Steric Effect on Carbon-13 Nuclear Magnetic Resonance Shifts in Poly(vinylnaphthalene)s

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From the point of view of the rotational isomeric state for the side groups (π- and o-conformation), the steric compression effect on the ^{13}C chemical shift of the aliphatic carbons in poly(1-vinylnaphthalene)(P1VN) and poly(2-vinylnaphthalene)(P2VN) were evaluated according to H. J. Schneider's method. In addition to the steric compression effect, the ring current effect by the naphthyl groups in P1VN and P2VN was taken into account. The numerical results suggested that the marked higher field shifts of the methine carbon of P1VN in comparison with that of P2VN, was attributed to the strong steric compression with the 1-naphthyl group (occupied the stable π-conformation) in the same monomer units. While in the P2VN chain, the resonances of the aliphatic carbons were calculated to be in the vicinity of those of polystyrene. Naphthyl ring current contribution to ^{13}C-NMR chemical shifts was found to be small in comparison to the dominant steric compression effect.

The two isomeric polymers of vinylnaphthalene (PVN), poly(1-vinylnaphthalene)(P1VN) and poly(2-vinylnaphthalene)(P2VN), differ from each other in some solution properties and the latter polymer behaves rather similar to polystyrene (PS) in a transition phenomenon[1,2] or ^1H-NMR spectral pattern.[3] In a previous paper,[4] we reported the results of evaluations of the steric energy of the RIS (Rotational Isomeric State) of the pendant groups in P1VN and P2VN. Since the naphthyl groups in P1VN or P2VN have no symmetry axis along the plane of the ring, there are distinguished two RIS (π- and o-conformation, see Fig. 1) of the side groups. The conclusions from the result are as follow; a) in the P1VN chain, the π-conformation is preferred but in paticular conditions, there are possibilities of formation of the o-conformations, and b) in P2VN chain, both the π- and o-conformations are stable; the choice of the RIS would not have a great influence upon the total stability of the P2VN chain and there are little conformational differences in the rotational states of P2VN and PS. We also pointed out a characteristic nonbonded interaction between the hydrogen atoms of a rotating 1-naphthyl ring and the methine hydrogen, found in the same monomer unit of P1VN chain.

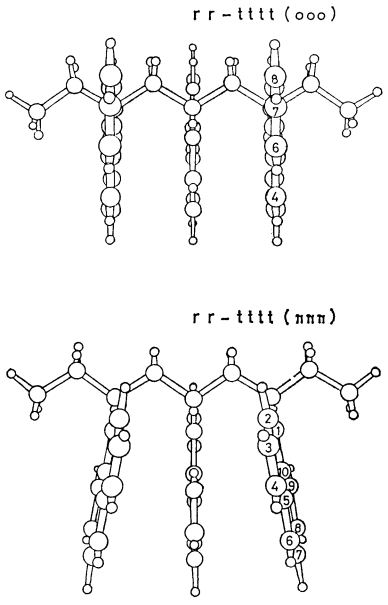

Fig. 1. Schematic representation of the rotational isomeric states of the side groups in (rr)-P1VN chain: (top) o-conformation; (bottom) π-conformation. In the P2VN chain, the α-carbon is bonded to the C(2) atom in the naphthyl group.

Recently, Tonelli[5] revealed that the ^{13}C-NMR chemical shifts of the aliphatic carbons in PS were attributable to a "γ-effect" (steric interaction between carbon atoms in the gauche arrangement) and to the ring current shielding effect (RCSE) of the aromatic groups. The γ-effect in PS depended on the stereoregularity or the skeletal conformations of the polymer chain. The apparent resemblance of the conformational situation between P2VN and PS described above suggests that the ^{13}C chemical shift of the former would be elucidated by γ-effect and RCSE of the aromatic rings, as reported by Tonelli for PS.[5] In the P1VN chain, the characteristic steric compression produced by the π-conformation would control the chemical shifts of the methine carbons. This effect depends only on the range accesible to the rotation of the 1-naphthyl ring, so that it would not depend on the steric regularity of the chain.

In this paper, we will discuss the distinct differences of the observed ^{13}C-NMR spectral patterns between P1VN and P2VN, based on the steric compression effect. In this spectra of P2VN and PS, there is no such unique effect as in P1VN, in addition to the γ-effect and RCSE.

