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Proximity and Conformational Effects on ^{13}C Chemical Shifts at the γ Position in Hydrocarbons

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Abstract: Using the modified-INDO finite perturbation theory of ^{13}C chemical shifts, a set of "computer experiments" was performed to explore the geometrical dependence of the shielding of methyl groups in systems where steric γ effects may be expected. The conformational dependences of the computed methyl-group ^{13}C shielding constants in *n*-butane and 2-butene systems were found to be substantial and to be qualitatively consistent with trends that have been popularly referred to as the γ effect. However, inspection of the computed electron density distributions and details of the geometrical dependences lead to the suggestion that the mechanism of the γ effect may be considerably more complex than the popularly accepted C–H bond polarization by nonbonded H⋯H interactions. Calculations on systems in which two methane or ethane molecules are brought close enough together to emphasize intermolecular H⋯H interactions and calculations on *n*-pentane conformers similarly lead to a conclusion that the nature and conformational relationship of the bonding connecting the interacting methyl groups may be at least as important as the proximity of nonbonded hydrogens.

(A) Steric Effects on ^{13}C Shielding and the γ Effect. In the early 1960's, as Paul and Grant[1] were examining the ^{13}C chemical shifts of linear alkanes with attention focused upon the possible existence of additivity relationships, an interesting pattern was uncovered. As Grant and Paul noted, and as can be seen in Table I in proceeding down the series from methane to propane, the chemical shift of the terminal carbon (C_1) moves increasingly toward lower shielding. The trend is reversed, however, for butane, in which the terminal carbon is more shielded than the terminal carbon of propane. This apparent reversal in trend has been noted in many saturated systems and has become known as "the γ effect". This effect, as noted by Woolfenden and Grant,[2] is also present in the alkenes but not in cumulenes or aromatics. An example of the γ effect in alkenes is included in Table I, where it can be seen that the methyl carbons on both isomers of 2-butene are more shielded than the methyl carbon on propene. The effect is far greater for the cis isomer. This type of data led Woolfenden and Grant[2] to suggest that the γ effect was due to a through space interaction of "groups which have coiled back upon one another". Grant et al.[2,3] went on to propose that this effect arose from electron repulsions between interacting C–H systems, which cause significant increases in the electron density about the carbon nucleus and, hence, it was argued, an increase in shielding. As a shorthand notation, we will refer to this as the "C←H⋯H→C" interpretation. As a specific example, let us consider *n*-butane, which is shown in both cis and trans configurations in Figure 1. In a gauche or cis configuration, the hydrogen atoms on the terminal methyl groups are close enough to one another to give rise, in the popular interpretation of the γ effect, to electronic repulsions, inducing a polarization of electron density down the H–C bond toward carbon.

The idea of a γ effect, originally applied only to hydrocarbons, has been extrapolated to systems with heteroatoms involved. A "generalized" γ effect has been found experimentally to exist in hydrocarbon derivatives, where a methyl group is replaced by a halogen atom,[4] a hydroxyl group,[5] or an amino group.[6] Through-space steric repulsion has been invoked as the probable cause of the generalized γ effect, although the mechanism has not been explored in detail, and, as Pehk and Lippmaa[7] have pointed out, hydrogen–hydrogen interactions cannot be invoked to explain all of the heteroatom effects, particularly when halogens are involved. This does not rule out steric repulsions completely, and indeed, arguments have been presented along these lines.[4] One would not necessarily expect a repulsive electronic interaction between a methyl hydrogen and a halogen or hydroxyl group. In fact, a microwave study[8] on propanol has shown that a *gauche* conformation is the most stable, being about 0.29 kcal lower in energy than the trans conformation, and ab initio calculations on propanol are in agreement with this result.[9]

In a more recent ^{13}C study, Grover, Guthrie, Stothers, and Tan[10] uncovered a result which seems very damaging to arguments in favor of a γ effect induced by heteroatoms by a steric mechanism of the type proposed by Grant and coworkers for hydrocarbons. Stothers and co-workers studied the conformational dependence of the effect on the ^{13}C chemical shift of substituents situated at the δ position. That study included the conformation I, which should be ideally constructed to exaggerate the kind of steric repulsion (between C(δ) and X) that has been invoked to explain the "generalized" γ effect. The authors found, for X = OH, that conformation I indeed exhibited the largest C(δ) shift from that of the unsubstituted analogue; however, the shift was to lower shielding, directly

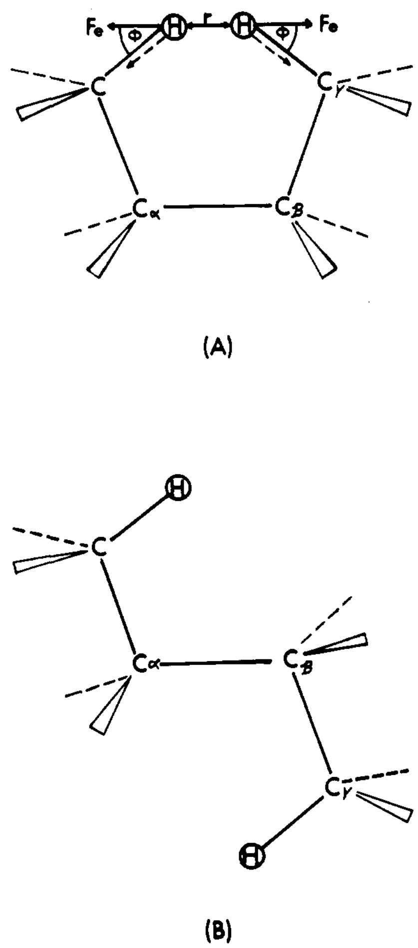

Figure 1. A pictorial representation of the γ effect as hypothesized by Grant and co-workers, using n-butane as an example. (A) The cis case. Fe is a vector representing the force due to electron-electron repulsion. θ is the angle between the force vector, Fe, and the bond between the interacting hydrogen and the methyl carbon. (B) The trans case. The interacting hydrogens are further apart and, hence, electron-electron repulsion is greatly reduced.

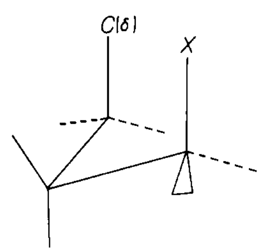

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Table I. Experimental ^{13}C Chemical Shifts of Some Hydrocarbon Systems Exhibiting the γ Effect[a]

	Alkanes C(methyl)	C(methylene)		
CH_4[b]	−2.1			
CH_3CH_3[b]	5.9			
$CH_3CH_2CH_3$[c]	15.4	15.8		
$CH_3CH_2CH_2CH_3$[c]	12.03	24.93		
	Alkenes	Methyl carbon[d]		
$CH_3CH{=}CH_2$		18.7		
$CH_3CH{=}CHCH_3$ (cis)		10.6		
(trans)		17.3		
	Methylcyclohexanes[e] C_α	C_β	C_γ	C_δ
Cyclohexane	27.26			
Methylcyclohexane	33.26	35.97	26.75	26.6
1,1-Dimethylcyclohexane	29.76	40.03	22.78	26.87
	Methylbenzenes	Methyl carbons[f]		
Toluene		−21.35		
o-xylene		−19.58		

[a] δ_C, ppm from TMS. [b] Reference 26. [c] Reference 1b. [d] Reference 27. [e] Reference 25. [f] Reference 2.

opposite that found for the γ effect of a hydroxyl group. While an explanation was not proposed, it was suggested that a theoretical explanation of the γ effect in terms of steric causes should be seriously reconsidered. This leads one to question whether there is more than one origin for the experimentally observed γ effect, even possibly in hydrocarbons, or whether there is only one type of origin which has little or nothing to do with sterically induced electronic repulsions.

The purpose of this investigation was to explore some of the possible origin(s) of conformational effects on γ carbons from a theoretical point of view. The approach adopted was to first test whether a theoretical method that has previously appeared to be promising, the modified-INDO finite perturbation method, could qualitatively reproduce conformational dependences consistent with what one would expect from the γ effect in hydrocarbons, i.e., larger *cis*- than *trans*-methyl shieldings in a four-carbon network. Having passed that test satisfactorily, this method was then applied to an exploration of steric interactions between methyl carbons by means of a systematic set of "computer experiments".

(B) Computational Methods. Ellis, Maciel, and McIver[11] reported a method of computing ^{13}C shielding constants at the INDO level,[12] using an approximate SCF-MO finite perturbation scheme.[13] The $\alpha\beta$ element (α or $\beta = x, y,$ or z) of the shielding tensor for nucleus M, $\sigma_{\alpha\beta}(M)$, was calculated using eq 1.

$$\sigma_{\alpha\beta}(M) = \sigma_{\alpha\beta}{}^{d}(M,M) + \sigma_{\alpha\beta}{}^{p}(M,M) + \sum_{K\neq M}^{\text{atoms}} [\sigma_{\alpha\beta}{}^{d}(M,K) + \sigma_{\alpha\beta}{}^{p}(M,K)] \quad (1)$$

In this equation, $\sigma_{\alpha\beta}{}^{d}(M,M)$ and $\sigma_{\alpha\beta}{}^{p}(M,M)$ are referred to as the local diamagnetic and paramagnetic contributions, respectively, to $\sigma_{\alpha\beta}(M)$ and $\sigma_{\alpha\beta}{}^{d}(M,K)$ and $\sigma_{\alpha\beta}{}^{p}(M,K)$ are contributions to that element of the shielding tensor for nucleus M due to the diamagnetic and paramagnetic currents, respectively, on the Kth atom. The two-center terms were computed using the long-range approximation of McConnell and Pople.[14] The one-center terms of eq 1 were calculated using eq 2 and 3, given by Ellis, Maciel, and McIver,[11]

$$\sigma_{\alpha\beta}{}^{d}(M,M) = 2\sum_{\mu}^{M}\sum_{\nu}^{M} R_{\mu\nu}{}^{(0)} \langle \chi_\mu{}^0 | h_{\alpha\beta}{}^{11}(M) | \chi_\nu{}^0 \rangle \quad (2)$$

$$\sigma_{\alpha\beta}{}^{p}(M,M) = 2\sum_{\mu}^{M}\sum_{\nu}^{M} \left(\frac{\partial R_{\mu\nu}}{\partial B_\alpha}\right)_0 \langle \chi_\mu{}^0 | h_{\beta}{}^{10}(M) | \chi_\nu{}^0 \rangle \quad (3)$$

