0.88			0.06	193.96
	C2			1.72			−0.22	196.28
	C3			1.54			0.03	196.40
n-butane								
basis I	C1	2.18	0.27	−0.86	0.44	0.56	0.34	205.97
	C2	3.41	1.70	1.56	0.22	0.09	0.05	204.48
basis II	C1	1.92	0.05	−0.91	0.33	0.52	0.33	197.67
	C2	3.93	1.48	1.84	0.10	0.02	0.05	189.68
2-methylbutane								
	C1[c]	2.16	−0.10	−1.04	0.48	0.56	0.26	197.76
	C2[b]	−3.54	−1.59	1.96	−0.19	−0.08	0.09	205.38
	C3[b]	−3.17	−1.59	1.39	−0.19	−0.10	0.07	198.55
	C4[b]	−2.62	0.82	−1.08	−0.26	−0.64	0.61	207.37
	C5[d]	2.17	−0.09	−1.07	0.49	0.57	0.24	197.75
2,2-dimethylbutane								
	C1[e]	2.24	−0.53	−1.18	0.53	0.53	0.19	190.52
	C2			2.38			0.12	208.72
	C3			1.42			0.08	193.04
	C4			−1.36			0.89	207.87

[a] All of the coefficients, A_1–A_6 and B, are in ppm. Standard deviations in the coefficients are less than 0.01 ppm except for C1 and C5 shielding of 2-methylbutane for which they are less than 0.14 ppm. [b] For this case the entries correspond to coefficients of cos $n\theta$, where $\theta = \phi - 120°$. [c] This and the entry for C5 correspond to the largest standard deviations of the calculated shielding (0.34 ppm); all others are less than 0.01 ppm. [d] For this case the entries correspond to coefficients of cos $n\omega$, where $\omega = \phi - 240°$. [e] For the C5 and C6 carbon shielding expression the coefficients are the same; however, the arguments of the trigonometric expression should be $\theta = \phi - 120°$, and $\omega = \phi - 240°$.

the isotropic shielding data for ethane are at least 0.9998, and the standard deviations of the estimated $\sigma(\phi)$ are less than 0.01 ppm. There are considerable differences in the magnitudes of the calculated isotropic shielding data for the four basis sets in Figure 1. However, the conformational dependence of σ on ϕ (as inferred from Figure 1 and by the magnitude of A_3 in Table V) is not as dependent on the size of the basis set. The fact that use of the IGLO method allows reproduction of the conformational dependencies with small basis sets (I and II) is of importance for this study because it is not yet routinely possible for us to perform shielding calculations with the larger basis sets (II–IV) for molecules having more than four carbon atoms.

It is of interest to examine certain inadequacies of the double-ζ (basis set I) set in comparison with those for the other basis sets. The ethane ^{13}C isotropic shielding for basis set II is 9.6 ppm less than for basis set I, whereas for methane in Table II the shielding difference for the same two basis sets is only 2.3 ppm. By comparing the data for any of the basis sets II–IV, it can be seen that the disparity in these differences is unique to basis set I. For example, basis set IV gives a value for ethane which is 22 ppm smaller than the value from basis set III, which is to be compared with a 20-ppm difference for methane for the same two basis sets. Schindler and Kutzelnigg[16] in noting this argued that there is an imbalance in the way in which the ^{13}C shieldings for C–C bonds are described in comparison with C–H bonds by the double-ζ set. In particular, the localized MO's for C–C bonds deviate more from spherical symmetry and have paramagnetic contributions which are larger in magnitude than the C–H bonds. The MO's for C–C bonds appear to be quite sensitive to the quality of the basis sets. For the purposes of this study the important implication is that *basis sets of double-ζ quality (basis set I) are not adequate to describe the conformationally independent part of the α-substituent effects on ^{13}C chemical shifts.* This is unfortunate because this is the basis set for which ab initio calculations can most easily be performed for the larger molecular systems of interest.

From the IGLO studies of ^{13}C shielding in hydrocarbons[15,16] it has been shown that the most important changes in the total shielding arise from paramagnetic contributions to the localized MO's. The individual bond paramagnetic contributions (basis set II) to the shielding from each of the four localized bonds and their totals for carbon atom C1 were fit in the least-squares sense to eq 3, and the coefficients are entered in Table VI. From these data it can be seen that the conformational dependence of the ethane ^{13}C shielding is almost entirely attributable to paramagnetic C–H and C–C bond terms, each of which follow a simple 3-fold dependence on dihedral angle. The amplitudes of the changes are about 0.5 ppm for each of the C–H bonds and about 1 ppm for the C–C bond. Conformationally induced changes are very small for the inner shell diamagnetic 1s (about 201 ppm) and local diamagnetic bond contributions (in these aliphatic systems these are about 12.5 ppm for C–H bonds and 12.0 ppm for C–C bonds). In fact, the total basis set II shielding value of 204 ppm for ethane follows from these values and the total σ^p of −46 ppm from Table VI. Comparison of the basis set II paramagnetic bond contributions (PBC) for ethane in Table VI with methane values (Table II) shows that an α-substituent-related downfield shift arises primarily from the more negative paramagnetic contributions for a C–C bond than a C–H bond as well as from slightly more negative PBC for the C–H bonds in ethane than in methane.

2. Propane. The IGLO isotropic ^{13}C shielding results for carbon atoms C1–C3 of propane **10** with a double-ζ basis set (basis set I in Table I) were calculated at 30° intervals of the dihedral
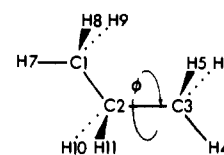
10

Table VI. Coefficients of Fourier Expansions for the Paramagnetic Bond Contributions (Basis Set II) to Total Isotropic Shielding Data for Ethane, Carbons C1–C3 of Propane, and the C1 and C2 Carbons of *n*-Butane[a]

atom/PBC	A_1	A_2	A_3	A_4	A_5	A_6	B
Ethane, Basis Set II							
C1: C1–H3			0.5				–10.0
C1–H4/C1–H5			1.0				–20.1
C1–C2			0.9				–13.5
total			2.4				–43.6
Propane, Basis Set II							
C1: C1–H7			–0.9				–13.0
C1–H8/C1–H9						–0.1	–22.7
C1–C2			0.2			–0.1	–17.7
total			–0.7			–0.3	–53.5
C2: C2–H10/C2–H11			1.0				–21.9
C2–C3			0.6				–15.6
C1–C2			0.8				–15.4
total			2.3				–52.9
C3: C3–H4	–0.3	–0.1	0.4	–0.4	0.3		–11.3
C3–H5/C3–H6	0.3	0.1	0.8	0.4	–0.3	0.1	–22.6
C3–C2			0.6				–17.4
total			1.8			0.1	–51.4
n-Butane, Basis Set II							
C1: C1–H7	0.5	–0.1	–1.0	0.1	0.2	0.1	–12.4
C1–H8/C1–H9	–0.1	–0.2		0.2	0.2	0.1	–22.5
C1–C2	1.3	0.3			0.1	0.1	–16.5
total	1.7		–0.9	0.3	0.5	0.3	–51.4
C2: C2–H10	0.3	0.4	0.6	–0.2	0.1		–11.4
C2–H11	1.0	0.5	0.2	0.2	–0.1	0.1	–12.0
C2–C3	1.5	0.6	0.6	0.1			–18.2
C1–C2	0.8	–0.2	0.5	0.1			–16.4
total	3.6	1.4	1.9	0.2		0.1	–58.0