Experimental

Instead of PVN polymers of high molecular weight, we used polymer samples of relatively low molecular weight, to obtain better resolved NMR spectra. The monomer of P1VN and P2VN were prepared from methyl naphthyl ketones,[6] and polymerized[7] in THF at -78 °C, using sodium naphthalenide as an initiator. The polymers were precipitated in about 10 times their volume of methanol in order to free them from any residual monomer and initiator, and were dried *in vacuo*.

The number-average molecular weights of these polymers were determined using a "KUNAUAR's Vapor Pressure

Osmometer" in chloroform solutions at 37 °C. The number-average degrees of polymerization ($\overline{DP}$) of the polymer samples were 80 for P1VN and 60 for P2VN. The molecular weight distributions of the polymers were determined by gel permeation chromatography ($\overline{Mw}/\overline{Mn}$: 1.90 for P1VN and 1.22 for P2VN).

^{13}C-NMR spectra were obtained using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.03 MHz, and a EC-100 computer with a memory capacity of 16 kilo words. samples were contained in 8 mm O.D. glass tubes and were degassed. The solvent used was chloroform-d_1, obtained from E. Merck A. G. The polymer concentration was *ca.* 30%. The 45° pulse width was about 13 μs. The apparatus was equipped with an internal ^{2}D field-frequency lock and a noise-modulated proton decoupler. The time-domain signal was digitized in 8192 channels, to provide 4096 data points after Fourier transformation. All spectra were observed at 30 °C.

Calculation

The chemical shifts of sterically perturbed carbon atoms are generally found at higher magnetic fields than those of unperturbed carbons which are not spatially crowded by neighboring atoms. The magnitude of these shifts exhibits a strong dependence upon the repulsive interactions between the ^{13}C–H bond and its surrounding groups. In order to evaluate the extent of the steric compression effect on ^{13}C-NMR chemical shifts, some equations of the steric force vector were proposed.[8,9] The steric compression effect was found to be directly related to the force component along the direction of the ^{13}C–H bond associated with nonbonded repulsive interaction. The repulsive interactions between nonbonded atoms or groups are sensitive to small changes in their separation distances and are produced not only by the hydrogen atom but also by the carbon atom. The numerical results reported here were obtained according to the H. J. Schneider's method[9] which has been applied to the fully relaxed molecular model in Force Field Method (FFM).[10] In defining the force vector F on the ^{13}C–H bond, H. J. Schneider *et al.*,[9] proposed an equation which was derived from a potential for nonbonded interactions:[11]

$$F = 0.6952\times10^{-5}(18\varepsilon/r^*)((r^*/r)^{10} - (r^*/r)^7)\times\cos\theta, \quad (1)$$

where r represents the distance of the hydrogen atom attached to ^{13}C from the interacting H or C; θ is the angle between the force vector and the perturbed ^{13}C–H bond. Equation 1 was applied to the hydrogen-hydrogen interaction (ε=0.004109, r^*=3.632) and also to the carbon-hydrogen interaction (ε=0.026102, r^*=3.575).[11] ε is an energy parameter which measures the depth of the van der Waals energy minimum, and r^* is the parameter which is correlated to the combined van der Waals radii of atoms. The steric compression effect on the methine and methylene carbons for P1VN was estimated by using a pentamer and a tetramer model, respectively, in which the terminal naphthyl groups were replaced by methyl groups.

To estimate the steric compression effect on the methylene carbon, the conformations of a relaxed tetramer model were chosen by the following procedure. A set of the initial models of trial conformations were obtained by combinations of each RIS for side groups (π- and o-conformations) and the backbone bonds (t, g, and $\bar{g}$). Before optimization[4] was completed (mainly in terms of the variation of the internal rotation for side groups and main chain, and bond angles for CH_2–αC–CH_2 and αC–CH_2–αC of the energy of these conformers), we carried out several examinations of the rotational angle of the naphthyl ring from the plane made by the adjoining backbone bonds. If the rotational angle in the conformer exceeded 10°, the subsequent optimization was rejected and this model of conformation was excluded from the relaxed conformations. In the pentamer model, the conformation of the relaxed model and their steric energies were adopted from the results in the previous paper.[4]