In eq 2 and 3, $R_{\mu\nu}{}^{(0)}$ is the $\mu\nu$th element of the density matrix in the absence of a perturbation, and B_α is the x, y, or z component of the applied magnetic field strength. The definitions of $h_{\alpha\beta}{}^{11}(M)$ and $h_{\beta}{}^{10}(M)$ were given previously,[11] according to eq 4 and 5.

$$h_{\alpha\beta}{}^{11}(M) = \frac{e^2}{2mc^2}(\mathbf{r}_\nu \cdot \mathbf{r}_M \delta_{\alpha\beta} - r_{\nu\alpha} r_{M\beta})/|\mathbf{r}_M|^3 \quad (4)$$

Table II. Computed ^{13}C Shielding Constants for Alkanes[a]

Compd	Conform.[b]	θ,[c] deg	$\sigma_T(C_1)$[d]	$\sigma_T(C_2)$	$\sigma_T(C_1')$[e]	$\sigma_T(C_2')$
$CH_3(CH_2)_2CH_3$	A	0	−13.15	−23.78		
		30	−15.82	−25.47		
		60	−17.87	−26.27		
		90	−19.95	−28.48		
		120	−21.83	−30.61		
		150	−19.96	−28.46		
		180	−18.39	−26.52		
	B	0	−15.72	−25.70	−15.85	−25.98
		30	−15.09	−25.13	−15.46	−25.21
		60	−16.54	−25.92	−17.54	−25.75
		90	−17.67	−28.53	−19.96	−26.52
		120	−17.94	−30.75	−21.82	−26.87
		150	−17.99	−28.52	−20.01	−26.56
		180	−17.84	−26.53	−18.45	−26.30
	C	0	−16.24	−26.27		
		30	−16.16	−25.51		
		60	−16.73	−25.73		
		90	−17.71	−26.55		
		120	−17.95	−26.68		
		150	−17.98	−26.68		
		180	−18.57	−26.93		

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformations shown in Figure 2. [c] C_1-C_2-C_2'-C_1' dihedral angle as defined in Figure 2. [d] Total shielding (in ppm) computed for the indicated carbon. [e] $\sigma_T(C_1)$ and $\sigma_T(C_2)$ are equivalent to $\sigma_T(C_1')$ and $\sigma_T(C_2')$, respectively, for conformations A and C.

$$h_\beta{}^{10}(M) = \frac{eh}{mci}(\mathbf{r}_M \times \nabla)_\beta / |\mathbf{r}_M|^3 \quad (5)$$

In the modified INDO framework employed, a modified form of Slater's screening rules[15] was used to evaluate integrals of the types $\langle r^{-3}\rangle$ and $\langle r^{-1}\rangle$; this method is used to take into account the effects of different environments of nonequivalent carbon atoms on orbital size and takes the form of

$$\xi = [3.25 - 0.35(P - 4)]/2 \quad (6)$$

where ξ is the Slater exponent and P is the total valence-shell electron density of the carbon atom in question. Finally, the London approximation[16] was employed.

Ellis et al.[11,17] calculated ^{13}C shielding constants for a variety of molecules using this method and obtained fairly good qualitative agreement with experimental results. However, the method had some problems, among them the fact that for linear molecules the two-center portion of the core Hamiltonian reduces to the zero-order approximation under the London approximation, for certain directions of applied field. To alleviate this shortcoming Ellis and Seidman[18] modified the original theory by including certain two-center terms which had originally been neglected. If one expands the expectation value of the energy for a closed shell molecule in the presence of a combined magnetic field due to the presence of an external magnetic field, **B**, and the nuclear magnetic moments, μ_M, μ_K, . . . , one obtains for the two-center portion, using gauge invariant atomic orbitals[19] and the INDO approximation,[12] eq 7.

$$\begin{aligned} H_{\mu\nu}(\mathbf{B}) = \beta_{\mu\nu}S_{\mu\nu} &+ \beta_{\mu\nu}S_{\mu\nu}(ie/2hc)\mathbf{B}\cdot(\mathbf{R}_\mu \times \mathbf{R}_\nu) \\ &+ (ie/2hc)\beta_{\mu\nu}\mathbf{B}\cdot[\mathbf{R}_{BA} \times \textstyle\int \phi_\mu \mathbf{r}_\mu \phi_\nu d_\tau] \\ &+ (he/2mci)\mathbf{B}\cdot \textstyle\int \phi_\mu \mathbf{L}_\nu \phi_\nu d_\tau \end{aligned} \quad (7)$$

ϕ_μ and ϕ_ν are atomic basis functions, $S_{\mu\nu}$ is the overlap integral between ϕ_μ and ϕ_ν, and $\beta_{\mu\nu}$ is the atomic bonding parameter from the MO approximation at the INDO level;[12] $\mathbf{R}_\mu$ and $\mathbf{R}_\nu$ are vectors from the origin to the nuclear centers of atomic orbitals ϕ_μ and ϕ_ν, and $\mathbf{R}_{BA}$ is a vector from nucleus B to nucleus A. The operator $\mathbf{L}_\nu$ is given by

$$\mathbf{L}_\nu = \mathbf{r}_\nu \times \nabla \quad (8)$$

where $\mathbf{r}_\nu$ is a vector to the nuclear center of orbital ϕ_ν from an arbitrary point in space. The last term in eq 7 is called the two-center dipole term. These two terms were not included in the calculations reported by Ellis, Maciel, and McIver,[11] but were included in the modification introduced by Seidman and Ellis,[18] the form used in the calculations reported here. The details of this modification are given elsewhere.[18,20] Of course, in an approximate theory of this type, there are some two-center terms which are neglected (as well as all three-center and four-center terms).

This modified-INDO finite perturbation theory described above was employed to calculate ^{13}C shielding constants in the present study. Unless otherwise noted, standard geometries were used.[21] As in the previously reported work,[11] modified INDO parameters were employed. The $\frac{1}{2}(I + A)$ values used in this work are the same as those used in ref 11; the β^0 values used in this work: $\beta_C{}^0 = -15.0$ and $\beta_H{}^0 = -13.0$. Ab initio calculations were carried out using a "Gaussian 70" program employing a STO-3G basis set.[22]

In addition to the computed ^{13}C shielding constants, also presented in this paper are some of the electron distribution results obtained in the same calculations. These electron density results are *not* presented as a prime source of information on electronic distributions in these systems; more reliable sources would be ab initio results, or probably standard INDO or CNDO/2 results. These modified-INDO results are presented only to display the relationships between shielding constants and electron distributions in a self-consistent theory providing both types of information. In any case, there is a considerable amount of arbitrariness in partitioning electron density in any molecular orbital scheme, which should be kept in mind in considering the electron densities reported here.

Results and Discussion

(A) ^{13}C Shielding Constants for *n*-Butanes and 2-Butenes. Table II presents the calculated ^{13}C shielding constants for *n*-butane in a variety of conformations, specified in Figure 2. Table III presents the calculated ^{13}C shielding constants for 2-butene in a variety of conformations, also specified in Figure

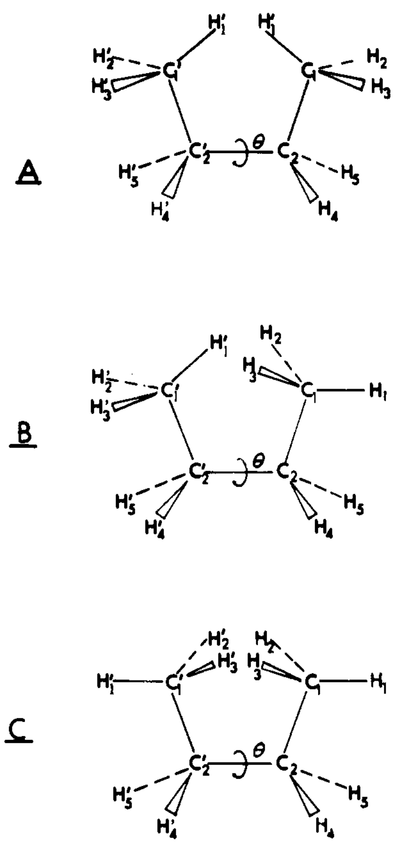


Figure 2. Configurations of *n*-butanes and 2-butenes employed in the calculations. θ is the C_1-C_2'-C_2-C_1 dihedral angle. Although only the *n*-butenes are shown, the same figures can be used to present the *cis*- and *trans*-2-butenes. The *cis*-2-butenes have the same key feature (the orientation of the methyl hydrogens). H_4 and H_4' will symbolize the ethylenic hydrogens attached to C_2 and C_2', respectively.

Table III. Computed ^{13}C Shielding Constants for Alkenes[a]

Compd	Conform.[b]	$\sigma_T(C_1)$[c]	$\sigma_T(C_2)$	$\sigma_T(C_1')$[d]	$\sigma_T(C_2')$
cis-CH_3CH=$CHCH_3$	A	−15.57	−143.62		
cis-CH_3CH=$CHCH_3$	B	−16.21	−144.76	−17.34	−145.59
cis-CH_3CH=$CHCH_3$	C	−17.06	−146.31		
trans-CH_3CH-=$CHCH_3$	B	−17.88	−144.88	−20.29	−145.50

[a] Computed by the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformations shown in Figure 2. [c] Total shielding (in ppm) computed for the indicated carbon. [d] $\sigma_T(C_1')$ and $\sigma_T(C_2')$ are equivalent to $\sigma_T(C_1)$ and $\sigma_T(C_2)$, respectively, for conformations A and C.

2. The calculated results shown in Table II tend to indicate the presence of a strong conformational dependence of a type generally consistent with what the traditional arguments would predict for a γ effect in the *n*-butane system, i.e., a higher shielding for cis than for trans C-C-C-C conformations. For a dihedral angle of 0°, the shielding is found to be the greatest for the sterically most crowded configuration A and the least for configuration C.