[a] Standard deviation in the computed value of PBC is less than 0.02 ppm.

angle ϕ, which is measured about the C2–C3 bond.[31,32] From the linear regression results in Table V it can be seen that the conformational dependencies are well represented by simple trigonometric forms having 3-fold terms and small 6-fold terms. Neglecting terms in Table V with coefficients less than 0.1 ppm are as follows:

$$\sigma_{C1}(\phi) = -0.7 \cos 3\phi + 203.7 \text{ ppm} \tag{6a}$$

$$\sigma_{C2}(\phi) = 2.0 \cos 3\phi + 211.7 \text{ ppm} \tag{6b}$$

$$\sigma_{C3}(\phi) = 1.2 \cos 3\phi + 205.6 \text{ ppm} \tag{6c}$$

For propane (as in ethane) the ^{13}C isotropic shieldings for carbons C1–C3 are dominated by the 3-fold term cos 3ϕ, but several of the carbons in the three basis sets require 6-fold contributions. Since the latter are less than 0.1 ppm, they do not appear in eqs 6a–c. The problem of imbalance in the double-ζ basis set, which was noted for ethane in the previous section, is most evident for the C2 carbon of propane in eq 6b. The experimental chemical shifts are about the same for the C1 and C2 carbons of propane (see Table III) so that the C2 shielding is underestimated by about 7 ppm with this basis set.

The IGLO ^{13}C shielding results for propane using basis set II are plotted in Figure 2 as a function of the dihedral angle ϕ,[31,32] which is measured about the C2–C3 bond. Note in Figure 2 that the ^{13}C shieldings for the C1 and C3 carbons only coincide for the all trans arrangement as the C3 methyl group is rotated about the C2–C3 bond. With basis set II the calculated shielding data for the C2 carbon actually fall *below* those for C1 carbon. However, with basis set III (see Table V) there is overlap of the shielding curves for carbons C1 and C2 for most of the range of dihedral angles. Moreover, note that the coefficients of the 3-fold terms agree more closely between basis sets I and III in Table V. The solid lines through the calculated data points in Figure 2 correspond to the linear regression results of the basis II propane shielding data from Table V. Neglecting terms with coefficients
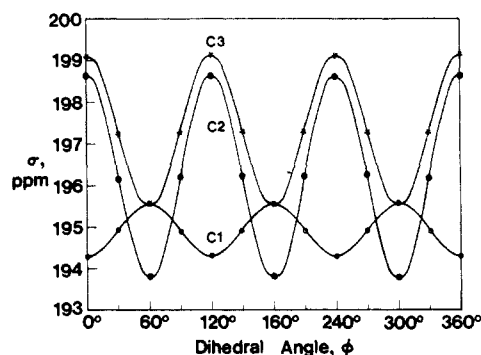

Figure 2. Calculated (basis set II) ^{13}C isotropic shielding data σ for the C1–C3 carbons in propane plotted as a function of the dihedral angle ϕ for (O), C1; (●), C2; and (*), C3. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression from Table V.
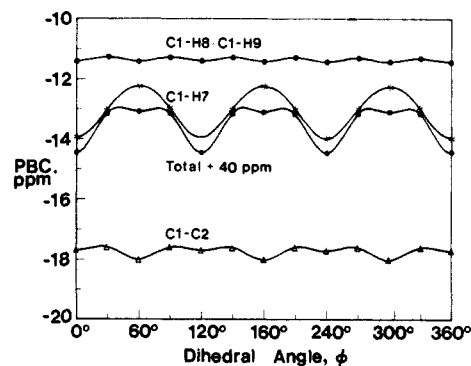

Figure 3. Angular dependence of the local bond paramagnetic contributions PBC to the shielding for the C1 carbon of propane 10 using basis set II: (O), average for the C1–H8 and C1–H9 bonds, (*), C1–H7 bond; (△), C1–C2 bond; (●), total (+40 ppm) for all bonds on C1.

less than 0.1 ppm, the resulting expressions for the conformational dependencies of the C1–C3 shielding, are given by

$$\sigma_{C1}(\phi) = -0.6 \cos 3\phi + 194.9 \text{ ppm} \tag{7a}$$

$$\sigma_{C2}(\phi) = 2.4 \cos 3\phi + 196.2 \text{ ppm} \tag{7b}$$

$$\sigma_{C3}(\phi) = 1.8 \cos 3\phi + 197.3 \text{ ppm} \tag{7c}$$

which will be used in the section on α-, β-, and γ-substituent effects. Since the simplest model for all three of these effects makes use of the differences between the chemical shielding (or chemical shifts) of propane and *n*-butane, their origins stem from the electronic factors which determine the shielding for *both* of these compounds. For the C1 carbon of propane the most important contributions to the angular dependence of the shielding (basis set II) arise from the four localized bonds on C1. The paramagnetic bond contributions (PBC) associated with each of the four localized bonds and the totals for each of the carbon atoms C1, C2, and C3 were fit in the least-squares sense to eq 3, and the coefficients A_n are entered in Table VI. The *sum* of contributions from C–H bonds on either side of the C1–C2–C3 plane, e.g., C1–H8 and C1–H9, is nearly constant and can more easily be fit to eq 3 with high precision than the contribution from individual C–H bonds. In Table VI, data for each of C1's four bonds are plotted in Figure 3 as a function of the dihedral angle ϕ about the C2–C3 bond.[32] For example, the curve (open circles) at the top of the figure is the average of the contributions from the C1–H8 and C1–H9 bonds, which are gauche to the C3 carbon as depicted in 10. The curve (triangles) at the bottom of Figure 3 corresponds to the PBC from the C1–C2 localized MO. Since PBC contributions from C1–H8, C1–H9, and C1–C2 have only a small dependence on dihedral angle, only that PBC associated with the C1–H7 bond trans to C3 (asterisks in Figure 3) exhibits a significant dependence on dihedral angle about the C2–C3 bond. Clearly, the PBC of C1–H7 are most important for the total PBC
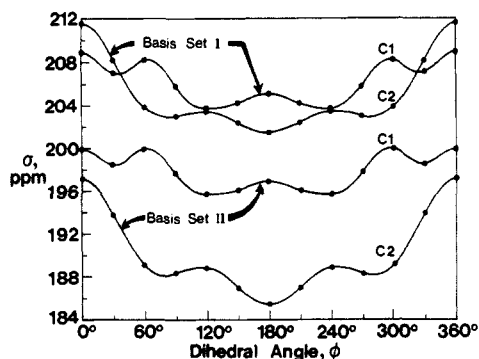
Figure 4. Plots of the ^{13}C isotropic shielding σ for the C1 and C2 carbons in *n*-butane **11** versus ϕ for basis set I and II: (O), C1 and (●), C2. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression from Table V.