In addition to the steric compression effect, the ring currents of the naphthyl groups in PVN may also affect the ^{13}C-NMR chemical shift. The shift parameter $(\delta)_{RC}$ for this effect can be approximately calculated from the equation of McConnell,[12]

$$\delta_{RC} = \Delta\chi(1-3\cos^2\Omega)/3r^3, \quad (2)$$

where r is the distance of ^{13}C from the center of each ring, Ω is the angle made by the r vector and the plane of the ring, and $\Delta\chi$ is the anisotropy of the magnetic susceptibility. In naphthalene, the intensity of the ring current of each ring will be 1.093 times[13] larger than that of the benzene ring.[14] Therefore, we used -65.5×10^{-6} cm^3 mol^{-1} as the values of $\Delta\chi$ for each ring of naphthalene. The ring anisotropic effects on the methine and the methylene carbon were evaluated by using a pentamer and a hexamer model, respectively. In previously calculated results[4] of steric energies for pentamer models, the optimized rotational angles of the 1- and 2-naphthyl ring did not exceed ±4.5°, from the perpendicular position. Accordingly, it is resonable to consider that the naphthyl planes are almost perpendicular to the plane defined by adjoining skeletal bonds. The skeletal chains were assumed to have the same set of conformations which are generally preferred for vinyl polymers.[15]

Results and Discussion

Based on the calculation described above, we obtained six conformations as the relaxed conformations of PS, P1VN and P2VN, respectively. The steric energies of the relaxed conformations were shown in Table 1. The rotational angles for backbone bonds were denoted by the convention of Flory *et al.*[16] The steric interactions involving the bulky naphthyl group precluded $\bar{g}$ conformation. The backbones in PVN were limited to just two rotational states, the trans (t) and gauche (g) conformations, as in the case of PS.[16] The steric energy of the P2VN chain was hardly influenced by the change of RIS of the side groups. The steric energy of the P2VN chain, (except meso-tt conformer), was 0.5—0.9 kcal mol^{-1}**

** 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

Table 1. Steric energies[a] of the tetramer model of P1VN, P2VN, and PS with terminal methyl groups (kcal mol^{-1})

		Meso			Racemic		
		tt[b]	tg	gg	tt	tg	gg
PS		−0.71	1.24	3.64	0.0	2.10	2.59
P2VN	$\pi\pi$[c]	−2.29	1.77	4.23	0.0	3.04	3.19
	πo	−1.96	1.74	4.34	0.27	3.20	3.19
	$o\pi$	−1.96	1.74	4.40	0.27	2.84	3.19
	oo	−2.34	1.70	4.16	0.37	2.82	3.19
P1VN	$\pi\pi$	0.12	3.76	6.98	0.0	4.54	5.58
	πo	2.47	5.16	7.63	3.37	5.91	6.79
	$o\pi$	2.47	5.19	7.44	3.39	6.47	6.79
	oo	3.02	6.77	10.3	6.18	7.69	7.87

a) All values are evaluated relative to the each racemic-tt($\pi\pi$) state. b) Rotational Isomeric States (RIS) for backbone bonds are denoted by the convention of Flory *et al.* c) RIS for side groups in tetramer models.

larger than that of PS. The difference in the energy was attributed to the steric interaction of the bulky 2-naphthyl groups. In the meso-tt conformer, the 2-naphthyl planes are parallel to the adjoining one, and oriented in the same direction; the distance between the two planes was estimated to be about 2.87—3.64 Å. The nonbonded interaction energies between the two 2-naphthyl groups are mainly attributable to the attractive van der Waals force. The steric energy of the meso-tt conformer for P2VN was found to be smaller than that of PS.

The difference of the steric energies between racemic-tt($\pi\pi$) and other conformers of P1VN was obviously larger than that of PS and P2VN. In the conformers with the same skeletal conformation, $\pi\pi$-conformer is more stable than πo-, $o\pi$- and oo-conformer (represented by full line in Fig. 3). However, the $\pi\pi$-conformer may not always be of lower energy in comparison with another conformer, which has the skeletal conformation different from that of $\pi\pi$-conformer: m-tt(oo)<m-tg($\pi\pi$) and r-tt($o\pi$)<r-gg($\pi\pi$). In case of the tetramer model, in which the terminal naphthyl groups were replaced by methyl groups, the steric repulsion produced by o-conformation (the steric interaction of the adjacent naphthyl groups) was appreciably relaxed, and the total steric energy was underestimated. When the tetramer model containing four naphthyl groups was used, the curves in Fig. 3 might slope to the right. On the other hand, the summation of the force components, F_{sum}, along the methine or methylene bond, will not be affected by the choice of model. This is because the total steric energy would not be so much influenced by the steric interaction with respect to the F_{sum} values in this model.