Figures 3-5 present plots of the calculated ^{13}C shielding constants for both the methyl and methylene carbons of *n*-butane for configurations A, B, and C, respectively, vs. the dihedral angle in the carbon framework. As the dihedral angle

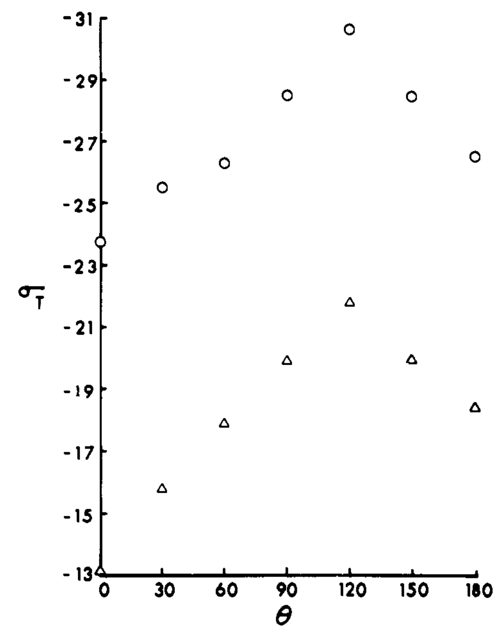


Figure 3. Plot of calculated ^{13}C shielding constants (σ_T, in ppm) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the A configuration of *n*-butane: (△) C_1; (○) C_2.

is changed from 0 to 180°, it is evident that configuration A is the most sensitive in terms of shifts of ^{13}C shielding constants. Configuration C shows the least response. Configuration B appears to act like a composite of configurations A and C with a few subtle differences. Essentially the plot of $\sigma_T(C_1')$ vs. the dihedral angle for configuration B closely parallels the plot for $\sigma_T(C_1)$ in configuration A, while the plot for $\sigma_T(C_1)$ in configuration B closely parallels the plot obtained for $\sigma_T(C_1)$ in configuration C. These results suggest that the dependence of the ^{13}C shielding of methyl carbon C_1 in *n*-butane upon the C_1'-C_2'-C_2-C_1 dihedral angle depends upon the conformational arrangement of the C_1 methyl group (e.g., the H_1-C_1-C_2-C_2') dihedral angle, ***but not on the conformational arrangement of the other methyl group.*** This is clearly not what one would expect for a γ effect based upon the C_1' $\leftarrow H_1' \cdots H_1 \rightarrow C_1$ interpretation, and suggests that the γ effect may be profitably considered, at least in part, as a manifestation of the conformational dependence of the entire bonding network, rather than just a result of nonbonded H⋯H repulsions. Furthermore, as the dependence of $\sigma_T(C_1)$ upon the C_1-C_2-C_2'-C_1' dihedral angle does not appear to depend significantly on the orientations of the hydrogen atoms on the C_1' methyl group, it might not be surprising if it did not depend even upon the *existence* of hydrogen atoms at that position. In these terms, the observation of a γ effect with "heavy atoms" that do not have attached hydrogen atoms (e.g., halogens) may be explainable. Also, as the orientation of the C_1' methyl hydrogens does not appear to be nearly as important as the orientation of the C_1 methyl hydrogens in determining the C_1 shielding, and as the orientation of C_1' itself (C_1-C_2-C_2'-C_1' dihedral angle) is highly important, perhaps the γ effect in hydrocarbons should be thought of more in terms of a 1-5 C_1'-C_2'-C_2-C_1-H_1 relationship than in terms of a 1-6 H_1'-C_1'-C_2'-C_2-C_1-H_1 relationship; the term "relationship" in this statement is not meant to imply a "steric interaction".

One of the most prominent features of the three plots of Figures 3-5 is that the behaviors of the ^{13}C shielding constants for the methylene carbons closely resemble the behavior of the methyl carbons in response to changes in the dihedral angle of the carbon framework, a feature that is readily apparent for conformations A and C in Figures 3 and 5, respectively. It is

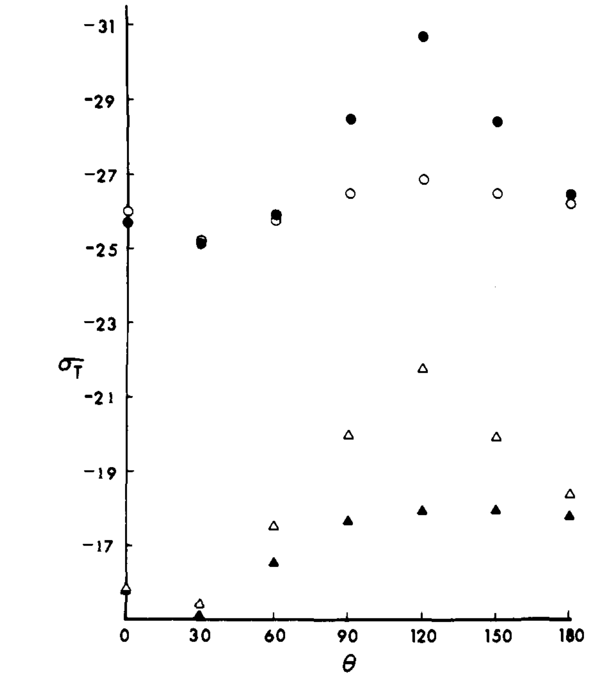


Figure 4. Plot of calculated ^{13}C shielding constants (σ_T, in ppm) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the B configuration of *n*-butane: (▲) C_1; (△) C_1'; (●) C_2; (○) C_2'.

interesting to note from Figure 4 that for configuration B, nonadjacent methyl and methylene carbons appear to behave in a similar manner. The variation in shielding of C_2' responds in a manner similar to that of C_1, while C_2 responds in a manner similar to C_1'. It is perhaps noteworthy that the plot of $\sigma_T(C_2)$ for B vs. the C_1'-C_2'-C_2-C_1 dihedral angle is nearly the same as that of $\sigma_T(C_2)$ for A, and the plot of $\sigma_T(C_2')$ for B vs. the C_1'-C_2'-C_2-C_1 dihedral angle is very similar to that of $\sigma_T(C_2)$ for C. Hence, as far as the dependence of $\sigma_T(C_2)$ or $\sigma_T(C_2')$ upon the C_1'-C_2'-C_2-C_1 dihedral angle is concerned, the orientations of the hydrogen atoms in the *adjacent* methyl group appears to be of no importance, but the orientation of the *nonadjacent* methyl group hydrogens is very important. This would tend to focus attention upon a 1-4 H_1'-C_1'-C_2'-C_2 relationship. In any case, the fact that conformational effects on $\sigma_T(C_2)$ and $\sigma_T(C_2')$ are predicted to be as important as those on $\sigma_T(C_1)$ and $\sigma_T(C_1')$ indicates that the substantial effects detected in these calculations are not due to the popular C←H⋯H→C mechanism, which could apply only indirectly to $\sigma_T(C_2)$, as the only mechanism responsible for observed γ effects. Such $\sigma_T(C_2)$ effects would typically be difficult to recognize experimentally, because of the uncertainties generally associated with conformational relationships or with other structural effects in rigid systems.

In order to gain additional insight into long-range geometrical effects on ^{13}C shifts, a set of calculations was carried out on the A configuration of *n*-butane in which the C_2-C_2' bond distance was varied from 1.48 to 1.70 Å. The results are shown in Table IV (part a). This set of calculations was designed to alter the distance between the hydrogen atoms of the two methyl groups without changing the angular conformations. Of course, altering the central carbon-carbon bond length represents a substantial perturbation to the molecule; such a perturbation could have some effects on C_1 shielding that would have nothing to do with a C←H⋯H→C mechanism or a conformationally sensitive mechanism for altering the C_1' shielding. It was hoped that uncertainties regarding such effects could be reduced by carrying out the calculations at more than one C_1'-C_2'-C_2-C_1 dihedral angle. Dihedral angles of 0, 120, and 180° were chosen for these calculations.

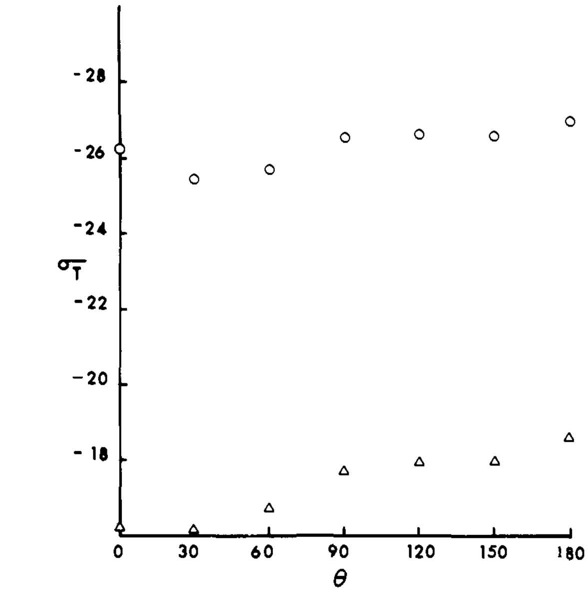


Figure 5. Plot of calculated ^{13}C shielding constants (σ_T, in ppm) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the C configuration of *n*-butane: (△) C_1; (○) C_2.

The results in Table IV indeed show that the computed ^{13}C shielding of the methyl carbons (as well as those of the methylene carbons) is sensitive to variation of the C_2'-C_2 distance. Inspecting only the results for a 0° dihedral angle, one sees that decreasing the C_2'-C_2 distance, which brings about a corresponding decrease in the H_1'-H_1 distance and the H_1'-H_1 overlap, results in an increased computed shielding for the methyl carbons; this could be taken as evidence for the popular C←H⋯H→C mechanism. An analogous, but much smaller, increase in computed shielding is obtained for the case of a 180° dihedral angle. However, the computed ^{13}C shielding results for a 120° dihedral angle show an even larger sensitivity to variation in the C_2'-C_2 distance, with a sense opposite to that of the 0 and 180° cases. The fact that the overall variation of computed methyl ^{13}C shielding with C_1'-C_2'-C_2-C_1 dihedral angle is greater for a shorter C_2'-C_2 is consistent with a γ-effect mechanism that is sensitively dependent upon the H_1'-H_1 distance. However, the fact that the sensitivity of the computed methyl shielding to variations in the C_2'-C_2 or H_1'-H_1 distances is even larger at a 120° dihedral angle (for which H_1'-H_1 overlap is negligible) than at 0° strongly suggests that factors other than the proximity and orientation of the C_1'-H_1' and H_1-C_1 moieties are important in determing the overall long range chemical shift effect.