(shifted by 30 ppm and represented by the line with filled circles in Figure 3) for the four bonds on C1.

A somewhat different picture emerges for the origin of the dominant contributions to the C2 carbon shielding. The conformational dependencies of the paramagnetic bond contributions (basis set II) arising from each of the four bonds are given in Table VI. In this case all four of the bonds on C2 as well as their sum exhibit 3-fold dependencies of the PBC. The situation for PBC to shielding for the C3 carbon of propane, which are also given in Table VI, is slightly more complex: as the C3 methyl is rotated about the C2–C3 bond, each of the three C–H bonds has conformational dependencies which are shifted by 120°, so that the sum depends on cos 3ϕ. The PBC associated with the C2–C3 bond also have this 3-fold symmetry.

3. *n*-Butane. (a) Dependence of the Shielding on the Dihedral Angle ϕ About the C2–C3 Bond. To explore the origin of the γ-effect Seidman and Maciel[5] performed highly parameterized, semiempirical GIAO calculations for *n*-butane as a function of the torsional angle ϕ. In some cases their results for *n*-butane have qualitative similarities to the ab initio data reported here. Seidman and Maciel[5] concluded that C–H bond polarization by nonbonded hydrogens was not sufficient to explain the origins of the γ-substituent effects.

The IGLO isotropic ^{13}C shielding results[31] for carbon atoms C1 (C4) and C2 (C3) of *n*-butane (**11**) with a double-ζ basis set (basis set I in Table I) are plotted in Figure 4 at 30° intervals of the dihedral angle ϕ, which is measured about the C2–C3 bond.[31,32] Clearly, the angular dependencies are complex, and
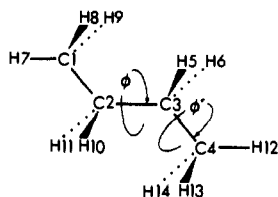
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it is not surprising that all six terms are required to obtain a precise representation of the calculated data points in Figure 4. The explicit dependencies of the calculated IGLO shielding results for carbons C1 and C2 with basis set I are given by (neglecting terms in Table V with coefficients less than 0.1 ppm)

$$\sigma_{C1}(\phi) = 2.2 \cos \phi + 0.3 \cos 2\phi - 0.9 \cos 3\phi + 0.4 \cos 4\phi + 0.6 \cos 5\phi + 0.3 \cos 6\phi + 206.0 \text{ ppm} \quad (8a)$$

$$\sigma_{C2}(\phi) = 3.4 \cos \phi + 1.7 \cos 2\phi + 1.6 \cos 3\phi + 0.2 \cos 4\phi + 204.5 \text{ ppm} \quad (8b)$$

The conformational dependencies in eqs 8a and 8b are dominated by the cos ϕ terms which have maxima at 0° and minima at 180°. The cos 2ϕ terms have relative maxima at 0° and relative minima at 90°. The "wiggles" near 60° and 180° arise from the 3-fold

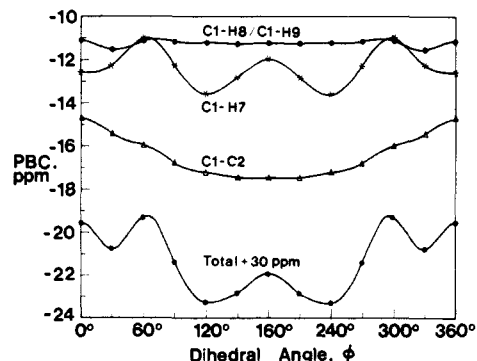**Figure 5.** Calculated local bond paramagnetic contributions PBC to the ^{13}C isotropic shielding for carbon C1 (C4) (basis set II) in *n*-butane plotted as a function of ϕ: (O), average for the C1–H8 and C1–H9 bonds; (*), C1–H7 bond; (△), C1–C2 bond; (●), total (+30 ppm) for all bonds on C1. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression.

term (cos 3ϕ); a difference in sign for this term between eqs 9a and 9b leads to relative maxima for the C1 shielding (open circles) and relative minima for the C2 shielding (filled circles) in Figure 4. The remaining terms in eqs 9a and 9b are small. As in ethane and propane the calculated shielding for the C2 or α-carbon of *n*-butane is badly underestimated at the double-ζ level. Improvement is noted for basis set II, for which the calculated shielding data[31] are also plotted in Figure 4.[32] Conformational dependencies for the C1 and C2 carbon shielding data of *n*-butane (basis set II, neglecting terms in Table V with coefficients less than or equal to 0.1 ppm) are given by

$$\sigma_{C1}(\phi) = 1.9 \cos \phi - 0.9 \cos 3\phi + 0.3 \cos 4\phi + 0.5 \cos 5\phi + 0.3 \cos 6\phi + 197.7 \text{ ppm} \quad (9a)$$

$$\sigma_{C2}(\phi) = 3.9 \cos \phi + 1.5 \cos 2\phi + 1.8 \cos 3\phi + 189.7 \text{ ppm} \quad (9b)$$

The conformational features as determined by the coefficients of the trigonometric functions are not significantly altered on increasing the quality of the basis set: the largest change is 0.5 ppm between the cos ϕ terms in eqs 8b and 9b. Clearly, the major changes are the 8.3 and 14.8 ppm decreases in the constant values (*B* in eq 3) for C1 and C2, respectively. The substantial improvements are reflected in the 3–10 ppm separations between the calculated C1 and C2 carbon shieldings (open circles and filled circles, respectively, in Figure 4) for basis set II.