Figure 2 shows the correlation of the steric energy E_{steric} for the pentamer model with the steric force F_{sum} directed along the methine bond, where F_{sum} is the arithmetical average of the steric forces directed along each methine bond in the same model chain.

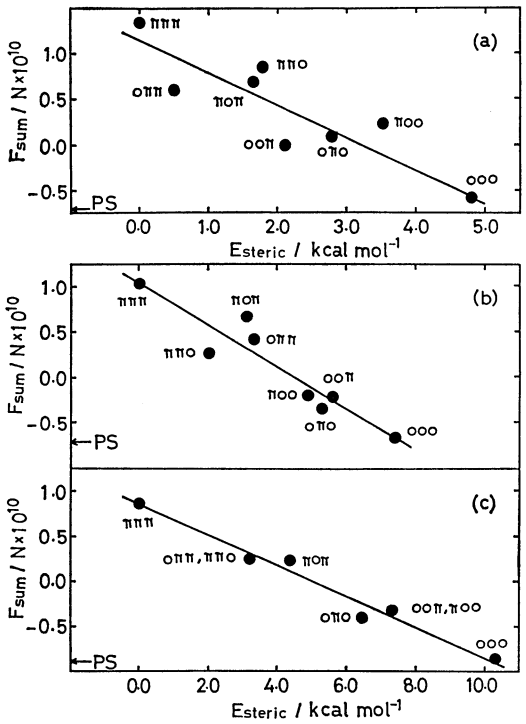

Fig. 2. Correlation of the steric energy E_{steric} of P1VN chain with the steric force F_{sum} directed along the methine bond. An arrow designates the calculated values of F_{sum} for PS chain.
(a): mm-tgtg conformer, (b): mr-tttg conformer, and (c): mm-tgtg conformer.

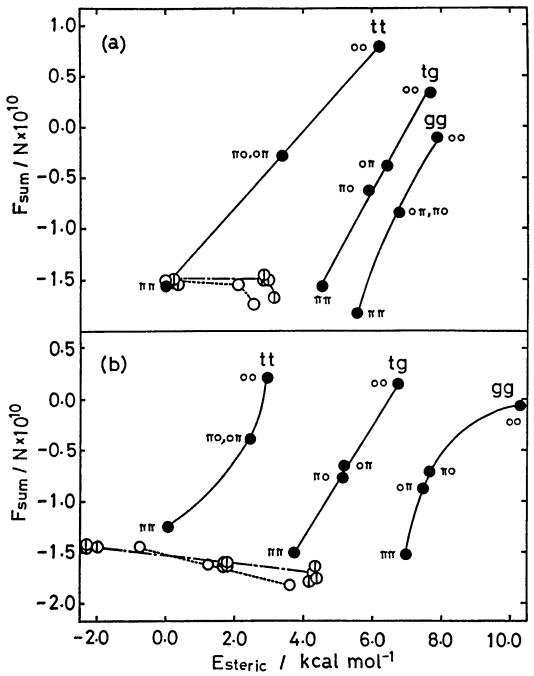

Fig. 3. Correlation of the steric energy E_{steric} for the tetramer model with the steric force F_{sum} directed along the central methylene bond.
●: P1VN chain, ⓘ: P2VN chain, and ○: PS chain.
(a): Racemic and (b): meso.