A related set of calculations was carried out on an *n*-butane system with standard bond lengths, but with the C_1-C_2-C_2' angle varied (104, 109.5, and 114°); in these calculations the C_1-C_2-C_2'-C_1' dihedral angle was either 0 or 120°. The results are shown in part b of Table IV. For a 120° value of the C_1-C_2-C_2'-C_1' dihedral angle, $\sigma_T(C_1)$ varies monotonically over a small range as the C_1-C_2-C_2' angle is varied, presumably for reasons that have little to do with steric or conformational relationships between the methyl groups, as $\sigma_T(C_1')$ remains nearly constant. For a 0° value of the C_1-C_2-C_2'-C_1' dihedral angles, the smallest value of the C_1-C_2-C_2' angle (104°), which also corresponds to the smallest H_1-H_1' distance, corresponds to the largest computed shieldings of C_1 and C_1'. However, increasing the C_1-C_2-C_2' angle from 109.5 to 114° yields no appreciable change in $\sigma_T(C_1)$ or $\sigma_T(C_1')$. These results for the 0° dihedral angle, comparing the 104 and 109.5° cases, are consistent with what one would expect for a C_1←H_1⋯H_1'→C_1' effect. Comparing the 109.5 and 114°

Table IV. Computed ^{13}C Shielding Constants and Overlap Integrals as a Function of Geometry for Configuration A of *n*-Butane[a,b]

(a)

C_2-C_2' distance, Å[c]	$\sigma_T(C_1)$	$\sigma_T(C_2)$	$r_{H_1-H_1'}$[d]	$S_{H_1-H_1'}$[e]
		Dihedral angle = 0°		
1.48	−12.72	−21.98	0.81	0.6335
1.54	−13.15	−23.78	0.87	0.5962
1.60	−13.48	−26.07	0.93	0.5595
1.70	−13.89	−30.06	1.03	0.4980
		Dihedral angle = 120°		
1.48	−22.42	−27.91	3.79	0.0063
1.54	−21.83	−30.61	3.80	0.0062
1.60	−21.06	−32.65	3.82	0.0060
1.70	−20.41	−38.07	3.84	0.0058
		Dihedral angle = 180°		
1.48	−18.29	−24.45	4.35	0.0022
1.54	−18.39	−26.51	4.36	0.0022
1.60	−18.44	29.07	4.37	0.0022
1.70	−18.41	−34.05	4.38	0.0021

(b)

C_1-C_2-C_2' angle,[f] deg	$\sigma_T(C_1)$	$\sigma_T(C_1')$	$\sigma_T(C_2)$	$\sigma_T(C_2')$	$r_{H_1-H_1'}$[d]	$S_{H_1-H_1'}$[e]
		Dihedral angle = 0°				
104.0	−11.86	−11.43	−21.72	−22.63	0.69	0.7089
109.5	−13.15	−13.15	−23.78	−23.78	0.87	0.5962
114.0	−13.11	−13.37	−23.72	−23.95	1.06	0.4823
		Dihedral angle = 120°				
104.0	−23.35	−21.67	−30.24	−32.23	3.73	0.0070
109.5	−21.83	−21.83	−30.61	−30.61	3.80	0.0062
114.0	−20.73	−21.96	−30.34	−29.44	3.87	0.0055

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Numbering of atoms given in Figure 2. [c] Standard bond angles maintained. [d] Distance (in ågströms) between H_1 and H_1' hydrogens. [e] Overlap integral between indicated 1s orbitals. [f] Standard bond distances maintained.

Table V. Computed Carbon Valence-Shell Electron Densities for Alkanes[a]

Compd	Conform.[b]	θ,[c] deg	$P(C_1)$[d]	$P(C_2)$	$P(C_1')$[e]	$P(C_2')$
$CH_3CH_2CH_2CH_3$	A	0	4.0669	3.9242		
		30	4.0106	3.9691		
		60	3.9905	3.9691		
		90	3.9901	3.9715		
		120	3.9912	3.9740		
		150	3.9918	3.9716		
		180	3.9917	3.9695		
	B	0	3.9980	3.9701	4.0219	3.9677
		30	3.9995	3.9691	4.0161	3.9684
		60	3.9910	3.9681	3.9928	3.9701
		90	3.9864	3.9706	3.9901	3.9718
		120	3.9858	3.9730	3.9911	3.9728
		150	3.9877	3.9706	3.9910	3.9717
		180	3.9890	3.9687	3.9907	3.9707
	C	0	3.9916	3.9692		
		30	3.9908	3.9695		
		60	3.9908	3.9691		
		90	3.9868	3.9707		
		120	3.9857	3.9716		
		150	3.9869	3.9707		
		180	3.9867	3.9688		

[a] Computed using the modified INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformations shown in Figure 2. [c] C_1'-C_2'-C_2-C_1 dihedral angle as defined in Figure 2. [d] Total valence-shell electron density, $P = P_{2s2s} + P_{xx} + P_{yy} + P_{zz}$, for the carbon atom being considered. [e] $P(C_1')$ and $P(C_2')$ are equivalent to $P(C_1)$ and $P(C_2)$, respectively, for conformations A and C.

cases would appear to indicate that steric interactions between 1,4 methyl groups, which might be expected to increase the average values of the C_1-C_2-C_2' angle, are not expected to increase the C_1 shielding in cisoid conformations (which is where the angular perturbations would be expected), but could perhaps give rise to increased C_1 shieldings if the C_1-C_2-C_2' angular perturbation could be maintained (at least partially) through rotation about the C_2-C_2' bond.

Table VI. Computed Carbon Valence-Shell Electron Densities for Alkenes[a]

Compd	Con-form.[b]	$P(C_1)$[c]	$P(C_2)$	$P(C_1')$[d]	$P(C_2')$
cis-$CH_3CH{=}CH$-CH_3	A	3.9916	4.0129		
cis-$CH_3CH{=}CH$-CH_3	B	3.9756	4.0146	3.9830	4.0126
cis-$CH_3CH{=}CH$-CH_3	C	3.9768	4.0139		
trans-$CH_3CH{=}C$-HCH_3	B	3.9772	4.0140	3.9769	4.0136

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformations shown in Figure 2. [c] Total valence-shell electron density, $P = P_{2s2s} + P_{xx} + P_{yy} + P_{zz}$, for the carbon atom being considered. [d] $P(C_1)$ and $P(C_2')$ are equivalent to $P(C_1)$ and $P(C_2)$, respectively, for conformations A and C.

Turning our attention to the results computed for the 2-butenes, one finds from Table III that the calculated ^{13}C shielding constants for the methyl carbons of the *cis*-2-butenes are larger for all three configurations studied than the shielding constant of the one trans configuration on which calculations were carried out. This is consistent with the experimental difference, although considerably smaller in magnitude. The experimental values are, of course, averages over all populated methyl conformations. It is interesting that analogous configurations of 2-butene and *n*-butane have shieldings that fall in the same order, cis A > cis B > cis C > trans B.

(B) Electron Densities for the *n*-Butanes and 2-Butenes. Tables V and VI present the total carbon valence-shell electron densities obtained for the *n*-butanes and 2-butenes, respectively, from the ^{13}C shielding calculations. Tables VII and VIII present the corresponding hydrogen electron densities. According to the hypothesis of Grant and co-workers, one should find an increase in electron density on carbon atoms which exhibit a ^{13}C γ effect and, correspondingly, one should find a decrease in electron density on hydrogen atoms which interact with one another in the manner postulated by those workers. Consider the three configurations of *n*-butane (A, B, and C of Figure 2) with dihedral angles of 0 and 30°. These cases exhibit the largest computed shielding for the methyl carbons. One sees in Table V that, in almost every case, there is indeed a larger electron density on the methyl carbons for those dihedral angles relative to conformations with larger dihedral angles. The only exception to the pattern is the C_1 methyl carbon in configuration B with a 0° dihedral angle.

It is important to note that there is no simple correlation between the computed electron densities (Table V) and the corresponding computed ^{13}C shielding constants (Table II) for the alkanes or alkenes studied, as is demonstrated in Figures 6 and 7. That is, a larger computed ^{13}C shielding constant does not necessarily mean a larger computed electron density on the ^{13}C nucleus. This result runs counter to the sizable portion of the ^{13}C NMR literature based upon interpretations of ^{13}C shifts which *assume* a linear (or at least monotonic) relationship between ^{13}C shielding and carbon electron density (including the γ effect model of Grant and co-workers). The present study is not based upon such an assumption. The electron densities computed for the interacting methyl hydrogens generally show decreases relative to the corresponding hydrogens in noninteracting situations (e.g., trans conformations), as would be predicted by the hypothesis of Grant and co-workers.

Inspection of Tables V and VII leads one to conclude that the electron densities of the methyl carbon and of the interacting methyl hydrogens of the *n*-butanes are most sensitive to changes in dihedral angles for configuration A, and least sensitive for configuration C. This is also found to be the order of sensitivity of the computed ^{13}C shielding constants toward changes in dihedral angle.