To study the origin of the angularly dependent substituent effects, the individual bond paramagnetic contributions to the shielding from the four localized bonds and their totals for carbon atoms C1 and C2 were fit in the least-squares sense to eq 3, and the coefficients were entered in Table VI. Data are included for basis set II. As with propane, it was found that the *sum* of C–H bond contributions on either side of the C1–C2–C3 plane is nearly constant and gives a much better fit to eq 3 than the contribution from individual C–H bonds. The terms in the trigonometric expansions in eqs 8 and 9, which are the major contributors to each trend, are shown in Table VI.

For *carbon C1* (and C4) of *n*-butane the PBC are plotted as a function of the dihedral angle ϕ in Figure 5.[31,32] The average of the PBC from the C1–H8 and C1–H9 bonds (open circles) is essentially constant. The angularly independent changes involving the C1–H7 bond and the C1–C2 bond (asterisks and triangles, respectively, in Figure 5) are major terms in the total from the four bonds (filled circles in Figure 5). The paramagnetic bond contributions from the C1–C2 bond are determining factors in the cos dependence on dihedral angle in eqs 8a and 9a. The next most important contribution to the angular dependence arises from the C1–H7 bond *which is directed away from the C4 methyl.* The angular dependence of the C4 shielding is related to the origin of the γ-effect. Therefore, it is surprising that the *bonds on the C1 carbon which are in closest proximity to the C4 methyl make*

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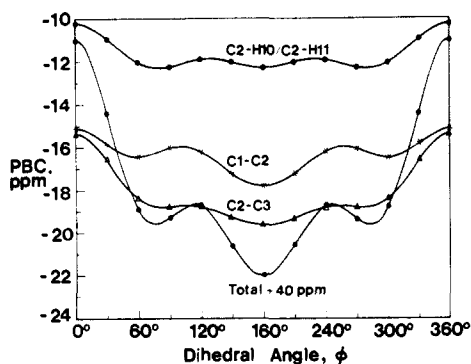
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Figure 6. Plots of the calculated local bond paramagnetic contributions PBC to the ^{13}C isotropic shielding for carbon C2 (C3) (basis set II) in *n*-butane versus ϕ: (O), average for the C2-H10 and C2-H11 bonds; (*), C1-C2 bond: (Δ), C2-C3 bond: (●), total (+40 ppm) for all bonds on C2. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression.
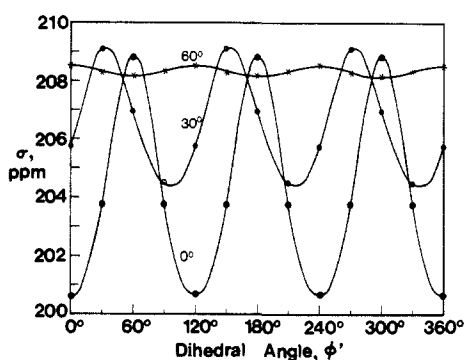
Figure 7. Plots of the calculated ^{13}C isotropic shielding σ (basis set II) for the C1 carbon in *n*-butane 11 versus ϕ' for ϕ = 0° (●), 30° (O), and 60° (*). The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression.

the least important contributions to the C1 isotropic shielding!

Factors which influence the angular dependencies of the α- and β-effects are examined with the help of Figure 6. The PBC for the ^{13}C shielding of the C2 (C3) carbon, which are found in the IGLO calculations for *n*-butane with basis set II, are plotted as a function of the dihedral angle ϕ. The PBC which represent averages for the C2-H10 and C2-H11 bonds (open circles in Figure 6) are relatively constant between 60° and 300°, and they are 6-8 ppm less negative (more shielded) than the PBC of the C1-C2 and C2-C3 bonds (asterisks and triangles). It was noted previously that the downfield shifts and approximate additivity associated with α- and β-effects are attributable, in large part, to the fact that the angularly independent part of the PBC for C-C bonds are more negative than for C-H bonds. However, the angularly dependent part of the total C2 shielding (filled circles in Figure 4 and 6) varies by about 10 ppm over the entire range of dihedral angles.

(b) Dependence of the Shieldings on the Dihedral Angle ϕ' About the C3-C4 Bond and ϕ About the C2-C3 Bonds—Mechanisms of the γ-Effects. To further investigate the dependence of the ^{13}C isotropic shielding on the proximity and orientation of the C1 and C4 methyl groups, a series of calculations (basis set I only) were performed in which the dihedral angle ϕ', which is measured about the C3-C4 bond in 11, was varied at 30° intervals. The ^{13}C isotropic shielding data[31] for the C1 carbon are plotted in Figure 7[32] as a function of the torsional angle ϕ' for ϕ = 0, 30, and 60°. It can be seen that the C1 shielding varies by about 8 ppm as ϕ' is varied with the dihedral angle ϕ, which is measured about C2-C3, fixed at 0° (filled circles in Figure 7). A most interesting feature in Figure 7 is the minimum which occurs in this curve for ϕ = 0°. In this arrangement the C4-H12 bond is pointed toward the C1 methyl group. The calculated minimum of about 201 ppm for the ^{13}C isotropic shielding would correspond
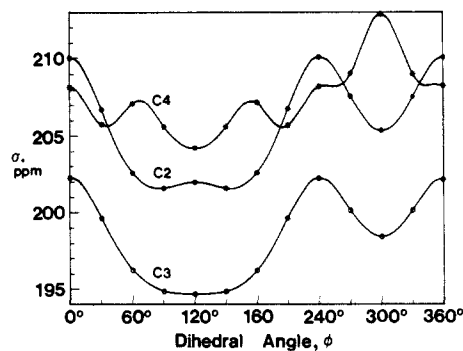

Figure 8. Angular dependence of the calculated (basis set I) ^{13}C isotropic shielding σ for the C2-C4 carbons in 2-methylbutane plotted as a function of the dihedral angle ϕ: (●), C2; (O), C3; and (*), C4. The IGLO results are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression from Table V.

to a downfield γ-effect of about 2 ppm. Thus, it appears that *γ-substituent effects of positive sign are possible depending on the 1,4-orientations* associated with both the carbons and the hydrogens.

