The Interpretation of Carbon Nuclear Magnetic Resonance Shifts. Part 2.[1] The Alkane (Empirical) Shielding Parameters, and an Absolute Scale for Carbon Shielding

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Grant has shown that the nuclear magnetic shielding of ^{13}C in the alkanes can be predicted as a sum of $\sigma(^{13}CH_4)$ and substituent parameters S_k for the kth position. Using Flygare's equation, we can obtain the molecular diamagnetic shielding term σ_d as a sum of $\sigma_d(^{13}CH_4)$ and substituent contributions D_k. The paramagnetic term can therefore be parameterised similarly, and the substituent contributions P_k have been obtained by subtracting D_k(calc) from S_k(obs). The unusual fall-off with distance of Grant's substituent parameters is interpreted as the difference between the smooth fall-off of the diamagnetic parameters with distance (as r^{-1}), and the less regular fall-off of the paramagnetic parameters, because of the dependence on the conformation of the γ, δ, *etc.*, substituents. The variation with chain length of the n-alkyl substituent parameters can be interpreted similarly. Absolute shielding terms for ^{13}C are derived from Ozier, Crapo, and Ramsey's molecular beam resonance measurements of the spin-rotation constant for ^{13}CO.

GRANT and PAUL[2] have shown that ^{13}C chemical shifts in alkanes can be predicted from a set of empirical parameters (α—ε). These are given (as S_k) in Table 1 so as to represent increments in the shielding of an alkane carbon for substitution of α, β, γ, *etc.*, hydrogen by alkyl carbon. (Note that the shielding parameters are opposite in sign to chemical shift parameters that are positive downfield.) The fall-off of these parameters with distance from the nucleus of interest is unexpected. The α and β parameters are nearly equal, the γ parameter is opposite in sign to the others, and the contribution of δ and ε carbons is still significant; as Grant and Paul showed,[2] the observed contributions from 'distant' substituents are much larger than those calculated by the dipole approximation with reasonable values of the magnetic anisotropy of the C–C bond.

Grant and Paul[2] gave further additive parameters for chain branching, and these were found to be unnecessary if an atom-plus-ligand local term, which we now call σ_d^{AL}, was used as diamagnetic correction of the observed shifts.[1] The resonant nucleus (A) was taken as

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[1] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038, is taken as Part 1.

[2] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

gauge origin and σ_d^{AL} summed over the nucleus A and its α-substituents (L for ligand) according to Flygare's equation[3] (which is equivalent to an observation by Ramsey[4]). Subtraction of σ_d^{AL} from the chemical shift δ gives a measure of σ_p^{AL}, an atom-plus-ligand paramagnetic term, which shows better 'chemical' correlations,[1] such as additivity of substituent effects, or periodic variation with atomic number of the ligand, than do the observed shifts, or the commonly used (atomic) local term σ_p^A.

TABLE 1

Diamagnetic, paramagnetic, and resultant (observed) substituent parameters for ^{13}C shielding in the acyclic alkanes

Substituent (weighting)	r/pm	Shielding parameter S_k/p.p.m. (obs.)	Diamagnetic parameter D_k/p.p.m. (calc.)	Paramagnetic parameter P_k/p.p.m (by difference)
α	153	−9.1	41.5	−50.6
β	254	−9.4	27.3	−36.7
γ_g (40%)	311	6.4	23.1	−16.7
γ_m	358	2.5	19.9	−17.4
γ_a (60%)	390	0.0	18.2	−18.2
$\delta_{g\pm g\pm}$ (12%)	390		18.4	
$\delta_{ag\pm}$ (28%)	450		16.3	
$\delta_{a\pm g}$ (28%)				
δ_m	461	−0.4	15.8	−16.2
δ_{aa} (32%)	507		14.3	
ε_m	564	−0.2	12.4	−12.6