Table IX gives the valence-shell electron densities obtained in the ^{13}C shielding calculations summarized in Table IV. For 0° dihedral $C_1'C_2'$-C_2-C_1 angle it can be seen that, corresponding to an increase in computed shielding with smaller C_2'-C_2 distance, there is also an increase in computed methyl carbon electron density. The results for 120 and 180° dihedral angles are very similar to each other, with only very small variation in the computed carbon electron densities. The fact that these results for the methyl carbon of the 120 and 180° cases are uniformly smaller than those for 0° and the fact that the corresponding H_1 electron densities are uniformly larger

Table VII. Computed Hydrogen Electron Densities for the *n*-Butanes[a]

Conform.[b]	θ,[c] deg	$P(H_1)$[d]	$P(H_2)$	$P(H_3)$	$P(H_4)$	$P(H_5)$	$P(H_1')$[e]	$P(H_2')$	$P(H_3')$	$P(H_4')$	$P(H_5')$
A	0	0.9324	1.0049	1.0049	1.0131	1.0131					
	30	0.9824	1.0047	1.0085	1.0125	1.0122					
	60	1.0029	1.0058	1.0063	1.0142	1.0111					
	90	1.0035	1.0067	1.0057	1.0139	1.0086					
	120	1.0024	1.0068	1.0067	1.0116	1.0070					
	150	1.0035	1.0063	1.0071	1.0104	1.0092					
	180	1.0044	1.0065	1.0065	1.0106	1.0106					
B	0	1.0142	0.9995	0.9995	1.0121	1.0121	0.9740	1.0075	1.0075	1.0128	1.0128
	30	1.0097	0.9889	1.0042	1.0120	1.0131	0.9806	1.0074	1.0054	1.0123	1.0129
	60	1.0074	1.0017	1.0058	1.0139	1.0116	1.0007	1.0065	1.0057	1.0112	1.0133
	90	1.0082	1.0060	1.0054	1.0142	1.0091	1.0035	1.0059	1.0067	1.0096	1.0129
	120	1.0092	1.0060	1.0058	1.0124	1.0078	1.0024	1.0065	1.0067	1.0092	1.0112
	150	1.0088	1.0057	1.0062	1.0109	1.0096	1.0035	1.0069	1.0062	1.0103	1.0106
	180	1.0083	1.0060	1.0060	1.0108	1.0108	1.0045	1.0064	1.0064	1.0109	1.0109
C	0	1.0118	1.0011	1.0011	1.0126	1.0126					
	30	1.0100	0.9999	1.0050	1.0125	1.0122					
	60	1.0078	1.0057	1.0016	1.0116	1.0134					
	90	1.0081	1.0055	1.0055	1.0101	1.0132					
	120	1.0091	1.0057	1.0058	1.0120	1.0100					
	150	1.0086	1.0057	1.0062	1.0110	1.0107					
	180	1.0086	1.0065	1.0065	1.0114	1.0114					

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts, described in the introductory section. [b] Conformations are shown in Figure 2. [c] C_1'–C_2'–C_2–C_1 dihedral angle is defined in Figure 2. [d] The hydrogen electron density, $P = P_{1s1s}$, for the specified atom. [e] $P(H_1)$ through $P(H_5)$ are equivalent to $P(H_1')$ through $P(H_5')$, respectively, for conformations A and C.

Table VIII. Computed Hydrogen Electron Densities for the Alkenes[a]

Compd[b]	$P(H_1)$[c]	$P(H_2)$	$P(H_3)$	$P(H_4)$	$P(H_1')$[d]	$P(H_2')$	$P(H_3')$	$P(H_4')$
$CH_3CH{=}CHCH_3$								
A, cis	0.9892	1.0029	1.0029	1.0003				
B, cis	1.0095	1.0003	1.0003	1.0005	0.9987	1.0022	1.0022	1.0003
C, cis	1.0085	1.0002	1.0002	1.0002				
B, trans	1.0088	1.0016	1.0016	0.9972	1.0039	1.0036	1.0036	0.9977

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformations are shown in Figure 2. [c] The hydrogen electron density, $P = P_{1s1s}$, for the indicated atom. [d] $P(H_1)$ through $P(H_4)$ are equivalent to $P(H_1')$ through $P(H_4')$, respectively.

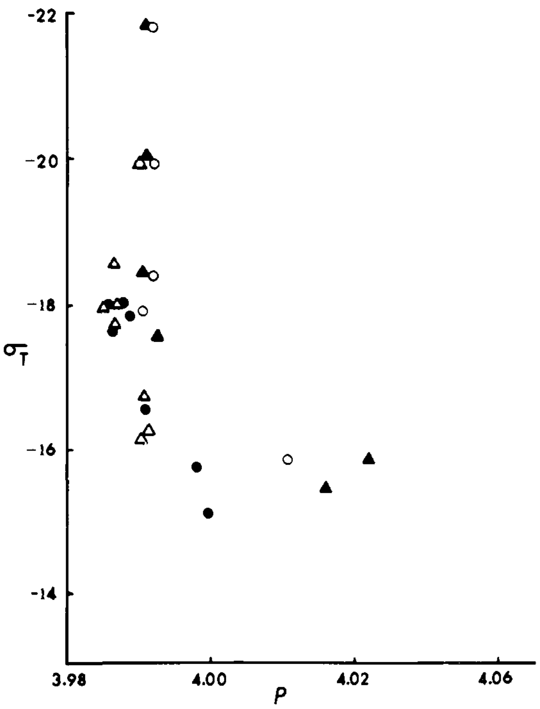


Figure 6. Plot of calculated ^{13}C shielding constants (σ_T, in ppm) vs. corresponding computed valence-shell electron densities (P) for the methyl carbons of the n-butane systems: (○) configuration A; (●) C_1 of configuration B; (▲) $C_{1'}$ of configuration B; (△) configuration C.

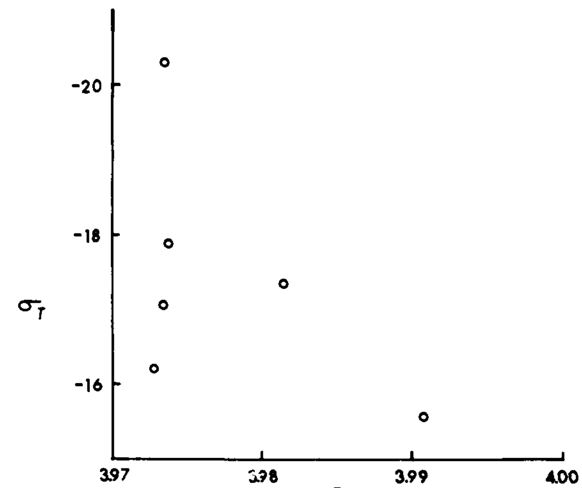


Figure 7. Plot of calculated ^{13}C shielding constants (σ_T, in ppm) vs. corresponding computed valence-shell electron densities (P) for the methyl carbons of the 2-butene systems.

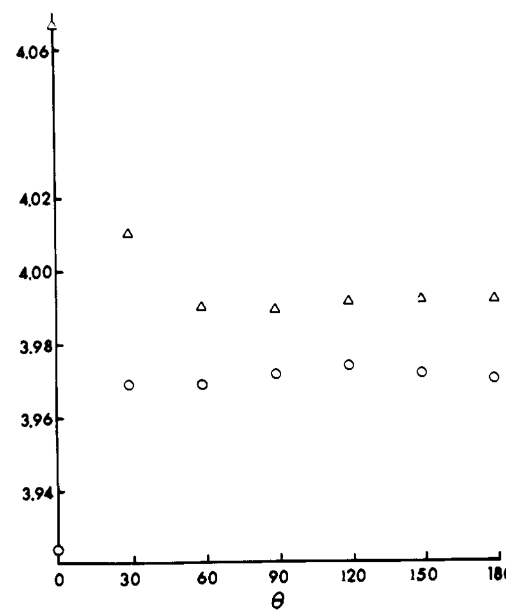


Figure 8. Plot of computed carbon valence-shell electron densities (P) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the A configuration of n-butane: (△) C_1; (○) C_2.

for the 120 and 180° cases lend credence to the mechanism of C-H bond polarization visualized in Figure 1. This point of view is further supported by the fact that the carbon and hydrogen electron densities for the 120 and 180° cases are closest to those of the 0° case for the 1.70 Å C_2'-C_2 distance, for which the postulated H_1'⋯H_1 interactions would be reduced relative to interactions expected at smaller C_2'-C_2 distances for the 0° case. On the other hand, the computed variation in the methyl ^{13}C shielding for the 120° case is an order of magnitude larger than that for the 180° case (see Table IV), while the variations in computed methyl carbon electron densities for these two cases are almost identical. Hence, while the $C_1' \leftarrow H_1'$⋯$H_1 \rightarrow C_1$ mechanism may be operable, it does not appear to be uniformly capable of accounting for the pattern of computed results.

Before leaving this section, mention should be made of the electron density on the methylene carbons. It has already been mentioned that Figures 3-5 tend to indicate that the ^{13}C shielding constants of nonadjacent methyl and methylene carbons respond in a similar manner to changes in the C_1'-C_2'-C_2-C_1 dihedral angle of the n-butanes. Figures 8-10, which present the results of electron density calculations as a function of C_1'-C_2'-C_2-C_1 dihedral angle, indicate that changes in electron density on these nonadjacent carbons within a given molecular system do not display a similar relationship. However, as with the case of computed shieldings, the calculated electron density results for C_1' of conformation B bear a close relationship to those for C_1 of conformation A, and the electron density results for C_1 of conformation B show substantial similarity with the corresponding results for C_1 of

Table IX. Computed Valence-Shell Electron Densities as a Function of C_2-C_2' Distance for Configuration A of *n*-Butane[a,b]

(a)

C_2-C_2' distance,[c] Å	$P(C_1)$	$P(C_2)$	$P(H_1)$
	Dihedral angle = 0°		
1.48	4.0814	3.9569	0.9212
1.54	4.0669	3.617	0.9324
1.60	4.0541	3.9718	0.9442
1.70	4.0366	3.9826	0.9563
	Dihedral angle = 120°		
1.48	3.9939	3.9684	1.0020
1.54	3.9912	3.9740	1.0024
1.60	3.9892	3.9791	1.0027
1.70	3.9861	3.9862	1.0029
	Dihedral angle = 180°		
1.48	3.9945	3.9630	1.0044
1.54	3.9917	3.9695	1.0044
1.60	3.9899	3.9754	1.0044
1.70	3.9863	3.9836	1.0043

(b)

C_1-C_2-C_2' angle,[d] deg	$P(C_1)$	$P(C_2)$	$P(H_1)$
	Dihedral angle = 0°		
104.0	4.1165	3.9625	0.8917
109.5	4.0669	3.9617	0.9324
114.0	4.0030	3.9694	0.9615
	Dihedral angle = 120°		
104.0	3.9937	3.9764	0.9997
109.5	3.9912	3.9740	1.0024
114.0	3.9885	3.9744	1.0042

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Numbering of atoms given in Figure 2. [c] Standard bond angles maintained. [d] Standard bond distances maintained.

conformation C. The electron densities of the methylene carbons behave similarly for all these systems as the C_1'-C_2'-C_2-C_1 dihedral angle is varied.