Table 2. Ring current shielding effect on the central methine and methylene carbon in model chain for the respective conformation

Chain conform.		Methine carbon (CH)			Methylene carbon (CH_2)		
		δ_{PS}[a]	$\delta_{P1VN}-\delta_{PS}$ $\pi\pi\pi\pi\pi$[b]	$\delta_{P2VN}-\delta_{PS}$[c] (h) (l)	δ_{PS}	$\delta_{P1VN}-\delta_{PS}$ $\pi\pi\pi\pi\pi\pi$	$\delta_{P2VN}-\delta_{PS}$ (h) (l)
iso	*gtgt[d]	−1.25	−0.54	−0.40—−0.44	−0.46	0.25	−0.18—−0.38
	*ttgg	−1.48	−0.92	−0.46—−0.52	−1.15	−0.76	−0.39—−0.67
	ggtt	−1.59	−0.93	−0.51—−0.62	−0.85	−0.57	−0.41—−0.66
syndio	*tttt	−0.63	−0.48	−0.30—−0.31	−0.35	−0.30	−0.20—−0.27
	ggtt	−1.72	−0.94	−0.55—−0.70	−0.67	−0.55	−0.32—−0.39
	ttgg	−1.34	−0.91	−0.42—−0.44	−1.63	−0.60	−0.58—−0.92
hetero*	tgtt	−1.11	−0.49	−0.36—−0.41	0.36	−0.03	0.26— 0.10
	gttt	−0.86	−0.64	−0.37—−0.37	0.36	−0.03	0.26— 0.10

a) The minus and plus signs represent paramagnetic and diamagnetic shielding, respectively. b) Rotational isomeric states for side groups in the P1VN chain. c) (h) and (l) represent ($\delta_{P2VN}-\delta_{PS}$) for the most upfield conformer and for the most downfield conformer, respectively. d) * represents the preferred conformation.

An arrow in Fig. 2 designates the calculated value of F_{sum} for the PS chain. When all RIS of the side groups in the model chain occupied the stable π-conformation ($\pi\pi\pi$-conformer), the methine group undergoes the maximum repulsive force in comparison with other conformers. The methine group in the *ooo*-conformer of this model experiences the same force as in the PS chain. The calculated values of F_{sum} for the P2VN model were located in the vicinity of that of the PS chain. Thus, the steric force directed along the methine bond in the P1VN chain was estimated to be $(1.73—2.08)\times10^{-10}$ N larger than that of PS or P2VN. As described above, whenever the P1VN chain occupies a π-conformation, the steric compression effect on the methine carbon was mainly caused by the intramolecular interaction of 1-naphthyl hydrogen in the same monomer unit. This effect was almost independent of the tacticity of the polymer chain. The methine group was slightly affected by other steric compression effects (*e.g.* γ-effect and detailed descriptions of γ-effect on the methine carbon in PS were given by Tonelli[5]). The backbones in PS are restricted to the trans and gauche states, excluding $\bar{g}$ state, and the methine carbons are always in the gauche arrangement with $C_{aromatic}$ connected to αC or CH_2 without regard to stereosequences, and should not exhibit any stereosequence-sensitive γ-effect. As the backbones in PVN are also restricted to the t and g, the methine carbons in PVN are not affected by the γ-effect and by the chain stereoregularity, as well as in PS.

The correlation of the steric energy E_{steric} for the tetramer model with the steric force F_{sum} directed along the central methylene bond is shown in Fig. 3. The numerical results of the γ-effect on methylene bond were excluded due to the interaction of the backbone atoms in the special case of the tetramer model. In contrast, with methine bond in P1VN chain, the methylene bond undergoes a repulsive force when the RIS of the side groups are in *o*-conformation. The repulsive force was produced by the steric overlap between the hydrogen in a rotating naphthyl ring and one of the methylenes. The magnitude of the steric force directed along the methylene bond in P1VN (occupied by the π-conformation) was not very different from that of the PS or the P2VN chain.

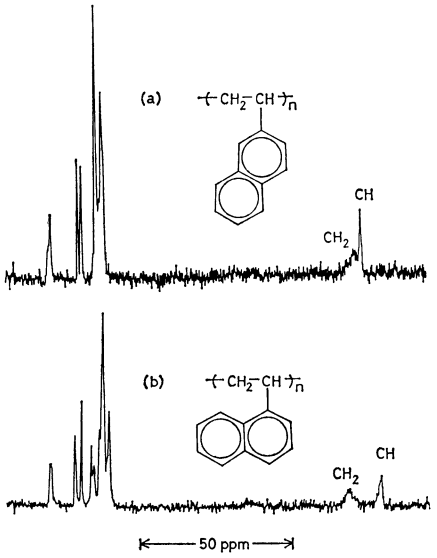

Fig. 4. Proton-decoupled, natural abundance ^{13}C FT NMR spectra of (a) P2VN and (b) P1VN in chloroform-d_1 at 25.03 MHz and 30 °C.