We now extend this argument to cover all (α, β, γ, . . .) substitution by alkyl carbon. The molecular term σ_d is given by the Flygare equation (1),[3] where e and

$$\sigma_d(A) = \sigma_d(\text{free atom}) + \frac{e^2}{3mc^2}\sum\frac{Z_k}{r_k} \qquad (1)$$

m are the electron charge and mass, c is the speed of light, Z_k is the atomic number and r_k the distance from the nucleus A of the kth nucleus, and k runs over all nuclei in the molecule except A. Accurate values of the free atom term (260.74 p.p.m. for carbon) have been published.[5] Flygare's equation shows that substituent contributions (α_d, β_d, γ_d, . . .) to the molecular (Ramsey) diamagnetic term are linearly additive, and so then must be the corresponding paramagnetic contributions (α_p, β_p, γ_p, . . .) by difference from the observed shielding parameters. Thus the Ramsey (molecular) terms[6] for the ^{13}C nucleus A are given by equations (2)—(4), D_k

$$\sigma(A) = \sigma_d(A) + \sigma_p(A) \qquad (2)$$

$$\sigma_d(A) = \sigma_d(CH_4) + \sum_k D_k \qquad (3)$$

$$\sigma_p(A) = \sigma_p(CH_4) + \sum_k P_k \qquad (4)$$

being the diamagnetic shielding parameters (α_d, β_d, γ_d, . . ., given in Table 1) for the kth position relative to the nucleus A, and k runs over all carbons in the molecule other than A; and similarly for the paramagnetic parameters P_k (*i.e.* α_p, β_p, γ_p, . . ., given in Table 1). We thus extend Grant's parameterisation [equation (5)] by setting S_k(obs.) = D_k(calc.) + P_k (*i.e.* $\alpha = \alpha_d + \alpha_p$, and

$$\sigma(A) = \sigma(CH_4) + \sum_k S_k \qquad (5)$$

similarly), calculating the diamagnetic parameters by Flygare's equation, and obtaining the paramagnetic parameters by difference from the observed increment in shielding.

The molecular dimensions for the alkanes used in the calculation of the diamagnetic terms were C–C 153 pm, C–H 110 pm, $\widehat{CCC}$ 112°, $\widehat{HCH}$ and $\widehat{HCC}$ 109°, and rotation angle $\phi = 0$ or $\pm 112.5°$, as reported for liquid alkanes at 27 °C.[7] Diamagnetic shielding terms calculated by Flygare's equation agree well, within 1 p.p.m. or so, with those obtained by *ab initio* methods[3] or by Sadlej's CNDO method.[8] The absolute shielding $\sigma(CH_4)$ for ^{13}C in methane as parent of the alkanes is obtained by referring the chemical shift to an absolute scale based on Ozier, Crapo, and Ramsey's measurement[9] of the spin-rotation constant for carbon in carbon monoxide by molecular beam magnetic resonance. This gives $\sigma_p(^{13}CO)$ as −323.4(1.6) p.p.m., which has been recalculated[10] as −323.2(0.3) p.p.m., and combined with $\sigma_d(^{13}CO)$ = 326.4 p.p.m. (calculated *ab initio*[10,11]) to give the absolute shielding of carbon in CO as 3.2(0.3) p.p.m. The known[12] chemical shift of ^{13}CO gives the absolute shielding of ^{13}C in tetramethylsilane[13] as 185.4 p.p.m., so that the shielding of carbon with chemical shift δ is σ = (185.4 − δ) p.p.m., and $\sigma(^{13}CH_4)$ is 190.6 p.p.m.[14] The value of $\sigma_d(^{13}CH_4)$ = 295.1 p.p.m. was obtained by Flygare's equation, and $\sigma_p(^{13}CH_4)$ = −104.5 p.p.m. by difference.

The contribution of the replaced hydrogen is important in the derivation of the substituent parameters: thus α_d is the difference between the diamagnetic contribution of α-CH_3 (50.0 p.p.m.) and that of α-H (8.5 p.p.m.), β_d is the difference between 31.6 p.p.m. for β-CH_3 and 4.4 p.p.m. for β-H, and so on. Different parameters are obtained for ring compounds because of the two hydrogens lost with each ring closure, as well as the effects of conformation, so the parameters in Table 1 are those for the acyclic alkanes. The γ, δ, and ε parameters depend on conformation and γ_m, δ_m, and ε_m given in Table 1 are mean values for liquid alkanes at

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[4] N. F. Ramsey, *Amer. Scientist*, 1961, **49**, 509.