(C) Ab initio Calculations on *n*-Butanes. In order to put the electron density patterns obtained via the modified-INDO approach in some perspective, ab initio calculations were performed on cis ($\theta = 0°$) and trans ($\theta = 180°$) conformers of *n*-butane (configuration A). The valence-shell and total electron densities for C_1 and C_2 are presented for both the modified-INDO and ab initio approaches in Table X. The ab initio overlap populations between H_1 and H_1' (the interacting hydrogens), between H_1 and C_1, and between H_2 and C_1 as well as the corresponding INDO bond orders are presented in Table XI.

Inspection of the ab initio results in Table X leads one to conclude that there is little, if any, change in the electron density in the 1s orbital of carbons C_1 or C_2 as the conformation changes from a 0 to 180° dihedral angle, and since we are concerned with relative differences between the conformers, discussion of the 1s orbitals can be neglected. One finds that differences in the computed valence-shell electron densities of both C_1 and C_2 between the two conformers are about three times greater for the modified-INDO method than for the ab initio method. For the 0 and 180° dihedral angles, the difference between the valence-shell electron density of C_1 is computed to be a little larger than 0.005 electron by the ab initio method. This rather small change in electron density would not seem to be large enough to account for an appreciable shift in the shielding constant of C_1, at least not with the magnitude

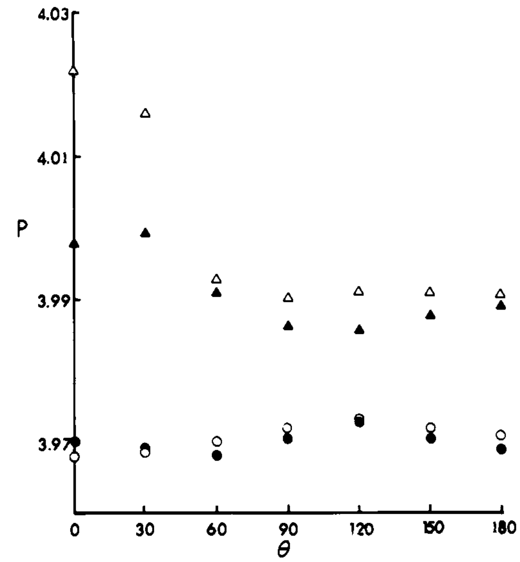


Figure 9. Plot of computed carbon valence-shell electron densities (P) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the B configuration of *n*-butane: (▲) C_1; (△) C_1'; (●) C_2; (○) C_2'.

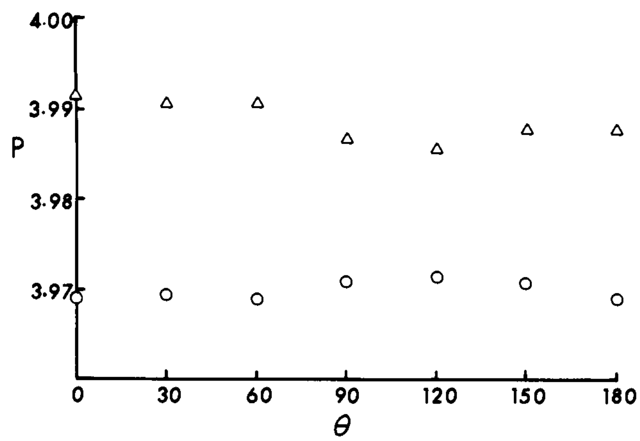


Figure 10. Plot of computed carbon valence-shell electron densities (P) vs. the C_1'-C_2'-C_2-C_1 dihedral angle, as defined in Figure 2, for the C configuration of *n*-butane: (△) C_1; (○), C_2.

normally exhibited by the γ effect, if one adopts the popular view of a linear relationship between electron density and ^{13}C shielding.

It is important to note that both of the MO methods employed indicate rather significant differences in orbital electron densities (as well as bond orders or overlap populations) between the conformers. In some cases these changes are individually far greater than the overall change in the net valence-shell electron densities. Changes in the individual orbital populations lead to changes in the electron *distribution* about the carbon atom, without necessarily altering the overall carbon electron density. Such changes in electron distribution about a nucleus are capable of causing substantial shifts in the shielding constant for that nucleus and are accounted for in chemical shift theory by what is commonly called the second-order paramagnetic terms.[24] It seems quite likely that changes in the electron *distribution*, not necessarily accompanied by comparable changes in the net electron *density* of the carbon atom, are responsible for the observed changes in ^{13}C shielding.

(D) The Dimethane System. In order to explore the nature of steric influences on the γ effect further and to test the $C_1' \leftarrow H_1' \leadsto H_1 \rightarrow C_1$ hypothesis by another approach, a set of

Table X. Computed Orbital, Valence-Shell, and Total Electron Densities for Configuration A of *n*-Butane (0 and 180° Dihedral Angles)[a]

Conform.[b]	Atoms[c]	$P_{1s,1s}$[d]	$P_{2s,2s}$	P_{xx}	P_{yy}	P_{zz}	P[e]	P_{TOT}[f]
A (θ = 0°)	C_1		1.0744	1.0080	0.9924	0.9921	4.0069	6.0069
		(1.9921)	(1.1833)	(1.0293)	(1.0138)	(0.9647)	(4.1911)	(6.1832)
	C_2		1.0452	0.9737	0.9748	0.9712	3.9242	5.9242
		(1.9920)	(1.1769)	(0.9675)	(1.0101)	(0.9594)	(4.1140)	(6.1060)
A (θ = 180°)	C_1		1.0340	0.9858	0.9882	0.9837	5.9917	5.9917
		(1.9921)	(1.1853)	(1.0159)	(1.0151)	(0.9695)	(4.1858)	(6.1779)
	C_2		1.0485	0.9735	0.9774	0.9701	3.9695	5.9695
		(1.9921)	(1.1781)	(0.9649)	(1.0061)	(0.9525)	(4.1016)	(6.0937)

[a] Computed using both the modified-INDO finite perturbation theory of chemical shifts described in the introductory section and ab initio program with a STO-3G basis set. [b] Conformation and definition of θ (C_1'-C_2'-C_2-C_1 dihedral angle) are found in Figure 2. [c] Refers to the specific carbon atom of *n*-butane being considered. [d] P_{1s1s}, P_{2s2s}, etc., are orbital electron densities for the carbon atom being considered. Numbers in parentheses are those computed using ab initio method. INDO does not consider inner-shell orbitals. Therefore, P_{1s1s} is blank. [e] P_C is the total valence shell electron density for carbon. $P = P_{2s2s} + P_{xx} + P_{yy} + P_{zz}$. [f] $P_{TOT} = P + P_{1s1s}$ is the total electron density for carbon. Since P_{1s1s} is neglected for the INDO method, $P_{TOT} = P + 2$.

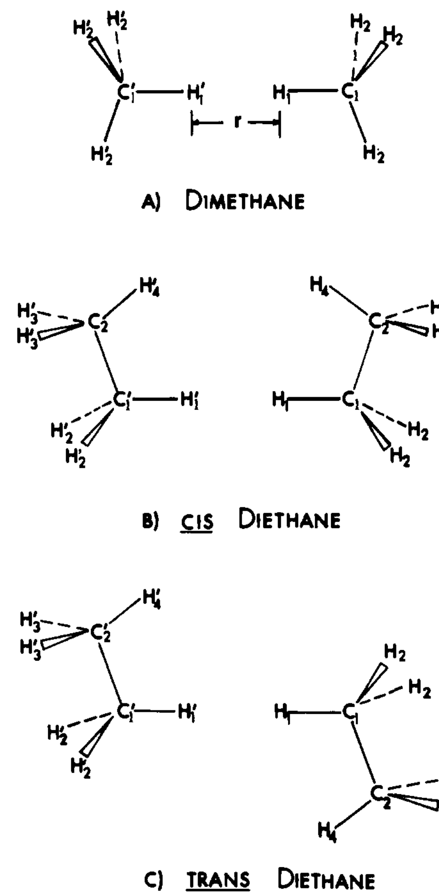


Figure 11. Dimethane and diethane systems employed in the calculations: (a) dimethane; (b) *cis*-diethane; (c) *trans*-diethane.

calculations was carried out based upon the approach of *emphasizing* the opportunity for nonbonded hydrogen-hydrogen interactions of the type proposed by Grant and co-workers, but not complicated by other features. The system chosen initially was two methane molecules, oriented as shown in Figure 11 and arranged so that the distance between H_1 and H_1' could be varied. At a distance of 5 Å (*r* in Figure 11), the calculations produced results that are essentially those of isolated methane molecules. As the two methane molecules were gradually moved together, effects from the hydrogen-hydrogen interactions could be studied systematically. This "dimethane" system has the advantage, relative to the *n*-butane case, that only the above mentioned interaction should be important. Other possible contributions, such as unknown conformationally dependent features of the molecular electronic structure of a four-carbon system, are nonexistent. Calculated ^{13}C shielding constants and hydrogen and carbon electron densities for this system are presented in Table XII. Relevant H-H and H-C bond orders, obtained fom the ^{13}C shielding calculations, are presented in Table XIII.

As can be seen from Table XII, there is no apparent interaction at 5 Å. At a distance of about 2 Å one begins to detect some small changes in the atomic electron densities and in the bond orders; however, one still does not see any change in the computed ^{13}C shielding constant. At H_1-H_1' distances of 1.2 Å, one begins to note some rather extensive changes in both atomic electron densities and bond orders. Each carbon atom has gained approximately 0.03 electron (relative to isolated methane), while each interacting hydrogen has lost approximately 0.03 electron. The noninteracting hydrogens have also lost electron density, but to a much smaller extent. The H_1-H_1' bond order is a rather large positive value, indicating a "bonding" interaction. The $C_1(2s)$-H_1 and $C_1(p_z)$-H_1 bond orders both show significant decreases, indicating an overall weakening of the C_1-H_1 bond. The C_1-H_2 bond orders do not change as drastically. If one inspects the data for distances of 1.0 and 0.8 Å, one finds the same trends as mentioned above only to a larger extent.