Again, it is instructive to examine the paramagnetic bond contributions at the C1 carbon as the C4 methyl is rotated: for ϕ = ϕ' = 0° the paramagnetic contribution from the C1-H7 bond assumes its most negative value in this basis set (-15.0 ppm compared with a value of -11.4 ppm for ϕ' > 60°), whereas contributions from the proximate C1-H8 and C1-H9 bonds are about 1 ppm more negative. Another unusual feature occurs for the C1 shielding in this conformation: there is a contribution of -1.3 ppm from the C4-H12 bond directed toward the C1 methyl group. Moreover, there appears to be little or no dependence of the shielding on the dihedral angle about C3-C4 in those cases in which the C2-C3 dihedral angle is greater than about 30° (Figure 7). Clearly, the methyl group orientations are exceedingly important for the γ-effects on ^{13}C chemical shifts, but major changes occur in the C1-H7 bond on C1 which is directed away from the proximate C4 methyl group.

4. 2-Methylbutane. The model compounds 2-methylbutane and 2,2-dimethylbutane should be more appropriate than *n*-butane because any experimental studies of the conformational dependencies of α-, β-, and γ-effects would most likely be performed in cyclic molecules in which the C1-C4 carbons are part of a ring structure. For example, structures 12a-c for a 2-methylbutane moiety correspond to dihedral angles of 60°, 180°, and 300°; if C4 and C1 are ring carbons of cyclohexane, then 12a and 12c correspond to C5 being an equatorial- and axial-substituted methyl, respectively. The transferability of the ^{13}C shielding conformational dependencies from simpler molecules (*n*-butane) to 2-methyl- and 2,2-dimethylbutanes is also of interest because of the potential for extension to more complicated molecular systems.

12a. ϕ =60°   12b. ϕ = 180°   12c. ϕ=300°
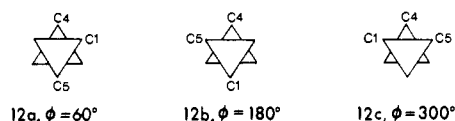
The IGLO isotropic ^{13}C shielding results for carbon atoms C1-C5 of 2-methylbutane were calculated with a double-ζ basis set and the data for carbons C2-C4 plotted in Figure 8 at 30° intervals of the dihedral angle ϕ.[31,32] The latter is measured about the C2-C3 bond. The calculated IGLO shielding data for the C2-C4 carbons of 2-methylbutane are poorly represented by the six-term Fourier series which depend on the torsional angle ϕ in eq 3. In fact, standard deviations in the calculated σ are as small as those for *n*-butane in Table V only if the linear regression analyses are performed with the dihedral angle θ = ϕ - 120° instead of ϕ in eq 3. This is precisely the result which would be expected from transferability of the paramagnetic bond contributions. If the angularly dependent contributions were strictly additive, then the dependencies of the shielding for carbons C2

Table VII. Coefficients of Fourier Expansions for the Paramagnetic Bond Contributions (PBC) to Total Isotropic Shielding Data for Carbons C2–C4 of 2-Methylbutane (Basis Set I)[a]

	atom/PBC	A_1	A_2	A_3	A_4	A_5	A_6	B
				Basis Set I				
C2:	C2–H6	−1.0	−0.7	0.3	−0.1			−9.6
	C2–C1/C2–C5	−0.9	−0.1	0.9		−0.1		−22.2
	C2–C3	−1.2	−0.4	0.5	0.1	0.1	−0.1	−12.0
	total	−3.0	−1.2	1.8				−43.8
C3:	C3–H10/C3–H11	−0.9	−1.2	0.6				−22.4
	C2–C3	−1.2	−0.5	0.5				−14.8
	C3–C4	−0.7	0.4	0.5				−12.3
	total	−2.8	−1.4	1.6				−49.6
C4:	C4–H7	−0.7	0.4	−1.0	−0.1	−0.2	0.2	−11.3
	C4–H8/C4–H9	−0.2	0.4	−0.1	−0.1	−0.2	0.2	−19.8
	C3–C4	−1.2	−0.1			−0.1	0.1	−11.4
	total	−2.1	0.7	−1.1	−0.2	−0.5	0.5	−42.5

[a] Standard deviation in the computed value of PBC are less than 0.01 ppm.

and C4 would involve the sum of $\sigma(\phi)$ for n-butane and $\sigma(\phi - 240°)$ which is defined for the C5 methyl at the C2 carbon of n-butane with a dihedral angle of $\phi - 240°$. A simple trigonometric identity,

$$A_n[\cos n\phi + \cos n(\phi - 240°)] = C_n \cos n(\phi - 120°) \quad (10)$$

where $C_n = -A_n$ for $n = 1, 2, 4,$ and $5, C_n = 2A_n$ for $n = 3$ and 6 provides the basis for excellent representations of the angular dependencies of the shielding by the Fourier series in $\theta = \phi - 120°$ in Table V. Equation 10 suggests an approximate "fragment model" in which the chemical shielding is obtained as the sum of the expressions for n-butane at the two dihedral angles. However, it is necessary to correct for replacement of a C–H bond by a C–C bond by subtracting the calculated propane shielding data for the same basis set. Thus, with this model the conformational dependence of the C4 shielding in 2-methylbutane for basis set I based on eqs 8a and 10 is given approximately by

$$\sigma_{C4}(\phi) = -2.2 \cos \theta - 0.3 \cos 2\theta - 1.0 \cos 3\theta - 0.4 \cos 4\theta -$$
$$0.6 \cos 5\theta + 0.6 \cos 6\theta + 208.2 \text{ ppm} \quad (11)$$

with similar expressions for shielding of the C2 and C3 carbons. This procedure leads to results which are consistent with calculated data for the C2–C4 carbons of 2-methylbutane in Table V.

The individual bond paramagnetic contributions to the shielding for basis set I from each of the four localized bonds and their totals for carbon atoms C2, C3, and C4 were fit in the least-squares sense to eq 3 and the coefficients entered in Table VII. Again, it was found that the *sum* of contributions from C–H bonds on either side of the C1–C2–C3 plane is nearly constant and gives a much better fit to eq 3 than the contribution from individual C–H bonds. The major contributors to each of the trends in the trigonometric expansion for the 2-methylbutane shielding can be seen in Table V.

The calculated IGLO ^{13}C shielding data for the C1 and C5 carbons of 2-methylbutane with basis set I, which were fit to six-term Fourier series in $\cos n\phi$ and $\cos n(\phi - 240°)$, respectively, are entered in Table V. The representations are not as good, e.g., $r^2 = 0.985$, as the almost exact agreement noted for most of the data in Table V. However, it is important to note that the angular dependencies of the shieldings for these carbons are close to those for n-butane obtained with the same basis set. The largest difference of 0.37 ppm between the coefficients A_2 occurs for the C1 carbon of n-butane and the C1, C5 carbons of 2-methylbutane in Table V; four of the six coefficients A_n are within 0.05 ppm.