[5] G. Malli and C. Froese, *Internat. J. Quantum. Chem.*, 1967, **1s**, 95.

[6] N. F. Ramsey, *Phys. Rev.*, 1950, [2], **78**, 699.

[7] A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, 1966, **88**, 631.

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[9] I. Ozier, L. M. Crapo, and N. F. Ramsey, *J. Chem. Phys.*, 1968, **49**, 2314.

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27 °C. The approximate statistical weighting of the *anti* (*a*) and *gauche* ($g^{\pm}$) states given in Table 1, and used to calculate the diamagnetic terms, was derived by Fawcett from Abe, Jernigan, and Flory's statistical mechanical studies [7] of n-alkanes at 27 °C.*

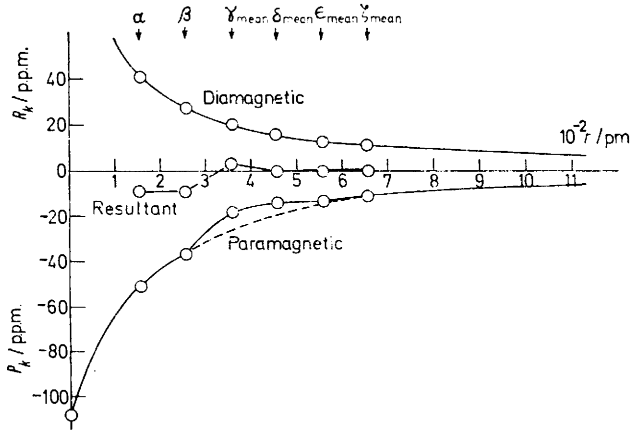

FIGURE 1 Diamagnetic, paramagnetic, and resultant ^{13}C shielding parameters in the alkanes

Figure 1 is a plot of the observed shielding parameters compared with their diamagnetic and paramagnetic parts, against the distance r of the substituent carbon from the observed nucleus (this differs little from the distance of the centre of mass or of electronic charge of the alkyl substituent). The diamagnetic parameter D_k falls off smoothly as (r^{-1}), and so too does the paramagnetic parameter P_k beyond the ζ-substituent at which the two shielding contributions become equal and opposite. Figure 1 thus illustrates the cancellation of long-range shielding contributions in large molecules which forms the basis of local-term approximations, and shows the observed variation of the neighbouring shielding contributions (α—ε) as arising from the difference in fall-off of the diamagnetic and paramagnetic parts. The fall-off of the paramagnetic parameters is not smooth, because of the differences in orientation of the successive substituent groups. Although the estimation of neighbouring contributions is a complex problem, and for other-nucleus shielding gives smaller values than those observed,[2,15-18] the angular dependence [17,18] of these contributions seems to be relevant to the irregularities in the plot of the paramagnetic parameters.[2] Thus for the dipole approximation (admittedly over-simple) the geometric factor $(1 - 3\cos^2\theta)$ becomes positive, giving a net shielding (diamagnetic) contribution when θ (the angle between the neighbouring bond and the distance vector to the nucleus A) exceeds 54.7°. This is so for γ_g, $\delta_{g\pm g\pm}$, or $\delta_{ag\pm}$ (though not $\delta_{g\pm a}$), the statistical weighting of such *gauche* states being *ca.* 40% both for the γ- and the δ-substituent at 27 °C, as shown in Table 1 (the $\delta_{g\pm g\mp}$ conformation is sterically excluded). Table 1 shows that γ_d increases by 4.9 p.p.m. as the substituent moves closer from *anti* to *gauche*, but the γ-parameter observed for rigid molecules [19] increases by 6.4 p.p.m., which means that the paramagnetic parameter has become slightly less negative, from γ_a to γ_g. When, therefore, sector rules can be developed for long-range shielding, we may find that regions of higher shielding for certain (*e.g. gauche*) conformations of the substituents account for the deviation of γ_p, δ_p, and perhaps ε_p from the smoother curve that can be drawn through the other P_k in Figure 1.