From our perspective, the most significant features of the data are the ^{13}C shielding constants. Despite the large changes found for electron densities and bond orders for distances of 1.2 Å and less, we find only small shifts in the shielding constants. Even at a H_1-H_1' distance of 0.8 Å, which is as short as any H_1'-H_1 distances encountered in the *n*-butane and 2-butene studies, an increase in shielding of only 0.58 ppm was obtained.

The flow of electron density found for the dimethanes is in good agreement with what Grant and co-workers proposed, i.e., the $C_1' \leftarrow H_1' \leadsto H_1 \rightarrow C_1$ mechanism. We see a depletion of electron density on the interacting hydrogens and a corresponding buildup of electron density on the carbon atoms. Very little change in the rest of the molecule is found as the H_1-H_1' distance is altered. However, the results on ^{13}C shielding constants indicate that, even if nonbonded hydrogen-hydrogen interactions of the type proposed by Grant and co-workers are at play, they cause only small changes in the ^{13}C shielding constants. Indeed, if the interacting hydrogens are more than 1.2 Å apart, as they are in most of the conformations of *n*-butane and 2-butene discussed in the preceding sections, the resulting contributions to the γ effect by this simple mechanism should be essentially insignificant.

(E) The Diethane System. The possibility was considered that there might be some requisite feature of an actual system ex-

Table XI. Computed[a] H_1–H_1 and H–C_1 Bond Orders[a] and Overlap Populations[b] for Configuration A of *n*-Butane (0 and 180° Dihedral Angles)

Conformer[c]	H_1–H_1[d]	C_1(2s)–H_1	$C_1(x)$–H_1	$C_1(y)$–H_1	$C_1(z)$–H_1	C_1(2s)–H_2	$C_1(x)$–H_2	$C_1(y)$–H_2	$C_1(z)$–H_2
A (θ = 0°)	−0.0008	0.1236	0.2538	0.0	0.0317	0.1054	0.0653	0.1877	0.0297
	(0.3243)	(0.4770)	(0.7496)	(0.0)	(0.2881)	(0.4836)	(0.4191)	(0.7030)	(0.2894)
A (θ = 180°)	0.000	0.1118	0.2501	0.0	0.0298	0.1097	0.0626	0.1877	0.0306
	(0.0047)	(0.4971)	(0.8092)	(0.0)	(0.2922)	(0.4937)	(0.4059)	(0.7031)	(0.2950)

[a] INDO bond orders are defined to be $P_{\mu\nu} = 2\Sigma_i^{occ} C_{\mu i}{}^*C_{\nu i}$, where the sum is over all occupied orbitals. Computed by the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. Values given are not in parentheses. [b] Overlap populations as defined in the Gaussian 70 ab initio program are $P_{\mu\nu}' = P_{\mu\nu}S_{\mu\nu}$ where $P_{\mu\nu}$ is as defined in (a) and $S_{\mu\nu}$ is the overlap integral between atomic orbitals μ and ν. For a detailed discussion of overlap populations see ref 23. Values given are in parentheses. [c] Conformations and θ (C_1'–C_2'–C_2–C_1 dihedral angle) are defined in Figure 2. [d] This notation refers to which orbitals are involved in the bond order or overlap population. C_1(2s)–H_1 means the bond order or overlap population between the 2s orbital on C_1 and the 1s orbital on H_1.

Table XII. Calculated Valence-Shell Electron Densities and ^{13}C Shielding Constants (ppm) for Dimethane

r (Å)[a]	$P(C_1)$[b,c]	$P(H_1)$	$P(H_2)$	$\sigma_T(C_1)$[d]
∞[e]	4.0027	0.9993	0.9993	−7.27
	(4.2706)	(0.9343)	(0.9343)	
5.0	4.0027	0.9993	0.9993	−7.27
	(4.2706)	(0.9343)	(0.9343)	
2.0	4.0054	0.9968	0.9968	−7.27
1.2	4.0356	0.9698	0.9982	−7.13
	(4.2724)	(0.9244)	(0.9364)	
1.0	4.0599	0.9489	0.9970	−6.98
	(4.2753)	(0.9188)	(0.9380)	
0.8	4.0983	0.9167	0.9950	−6.69
	(4.2752)	(0.9128)	(0.9400)	

[a] "Intermolecular" hydrogen-hydrogen distance (r) and dimethane configuration defined in Figure 11. [b] Valence-shell electron density of indicated atom computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. Vales in the parentheses are valence-shell electron densities computed using an ab initio program with a STO-3G basis set. [c] Numbering of atoms correlates with those shown in Figure 11. [d] Shielding constant of carbon computed using the modified-INDO finite perturbation theory described in the introductory section. [e] Isolated methane.

hibiting an experimental γ effect, a feature that depends upon the existence of four or more carbon atoms. If so, the dimethane calculations, by virtue of the small size of the interacting moieties (CH_4), would misrepresent the γ effect. Hence, a system analogous to the dimethane system, a "diethane" system, containing four carbon atoms, was studied. The diethane system consists of two ethane molecules placed together in either a cis or a trans conformation, as shown in Figure 11. The distances of separation considered were 1.4, 1.0 and 0.6 Å. Bond orders between H_4 and H_4' indicate that essentially the only interaction of major consequence is that between H_1 and H_1' (the value of the H_4–H_4' bond order being 0.0003 at 0.6 Å). Table XIV presents the various computed atomic electron densities and ^{13}C shielding constants for the diethanes, with ethane results for comparison.

The valence-shell electron densities given in Table XIV show similarities in their dependence on the H_1–H_1' distance to those found for dimethane. H_1 and H_2, especially the former, show a depletion of electron density, as does C_2, as the H_1–H_1' distance is decreased. As with the dimethanes, C_1 shows an increasing buildup of electron density as the two ethane fragments are brought closer together. The ^{13}C shielding constants for the diethanes show some interesting features. The most significant pattern is the small size of the variation for the C_1 shielding constant. It also appears that the C_1 shielding is not affected as much for the cis conformation as for the trans conformer. In fact, the C_1 shielding for the cis conformation is affected only slightly and there is no definite trend. It is found that, with decreasing H_1'–H_1 distance, the calculated C_2 shielding constant is shifted to lower values in both configurations, these shifts being of larger magnitude than those for the C_1 shielding. In any case, the critical point here is that we see only small changes in the shielding constant for C_1, even at 0.6 Å. This result is in agreement with the dimethane results. In summary, the dimethane and diethane computational experiments, which might have been expected to emphasize the kind of nonbonded H_1–H_1' interactions of the $C_1' \leftarrow H_1' \leadsto H_1 \rightarrow C_1$ model, provide no support for that popular hypothesis. Indeed, the fact that such small shifts were obtained in the dimethane and diethane calculations implies that a network such as the C_1'–C_2'–C_2–C_1 chain, in which some unknown, conformationally sensitive, intramolecular influences may be exerted, is a necessary ingredient for the manifestation of the γ effect.

(F) Ab inito Calculations on Dimethane. Ab initio calculations were carried out on the dimethane system to obtain another view into the patterns of changes in the electronic distribution associated with bringing the two molecules together. The resulting valence-shell electron densities and overlap populations are presented in parentheses in Tables XII and XIII, respectively.

The pattern of ab initio results for dimethane differs in some ways from the results obtained in the modified-INDO ^{13}C shielding calculations. The changes in electron density on the methyl carbon are found to be much smaller for the ab initio calculations, as was found to be the case for the *n*-butanes. This result casts further doubt on a simple electron density effect, due to a $C_1' \leftarrow H_1' \leadsto H_1 \rightarrow C_1$ mechanism, for altering the shielding of the methyl carbon. In the ab initio results, one notices a depletion of electron density on H_1 and an increase on H_2 as the methanes are brought closer together. One also finds an overall *increase* in the total overlap population between C_1 and H_1 (in contrast to indications of the modified-INDO results), as well as an overall increase in the C_1–H_2 overlap population. The total picture shows electron density flowing away from H_1 and toward H_2, whereas the results discussed above for the modified-INDO calculations indicate that the electron density flows away from H_1 and toward C_1, with very little change in the H_2 density. The ab initio results point to a significant change in the *distribution* of electron density about the methyl carbon, rather than to a significant change in the total electron density on the methyl carbon, a conclusion that is in agreement with what was found from the ab initio calculations on *n*-butane. It should be noted that the ab initio calculations indicate no trend in the total electron density on C_1 as the two methane molecules are moved closer together. C_1 has its largest electron density at 1.0 Å, not at 0.8 Å.