The correlation between the chemical shift and the steric force F_{sum} can be interpreted as follows, a) In the P1VN chain, the resonance of the methine carbon shifts to higher field in comparison with that of PS, owing to the steric interaction of the 1-naphthyl group (π) in the same monomer unit. The chemical shift of the methylene carbon is attributed to the γ-effect,[5] and the resonance peak is located in the vicinity of the position of PS. b) The resonance of the aliphatic carbons in the P2VN chain would appear at the same positions as the resonance of PS.

Figures 4a and 4b show the proton-decoupled ^{13}C-NMR spectra of P2VN ($\overline{DP}=60$) and P1VN ($\overline{DP}=80$), respectively. The experimental values of the chemical shifts of methine carbon or methylene carbon for PVN at 30 °C are represented relative to the chemical shifts of PS ($\overline{DP}=20$), and are summarized as follow.

$(\delta_{P1VN}-\delta_{PS})_{CH} = 6.83$, $(\delta_{P1VN}-\delta_{PS})_{CH_2} = 0.43$ ppm,

$(\delta_{P2VN}-\delta_{PS})_{CH} = -0.37$, $(\delta_{P2VN}-\delta_{PS})_{CH_2} = 0.85$ ppm.

The spectrum of the aliphatic region in the P2VN chain shows a similar pattern as that of PS. The resonance of the methine carbon in the P1VN chain appears at higher field in comparison with that of PS and P2VN. These experimental results correspond to the conclusion derived from Figs. 2 and 3.

The calculated results for ring anisotropic effect on methine and methylene carbon are given in Table 2. In RCSE on methylene carbon, the numerical results of those polymer chain (PS, P1VN, and P2VN) depend slightly on the chain regularity and conformation, indicating that the resonance of the methylene carbon spread to a broad band. On the other hand, the numerical results for RCSE on the methine carbon were little affected by the chain stereoregularity and backbone conformation. RCSE shifts of P2VN relative to PS, $(\delta_{P2VN}-\delta_{PS})_{CH,\,RCSE}$ for the preferred conformation were about -0.30——-0.44 ppm. The resonance of the methine carbon for the P2VN chain was not influenced by the steric interaction, resulting in an upfield shift of the methine in the P1VN chain, and was simply governed by the anisotropy of the 2-naphthyl ring. The experimental value of -0.37 ppm was in the range of the calculated values (-0.30——-0.44 ppm). For methine carbon in the P1VN chain, $(\delta_{P1VN}-\delta_{PS})_{CH,\,RCSE}$ the values for preferred conformations were about -0.48——-0.54 ppm. Evidently, the RCSE contributions to the observed ^{13}C chemical shift of methine carbon in P1VN are found to be small in comparison to the dominant steric compression effect.

Finally, we are tried to obtain the proportional constant between the magnitude of the steric compression force of methine bond in a P1VN chain and the chemical shift values. The shift values which depend on the steric compression effect only, could be obtained from substracting the $(\delta_{P1VN}-\delta_{PS})_{CH,\,RCSE}$ value from the experimental values. The constant obtained was $(3.5—4.2)\times10^{10}$ ppm N^{-1}. H. J. Schneider's constant was 20×10^{10} ppm N^{-1},[9] which was obtained for deshielded carbon atoms in substituted cyclohexane and in norbornane derivatives. D. M. Grant's constant for shielded carbon obtained from the non-relaxed model (*o*-xylene and methyl cyclohexane) was 1.30×10^{10} ppm N^{-1}.[8] Taking into account that the extent of the shift by the shielding force is smaller than that of the deshielding force, and that our constant was derived from shielding carbon in a relaxed model, the value of the calculated constant is considered to be resonable.

In ^{1}H-NMR spectra of P1VN, in addition to the RCSE by the 1-naphthyl ring, such a steric compression effect on the methine proton would also be revealed. However, it is difficult to estimate numerically this steric compression effect on the chemical shift of the proton in P1VN. The deshielding associated with the steric compression increases with increasing the repulsive interaction, but the distance between the hydrogen atoms does not simply relate to the extent of deshielding. Moreover, the nature of the deshielding mechanism by the steric interaction on the chemical shift of the proton is not very apparent at present.[17]

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