TABLE 2

Diamagnetic, paramagnetic, and resultant (observed) substituent parameters for n-alkyl substituents

Substituent	Shielding parameter observed (p.p.m.)	Diamagnetic parameter (calc.) (p.p.m.)	Paramagnetic parameter (by difference) (p.p.m.)
Me	−9.1	41.5	−50.6
Et	−18.5	68.7	−87.3
Pr	−16.0	89.0	−104.7
Bu	−16.3	105.1	−120.8
C_5H_{11}	−16.5	117.6	−133.4
C_6H_{13}	−16.5	128.6	−143.4

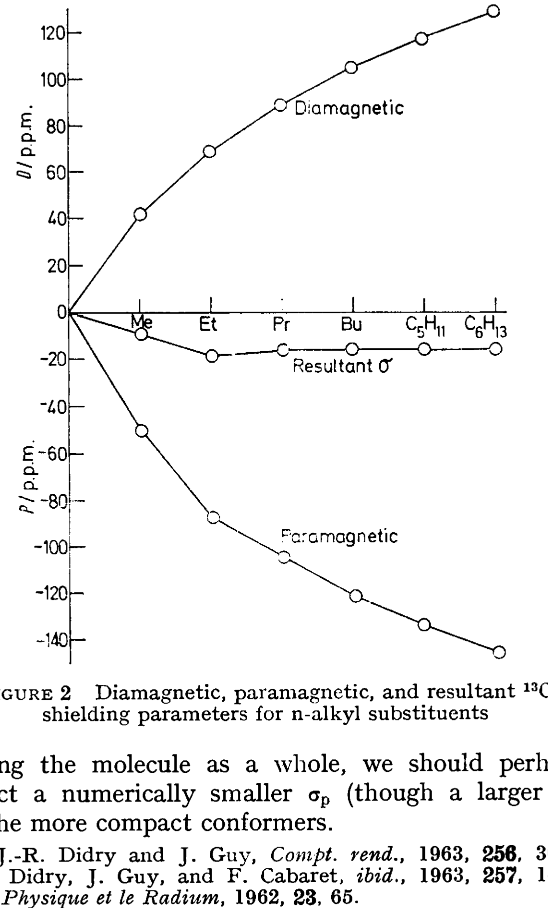

FIGURE 2 Diamagnetic, paramagnetic, and resultant ^{13}C shielding parameters for n-alkyl substituents

Taking the molecule as a whole, we should perhaps expect a numerically smaller σ_p (though a larger σ_d) for the more compact conformers.

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* I am grateful to Dr. Fawcett for this information.

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Table 2 gives the observed shielding parameters for *n*-alkyl substituents as a sum of diamagnetic and paramagnetic parts, and these are plotted in Figure 2. The parameters are derived from those in Table 1, and the fall-off of the resultant shielding parameter with the length of the alkyl chain can be interpreted in the same way.

Such analyses of observed shielding into diamagnetic and paramagnetic parts do not show, as has been suggested, that the diamagnetic term may be ' more important ' than the paramagnetic term in determining chemical shifts. The failure of neighbouring diamagnetic and paramagnetic contributions to cancel means that both may need to be taken into account: but the diamagnetic term is conceptually simple and fairly readily estimated, and can be used as a ' physical ' correction of the observed shift[3] to furnish an accurate estimate of the paramagnetic term, with which to interpret the observed variations in shielding in chemical terms of structure and bonding.

There has been argument also as to the gauge origin to be used when diamagnetic and paramagnetic contributions are separated. In theoretical calculations a choice of gauge origin closer to the electronic centre of the molecule reduces the error in the calculation of σ_p from incomplete basis sets, but there are no comparable problems in the calculation of σ_d. Our recent analyses[1,20] are based on the Flygare–Ramsey approximation, which avoids the need for wavefunctions in the calculation of σ_d, and on chemical shifts and spin-rotation constants, which naturally refer to the resonant nucleus as origin.

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