5. 2,2-Dimethylbutane. The IGLO isotropic ^{13}C shielding results for the C2–C4 carbons atoms of 2,2-dimethylbutane with a double-ζ basis set (basis set I in Table I), which were fit to functions with two terms under the summation in eq 3, are entered in Table V. Conformational dependencies of the shielding are of the form

$$\sigma(\phi) = A_3 \cos 3\phi + A_6 \cos 6\phi + B \quad (12)$$

which are completely consistent with the n-butane conformational

shielding dependence on application of a trigonometric identity obtainable from eq 10

$$\cos n\phi + \cos n(\phi - 120°) + \cos n(\phi - 240°) = 3 \cos n\phi \text{ if } n$$
$$= 3,6,...$$
$$= 0, \text{ otherwise}$$
$$(13)$$

Therefore, the angular dependence of the C4 carbon of 2,2-dimethylbutane can be estimated from the fragment model with the propane and n-butane shielding data in eqs 6a and 8a, respectively. For example, if it is assumed that C2 carbon of n-butane has two hydrogens replaced by C5 and C6 methyl groups having dihedral angles $\phi - 120°$ and $\phi - 240°$, respectively, then the C4 shielding is given by

$$\sigma_{C4}(\phi) = -1.3 \cos 3\phi + 1.0 \cos 6\phi + 210.6 \text{ ppm} \quad (14)$$

The excellent agreement of the conformational part with the data in Table V yields the likelihood that it will be possible to apply the fragment model with the basis set II to larger molecules. Expressions for $\sigma_{C2}(\phi)$ and $\sigma_{C3}(\phi)$, which are obtained in this way, are also in good agreement with the angular dependencies of the ^{13}C isotropic shieldings for 2,2-dimethylbutane in Table V.

The C1 carbon shielding for 2,2-dimethylbutane exhibits a dependence on dihedral angle ϕ in Table V which is roughly of the form noted for the C1 carbon of n-butane in Figure 4. The shielding expressions σ_{C5} and σ_{C6} have the same coefficients as for the C1 carbon; however, the arguments of the trigonometric functions are $\phi - 120°$ and $\phi - 240°$, respectively. An approximate expression for these shielding calculations can be based on the additive fragment scheme

$$\sigma_{n\text{-butane}}(\phi) + \sigma_{\text{neopentane}} - \sigma_{\text{propane}}(\phi)$$

which yields

$$\sigma_{C1}(\phi) = 2.2 \cos \phi + 0.3 \cos 2\phi - 0.2 \cos 3\phi + 0.4 \cos 4\phi +$$
$$0.6 \cos 5\phi + 0.3 \cos 6\phi + 191.9 \text{ ppm} \quad (15)$$

Except for the coefficients of the second and third terms, eq 15 is consistent with the corresponding expression in Table V.

C. Conformational Dependencies of the α-, β-, and γ-Substituent Effects. The usual criterion for determination of the magnitude of all three substituent effects is based on the difference between the values for compounds with and without the methyl group. Accordingly, the differences between the calculated ^{13}C isotropic shielding data for n-butane and propane with basis set I in Table V give the following substituent shifts:

$$\delta_\alpha(\phi) =$$
$$-3.4 \cos \phi - 1.7 \cos 2\phi - 0.4 \cos 3\phi - 0.2 \cos 4\phi + 1.1 \text{ ppm}$$
$$(16a)$$

$$\delta_\beta(\phi) =$$
$$-3.4 \cos \phi - 1.5 \cos 2\phi + 0.4 \cos 3\phi - 0.2 \cos 4\phi + 7.2 \text{ ppm}$$
$$(16b)$$

$$\delta_\gamma(\phi) = -2.2 \cos \phi - 0.3 \cos 2\phi + 0.2 \cos 3\phi - 0.4 \cos 4\phi -$$
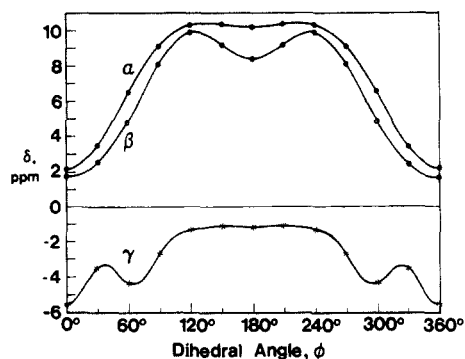$$0.6 \cos 5\phi - 0.3 \cos 6\phi - 2.2 \text{ ppm} \quad (16c)$$

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Figure 9. Angular dependencies of the α-, β-, and γ-effects δ for basis set II taken as the differences between the propane and n-butane shielding results: (●), α; (O), β; and (*), γ. The IGLO data are given at 30° intervals of the dihedral angle; the solid lines correspond to the results of the linear regression. Note that the shifts δ are measured in a direction opposite to σ.

It is important to note that both the α- and β-substituent effects in eqs 16a and 16b are in a range of about 8 ppm depending on torsional angle, even though the entire range of values for $\delta_\alpha(\phi)$ is about 8 ppm too small in magnitude. The equality of the first two coefficients in eqs 16a and 16b suggests a common mechanism for the angularly dependent parts of the α- and β-effects. Equation 16c is in accord with the major experimental criteria for the conformational dependence of γ-substituent effects which are described in the Introduction.

Because of the failure of basis set I to reproduce the shielding at the C2 carbons, it is important to discuss the conformational dependencies of α- and β-substituent effects obtained with basis set II:

$$\delta_\alpha(\phi) = -3.9 \cos \phi - 1.5 \cos 2\phi + 7.6 \text{ ppm} \quad (17a)$$

$$\delta_\beta(\phi) = -3.9 \cos \phi - 1.5 \cos 2\phi + 0.6 \cos 3\phi + 6.5 \text{ ppm} \quad (17b)$$

$$\delta_\gamma(\phi) = -1.9 \cos \phi + 0.3 \cos 3\phi - 0.3 \cos 4\phi - 0.5 \cos 5\phi - 0.3 \cos 6\phi - 2.8 \text{ ppm} \quad (17c)$$

The substituent shifts from these equations are plotted as a function of dihedral angle in Figure 9. The most important difference between the two sets of results occurs in the 6.5-ppm increase in the constant part of the α-substituent shifts. In all cases the shapes of the curves are similar for the same carbons with the two basis sets, and, except for the α-carbon, the results are the same within less than one ppm. In contrast to a prediction of only negative values for γ-substituent effects, the α- and β-effects are positive everywhere in Figure 9. The similarity of the curves for the α- and β-effects in Figure 9 comes as no surprise since both are derived from the shielding data for the C2 carbon of n-butane in Figure 4.