Table XIII. Calculated H-H and H-C Bond Orders[a] and Overlap Populations[b] for the Dimethanes

r (Å)[c]	H_1'-H_1[d]	$C_1(2s)$-H_1	$C_1(z)$-H_1	$C_1(2s)$-H_2	$C_1(x)$-H_2	$C_1(y)$-H_2	$C_1(z)$-H_2	$C_1(2s)$-H_1'	$C_1(z)$-H_1'
∞[e]	0.000	0.5000	0.8660	0.5000	0.4082	0.7071	0.2886	0.0000	0.0000
	(0.0000)	(0.1118)	(0.2799)	(0.1118)	(0.0622)	(0.1866)	(0.0311)	(0.0000)	(0.0000)
5	0.0003	0.5000	0.8660	0.5000	0.4082	0.7071	0.2886	0.0000	0.0000
	(0.0000)	(0.1118)	(0.2799)	(0.1118)	(0.0622)	(0.1866)	(0.0311)	(0.0000)	(0.0000)
2	0.0655	0.4993	0.8639	0.4998	0.4082	0.7071	0.2890	−0.0075	0.0046
1.2	0.2123	0.4927	0.8428	0.4975	0.4082	0.7071	0.2923	−0.0215	0.0202
	(−0.0002)	(0.1161)	(0.2803)	(0.1107)	(0.0622)	(0.1866)	(0.0315)	(−0.0073)	(−0.0093)
1.0	0.2849	0.4855	0.8235	0.4959	0.4082	0.7071	0.2947	−0.0237	0.0332
	(0.0008)	(0.1191)	(0.2813)	(0.1100)	(0.0622)	(0.1866)	(0.0318)	(−0.0144)	(−0.0171)
0.8	0.3544	0.4767	0.7979	0.4919	0.4082	0.7071	0.3001	−0.0242	0.0517
	(0.0062)	(0.1232)	(0.2829)	(0.1089)	(0.0622)	(0.1866)	(0.0323)	(−0.0275)	(−0.0312)

[a] INDO bond orders defined to be $P_{\mu\nu} = 2\Sigma_i^{occ} C_\mu^* C_\nu$ where the sum is over all occupied MO's. Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. Values are not in parentheses. [b] Computed using an ab initio method with an STO-3G basis set. Overlap populations as defined in the Gaussian 70 ab initio program are $P_{\mu\nu}' = P_{\mu\nu} S_{\mu\mu}$, where $P_{\mu\nu}$ is as defined in (a) and $S_{\mu\nu}$ is the overlap integral between atomic orbitals μ and ν. For a detailed discussion of overlap populations see ref 23. Values given in parentheses. [c] "Intermolecular" hydrogen-hydrogen distance (r) and actual orientation of two methane molecules shown in Figure 11. [d] This notation refers to which orbitals are involved in the bond order or overlap population. $C_1(2s)$-H_1 means the bond order as overlap population between the 2s orbital on C_1 and the 1s orbital on H_1. Numbering of atoms correlates with those given in Figure 11. [e] Isolated methane.

Table XIV. Calculated Valence-Shell Electron Densities and ^{13}C Shielding Constants for Diethanes[a]

Conform. (r, Å[b])	$P(C_1)$[c]	$P(C_2)$	$P(H_1)$	$P(H_2)$	$P(H_3)$	$P(H_4)$	$\sigma_T(C_1)$[d]	$\sigma_T(C_2)$
∞[e]	3.9812	3.9812	1.0068	1.0068	1.0068	1.0068	−16.71	−16.71
Cis (1.4)	3.9983	3.9784	0.9889	1.0060	1.0073	1.0076	−16.66	−16.92
Cis (1.0)	4.0861	3.9743	0.9545	1.0041	1.0088	1.0102	−16.64	−17.50
Cis (0.6)	4.1283	3.9651	0.8751	0.9982	1.0102	1.0146	−16.70	−19.09
Trans (1.4)	3.9984	3.9783	0.9889	1.0060	1.0073	1.0078	−16.57	−16.83
Trans (1.0)	4.0361	3.9737	0.9545	1.0040	1.0082	1.0110	−16.39	−17.19
Trans (0.6)	4.0374	3.9631	0.8751	0.9980	1.0100	1.0175	−16.01	−18.09

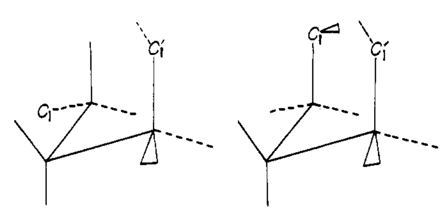
[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] "Intermolecular" hydrogen-hydrogen distance (r), orientation of the ethane molecules and numbering of atoms given in Figure 11. [c] The valence-shell electron density for the specified atom. [d] σ_T, the total shielding constant in ppm. [e] Isolated ethane with an eclipsed conformation.

Table XV. Valence-Shell Electron Densities and ^{13}C Shielding Constants for n-Pentane Conformers[a]

Conformer[b]	$P(C_1)$[c]	$P(C_1')$	$P(H_1)$[d]	$P(H_1')$	$\sigma_T(C_1)$[e]	$\sigma_T(C_1')$
II	3.9875	3.9910	1.0070[d]	1.0019	−17.85	−16.85
III	4.0963	4.0963	0.9055	0.9055	−19.74	−19.74

[a] Computed using the modified-INDO finite perturbation theory of chemical shifts described in the introductory section. [b] Conformers are shown in the text. [c] The valence shell electron density for the indicated atom. Numbering of atoms correlates with those shown for structures II and III in the text. [d] This number is an average of three similar values for the C_1 methyl hydrogens. [e] The calculated total shielding constant, σ_T, given in ppm.

(G) A Five-Carbon System. One additional approach which was taken to explore the effect that steric interactions between two methyl groups have on their ^{13}C shieldings was to consider the interactions between the terminal methyl groups of the n-pentane system. The two conformations on which calculations were carried out are shown as structures II and III. The



II III

pertinent calculated ^{13}C shielding constants and valence-shell electron densities for these two conformers are given in Table XV. The most noteworthy result is that the ^{13}C shielding constant is *lower* for the sterically more crowded methyl system, conformer III (for which the closest interacting methyl hydrogens are separated by 2.5 Å), relative to conformer II (for which the closest pertinent methyl hydrogens are separated by 5.1 Å).

The pattern of electron densities given in Table XV shows that for the sterically more crowded conformer, III, the electron densities of the interacting hydrogens (H_1 and H_1') are depleted relative to the "noniteracting" case, II. The methyl carbons in III have a higher computed electron density than in II (the difference being far more than found for either the n-butanes or 2-butenes). Thus, the methyl groups in conformer III behave, as far as electron distribution is concerned, according to what one would expect for an interaction of the $C_1' \leftarrow H_1' \rightsquigarrow H_1 \rightarrow C_1$ type, yet the shielding of the methyl carbon for that case is lower than that for the conformer in which there is no steric interaction between the methyl groups. This lower shielding for III is consistent with a methyl-methyl δ shift to lower shielding reported by Jones and co-workers[28] for

1,8-dimethylnaphthalene and with the *heteroatom* δ effect found by Grover et al.,[10] yet the electron density computed for the methyl carbon in III is larger than for II. If the popular assumption of a linear relationship between ^{13}C shielding and electron density were correct, one would expect this higher computed electron density on the methyl carbon for conformer III to occur along with a higher computed ^{13}C shielding constant. Of course, the possibility exists that totally different mechanisms operate for γ and δ effects.

(H) Summary and Conclusions. The results of this work can be summarized as follows:

1. The modified-INDO finite perturbation theory of ^{13}C chemical shifts predicts significant conformational effects on ^{13}C shielding, which are qualitatively what one would expect for the experimentally well-known γ effect.

2. The computed carbon electron densities appear to bear no simple relationship to the computed ^{13}C shielding constants.

3. Ab initio calculations indicate that changes in the electron distribution about a methyl carbon which experiences a steric crowding is much more substantial than changes in the total atomic carbon electron density.

4. The apparent dependence of the ^{13}C shieldings upon pertinent H_1'-H_1 distances is even larger for a 120° C_1'-C_2'-C_2-C_1 dihedral angle than for 0°.

5. The results for dimethane and diethane calculations indicate that an electron density increase by the $C_1' \leftarrow H_1' \rightsquigarrow H_1 \rightarrow C_1$ mechanism alone cannot account for the γ effect on ^{13}C shielding.

6. Calculations on *n*-pentane conformers predict the existence of a negative shielding increment associated with a steric interaction of methyl groups bearing a δ relationship to each other, whereas, the electron density patterns are consistent with a $C_1' \leftarrow H_1' \rightsquigarrow H_1 \rightarrow C_1$ mechanism.

There is no guarantee that the calculations performed in this work properly include all pertinent mechanisms that contribute to the experimental γ effect. However, it seems very unlikely that these calculations have created a spurious new source of long-range chemical shift effects. Thus, we believe, the substantial geometry-dependent effects that have appeared in these calculations should be taken into account in attempts to understand the γ effect. The somewhat diminished magnitudes of the computed effects (relative to experimentally determined γ effects) could be due either to an underestimation of all important contributions or to the omission of one or more especially important contributions. One can only conclude from this summary that changes in the magnitude of electron density on a methyl carbon are not the primary source of long-range chemical shifts brought about by a "crowded" γ methyl relationship. It is much more likely that the precise manner in which the electronic distribution about the methyl carbon changes is a key factor. That portion of the original hypothesis by Grant and co-workers pertaining to C-H polarization due to nonbonded H-H interactions may well represent one of the main sources of alterations in the distribution. However, it appears that the existence, number, and conformations of covalent bonds between the two methyl carbons involved are at least as important as the proximity of the interacting methyl groups.

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References and Notes

(1) (a) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1701 (1963); (b) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964).
(2) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966).
(3) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).
(4) J. B. Stothers, "Carbon-13 NMR Spectrocopy", Academic Press, New York, N.Y., 1972.
(5) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).
(6) H. Eggert and C. Djerrasi, *J. Am. Chem. Soc.*, **95**, 3710 (1973).
(7) E. Lippmaa and T. Pehk, *Org. Magn. Reson.*, **5**, 277 (1973).
(8) A. A. Abdurahmanov, R. A. Rahimova, and L. M. Manov, *Phys. Lett. A*, **32**, 123 (1970).
(9) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).
(10) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973).
(11) P. D. Ellis, J. W. McIver, Jr., and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 4069 (1972).
(12) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(13) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).
(14) (a) H. McConnell, *J. Chem. Phys.*, **27**, 226 (1957); (b) J. A. Pople, *ibid.*, **37**, 53 (1962).
(15) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).
(16) F. London, *J. Phys. Radium*, **8**, 397 (1937).
(17) P. D. Ellis, Ph.D. Thesis, University of California at Davis, 1970.
(18) K. Seidman, Masters Thesis, University of South Carolina, 1973.
(19) H. F. Hameka, *Rev. Mod. Phys.*, **34**, 87 (1962).
(20) C. J. Jameson and H. L. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).
(21) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(22) W. J. Hehre, R F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(23) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(24) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).
(25) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).
(26) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(27) A. J. Jones and D. M. Grant, cited in ref 4.
(28) A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Am. Chem. Soc.*, **92**, 2386 (1970).