For this discussion it is convenient to separate each of the α-, β-, and γ-substituent effects into a part δ^A, which is dependent on the dihedral angle, and a part δ^B which is not. The latter can be identified with the A_n and B terms in eq 3. Implicit in the empirical expression for ^{13}C chemical shifts (eq 1) is the assumption that the angular part δ^A vanishes in aliphatic systems for which there is rotational averaging about the C–C bonds. For a simple average over free rotation about the C2–C3 bond, the cos $n\phi$ terms in eq 3 vanish identically, and the average of the calculated substituent effects from eqs 17a–c are $\langle\delta_\alpha\rangle = 7.6$, $\langle\delta_\beta\rangle = 6.5$, and $\langle\delta_\gamma\rangle = -2.8$ ppm. Identification of these quantities with the angularly independent terms δ^B for each type of substituent and the assumption of additivity leads to eq 1. The calculated rotational averages are in reasonable conformity with the empirical values of 9.1, 9.4, and -2.5 ppm, respectively, from eq 1. An alternative to *free* rotation is the assumption of simple, hindered rotation about the C–C bonds: from eqs 17a–c this leads to the values $(2/3)\delta_{\text{gauche}} + (1/3)\delta_{\text{trans}} = 7.7$, 5.9, and -3.3 ppm for the α-, β-, and γ-effects, which are also in reasonable conformity with the empirical values from eq 1.
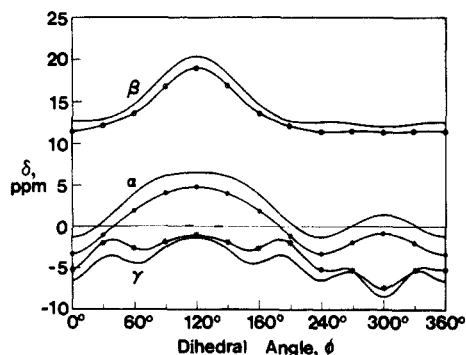
Figure 10. Angular dependencies of the calculated (basis set I) α-, β-, and γ-effects for 2-methylbutane plotted as a function of the dihedral angle ϕ: (●), α; (O), β; (*), γ. The data at 30° intervals of the dihedral angle were obtained as differences between the propane and 2-methylbutane shielding results. The solid lines through the data points correspond to the results of the linear regression. Also included are data for 2-methylbutane, which was obtained from the basis set I data for n-butane assuming additivity. The resulting curves, which do not have symbols, are only slightly displaced from those for 2-methylbutane.

The origins of the α-substituent effects δ_α^B, as usually defined, follow from the B terms in Tables VII and VIII wherein the paramagnetic bond contributions for C–C bonds are invariably larger in magnitude (more negative) by several ppm than for C–H bonds. Thus, replacement of a C–C bond by a C–H bond, such as by methyl group substitution, leads to a decrease in the total shielding, which should be approximately additive in the absence of conformational effects. The α- and β-substituent effects have a similar origin. This can be seen by comparing the ethane data with the propane data in Table VI. The introduction of a methyl group at the C2 carbon leads to a value of the C1–C2 bond paramagnetic contribution at C1 which is several ppm more negative than the ethane value. Contributions from each of the C1–H bonds are 2-3 ppm more negative than the ethane values. The *conformational dependencies* δ_α^A and δ_β^A of the α- and β-effects arise primarily from the cos ϕ terms which occur in the PBC associated with all four bonds at the C2 (C3) carbon atoms of n-butane in Table VI. Interestingly, the cos 3ϕ term in eq 18a disappears completely because the coefficients of this term are of opposite signs in eq 7c (the C3 carbon of propane) and in eq 9b (the C2 carbon of n-butane). However, complete cancellation of this term does not occur for the β-effects in eq 17b.

Appropriate model compounds for the angularly dependent α-, β-, and γ-substituent effects are 2-methylbutane and 2,2-dimethylbutane since experimental criteria for measurement of the effects require cyclic molecules such as in Table IV where carbons C1–C4 are part of a ring. Accordingly, α-, β-, and γ-substituent effects are taken to be the differences between the calculated ^{13}C isotropic shielding (basis set I) values for carbons C1–C3 of propane and carbons C2–C4 of 2-methylbutane from Table V. These are plotted as a function of the dihedral angle ϕ in Figure 10. The shapes of the curves in this figure might appear strange in comparison with those for the α-, β-, and γ-effects in Figure 9. In fact, all of these features are implicit in the data for n-butane. It is implicit in the fragment model (proposed in the previous section) that the substituent effects for 2-methylbutane will be given by the sum of the n-butane values in eqs 16a–c at ϕ and $\phi - 240°$

$$\delta_\alpha(\phi) = 3.4 \cos \phi + 1.7 \cos 2\phi - 0.8 \cos 3\phi + 0.2 \cos 4\phi + 2.2 \text{ ppm} \quad (18a)$$

$$\delta_\beta(\phi) = 3.4 \cos \phi + 1.5 \cos 2\phi + 0.8 \cos 3\phi + 0.2 \cos 4\phi + 14.4 \text{ ppm} \quad (18b)$$

$$\delta_\gamma(\phi) = 2.2 \cos \phi + 0.3 \cos 2\phi + 0.4 \cos 3\phi + 0.4 \cos 4\phi + 0.6 \cos 5\phi - 0.6 \cos 6\phi - 4.4 \text{ ppm} \quad (18c)$$

Data from eqs 18a–c are plotted (curves without symbols) in Figure 10 as a function of the dihedral angle ϕ. The agreement

between the two sets of data provides justification for the additivity of substituents, and it permits obtaining approximate α-, β-, and γ-effects equivalent to basis set II results for 2-methylbutane from the n-butane data in eqs 17a–c. A similar scheme, which makes use of the trigonometric identity (eq 13), can be used to relate the substituent shifts in 2,2-dimethylbutane to those in n-butane (eqs 16a–c or 17a–c).

It was noted previously that the conformational dependencies of the α-substituent effects appear in the experimental $\Delta\delta_\alpha$ values of 5.9 and 0.4 ppm for the C1 carbon of equatorial and axial methylcyclohexanes in Table IV. It is of interest to examine the 2-methylbutane results for this dependence. For 2-methylbutane as the model compound, the equatorial and axial arrangements of the methyl group in methylcyclohexane correspond to dihedral angles of 60° in **12a** and 300° in **12c**. The data in Figure 10 correspond to the effects of two methyl groups at C2, but the data for $\Delta\delta$ in Table IV were obtained by subtracting the data for the parent compound, thereby removing the effects of the ring carbons. Therefore, it is necessary to subtract the effects of the C1 carbon in **12a** and **12c**. For the equatorial and axial arrangements of methylcyclohexane the calculated values $\Delta\delta$ are 1.2 and −1.6 ppm, respectively. For basis set I it is not surprising that these are in poor agreement with the experimental data. In view of the discussion leading to eqs 18a–c, it seems likely that the substituent effects for 2-methylbutane could also be obtained with basis set II data for n-butane, as this should provide a better description of the α-substituent effects. The values predicted for $\Delta\delta_\alpha$ are 10.0 and 6.4 ppm in comparison with the experimental solution data of 5.9 and 0.4 ppm, respectively. This overestimation of the magnitude of the α-effects should not be surprising since the chemical shifts are overestimated with basis set II in Table III, and the analysis in terms of the calculated shielding data in n-butane does not include the nonadditivity of the angularly independent α-effects. For the α-substituent effects it appears that basis sets I and II greatly underestimate and overestimate the $\delta_\alpha{}^B$ term, respectively, whereas the difference in the $\delta_\alpha{}^A$ for the two basis sets is only about 1 ppm. A better basis set for n-butane would be very useful for α-effects.

The β-substituent effects inferred for equatorial and axial cyclohexanes, based on the 2-methylbutane basis set I data in Figure 10, are 7.5 and 5.3 ppm. However, results based on basis set II in eq 18b, using the fragment model described above, are 8.3 and 4.7 ppm, which are in remarkably good agreement with the experimental values of 8.3 and 4.8 ppm for the C2 carbon of equatorial and axial methylcyclohexanes, respectively, in Table IV. For the 2(*exo*)- and 2(*endo*)-methylbicyclo[2.2.1]heptanes, assuming that the dihedral angles for the methyl groups are +120° and −120°, respectively, from the plane of the ethylene bridge, a value of 9.9 ppm is obtained for both from eq 17b. These estimates compare favorably with the experimental $\Delta\delta_\beta$ values of 10.2 and 10.6 ppm, respectively, for the methylbicyclo-[2.2.1]heptanes in Table IV.

In Figure 10 the minimum in the curve for $\delta_\gamma(\phi)$ occurs for ϕ = 300° which is the arrangement **12c** for 2-methylbutane and corresponds to the γ-gauche effect as might be found for the C3 carbon in axial methylcyclohexane. The γ-substituent effects inferred for the C3 carbon of equatorial and axial cyclohexanes, based on the 2-methylbutane basis set I data in Figure 10, are −1.0 and −4.7 ppm. However, if the γ-substituent effects are based on eq 17c with the argument given above, the $\Delta\delta_\gamma$ are −1.3 and −4.4 ppm for these angles, values which are also in reasonable conformity with the experimental values of −0.4 and −6.5 ppm in Table IV. The value for the γ-eclipsed arrangement when ϕ = 0° in eq 18c is −5.6 ppm, which is in good agreement with the experimental value for $\Delta\delta_\gamma$ of −5.6 and −6.6 ppm for 2(*endo*),3-(*endo*)- and 2(*exo*),3(*exo*)-dimethylbicyclo[2.2.1]heptanes, respectively, in Table IV.

Conclusions

The IGLO studies of ^{13}C isotropic shielding in hydrocarbons show that the *angularly dependent* parts of the substituent effects are relatively insensitive to the size of the basis sets. The double-ζ basis sets, which can most easily be applied to larger molecules

of interest, unfortunately do not account for the angularly *independent* part of the α-substituent effects. However, even with this inadequacy the IGLO calculations for the ^{13}C isotropic shielding, applied to a number of methyl-substituted cyclohexanes and bicyclo[2.2.1]heptanes, gave an average deviation of 1.3 ppm in the $\Delta\delta$ for the 29 carbons which are not directly bonded to the methyl substituent. Although the larger basis sets give much better agreement with the experimental data and can be implemented with appropriate computer facilities, the computations could not routinely be performed at this time.

The IGLO method satisfactorily describes the α-, β-, and γ-substituent effects in the ^{13}C NMR spectra of aliphatic and alicyclic hydrocarbons. These conformational dependencies, which are not always clearly defined by the experimental data, seem not to have been elucidated in previous ab initio theoretical studies. It seems likely that difficulties of ascertaining the conformational dependencies of the γ-substituent effect are due in part to the failure to recognize the angular dependencies of α- and β-effects. Moreover, in aliphatic and unstrained hydrocarbons the additivity relationships work reasonably well because hydrogens can only be in gauche or trans positions.

When each of these effects is analyzed in terms of the variations in the IGLO C–H and C–C paramagnetic contributions, it is found for n-butane that each bond exhibits a different dependence of the shielding on dihedral angle, while the calculated shieldings in propane have a cos 3ϕ dependence on dihedral angle ϕ. In contrast to a steric compression model for ^{13}C γ-substituent effects, the angular dependence of the calculated shielding at the C1 carbon of n-butane is dominated by the changes at the C1–C2 bond and the C1–H bond which is directed away from the C4 methyl group. In fact, the least important changes associated with the conformation dependencies of the C1 isotropic shielding are from the bonds on the C1 carbon which are in closest proximity to the C4 methyl. The calculated conformational dependencies of the ^{13}C substituent effects for 2-methyl- and 2,2-dimethyl-butanes appear to be quite different from those obtained for n-butane: however, the results are consistent with additivity of the trigonometric form for the γ-substituent effect in the simpler molecule.

The study of conformational effects on ^{13}C isotropic shielding in aliphatic and alicyclic compounds represents only a small fraction of the more general topic of conformational effects in NMR shielding. In particular, in this study there was no consideration of the implications of the internal angle changes, such as would occur in strained multicyclic compounds. Exceptions were the bicyclo[2.2.1]heptanes in Table IV. No attempt was made here to deal with the vast topic of heteroatoms and functional groups such as –CN, –CO$_2$H, etc., all of which have been incorporated into the angle-independent, empirical scheme of eq 1. Investigations of the importance of torsional factors for δ-substituent effects were not attempted because of the substantial size of an adequate basis set for even the simplest model compounds. Finally, it should be noted that the determinations here of the angular forms of the α-, β-, and γ-substituent effects and the applicability of a "fragment model" offer promise of extension of the empirical scheme of eq 1 to include conformational effects in cyclic molecules.

Supplementary Material Available: Tables containing all of the calculated shielding data, energies, paramagnetic bond contributions for basis set I, and α-, β-, and γ-substituent effects (12 pages). Ordering information is given on any current masthead page.