Table I. Catalytic Hydrolysis by Fluorocarbon and Hydrocarbon Amphiphiles[a]

	catalyst					
	C^F_{10}–HA–C_4N^+			$2C_{18}$–HA–C_4N^+		
substrate	C^F_{10}–PNP	C_{12}–PNP	PNPA	C^F_{10}–PNP	C_{12}–PNP	PNPA
10^2k_1, s^{-1}	185	8.4	0.45	0.11	12	0.71
relative k_1	1700	76	4	1	110	6

[a] 30 °C, 0.02 M borate buffer, μ = 0.01 (KCl), [catalyst] = 1.0×10^{-4} M. [substrate] = 1.0×10^{-5} M.

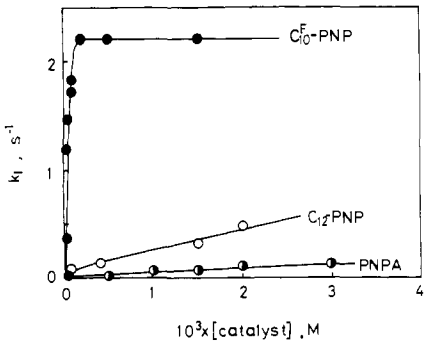
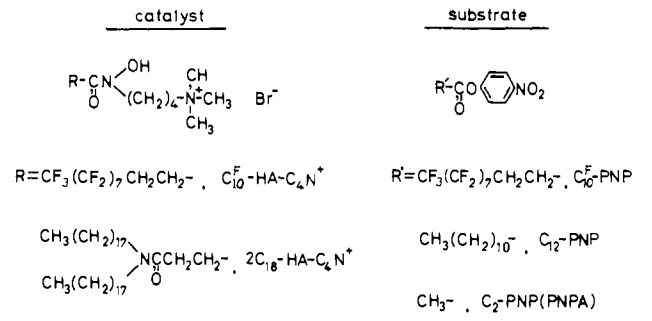


Figure 1. Catalytic hydrolysis of phenyl esters: 30 °C, 0.02 M borate buffer, μ = 0.05 (KCl), catalyst C^F_{10}–HA–C_4N^+, substrates 1.0×10^{-5} M.

Chart I



of C^F_{10}–HA–C_4N^+. The reaction of the hydrocarbon substrates, C_{12}–PNP and PNPA, proceeds less efficiently and without rate saturation.

The k_1 values at a catalyst concentration of 1.0×10^{-4} M are compared in Table I. The data obtained with the corresponding hydrocarbon (bilayer) catalyst, $2C_{18}$–HA–C_4N^+, are also included.[13] It is immediately apparent that both catalysts show analogous reactivities toward PNPA. This implies that the PNPA substrate is not strongly (or not deeply) bound to these catalytic aggregates, as expected from its lessened hydrophobicity. In the absence of strong binding, the difference in the long-chain portion (hydrocarbon vs. fluorocarbon) of the catalyst would not be influential in the reaction. In contrast, the catalytic reactivities toward C^F_{10}–PNP are very different; the fluorocarbon catalyst being 1700 times more efficient than the hydrocarbon catalyst. The saturation kinetics shown in Figure 1 strongly indicate that this remarkable rate difference arises from much enhanced binding of the fluorocarbon substrate to the fluorocarbon catalyst.

Interestingly, in the case of the C_{12}–PNP substrate, the two catalysts gave relatively large efficiencies of similar magnitude. This result appears strange, if the selective binding of hydrocarbon and fluorocarbon components produces a large rate difference as discussed above. It must be noted, however, that the hydrophobic portion of the fluorocarbon catalyst is made of hydrocarbon ($-C_4H_8-$) and fluorocarbon ($C_8F_{17}-$) components. C_{12}–PNP is probably bound to the hydrocarbon region of the fluorocarbon micelle.

In conclusion it is established that enhanced selectivities in catalysis can be created by a combination of micellar rate enhancements and discriminatory binding of hydrocarbon and fluorocarbon components.

(13) The reactivity of $2C_{18}$–HA–C_4N^+ is close to those of single-chain (hydrocarbon) zwitterionic hydroxamate.[11] Therefore, it appears that the aggregate morphology (micelle vs. bilayer) does not exert a significant influence on the hydroxamate reactivity. An attempt to synthesize a single-chain hydroxamate corresponding to $2C_{18}$–HA–C_4N^+ failed, because the final product obtained upon debenzylation lost its hydroxamate activity quickly when dissolved in water.

Conformational Origin of the Nonequivalent ^{13}C NMR Chemical Shifts Observed for the Isopropyl Methyl Carbons in Branched Alkanes

A. E. Tonelli,* F. C. Schilling, and F. A. Bovey

AT&T-Bell Laboratories
Murray Hill, New Jersey 07974

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Over 25 years ago, Drysdale and Phillips[1] observed geminal nonequivalence of ^{19}F nuclei in acyclic compounds by NMR. Nair and Roberts[2] confirmed these results and rationalized them in terms of conformational preference. Shoolery and Crawford[3] observed a corresponding nonequivalence of ^{19}F scalar couplings. Waugh and Cotton[4] noted that even in the absence of a conformational preference the geminal nonequivalence would still persist. Gutowsky[5] considered this latter aspect in greater detail. More recently van Gorkom and Hall[6] and Jennings[7] have reviewed the chemical shift nonequivalence of geminal groups in NMR spectra.

In the present paper we consider the ^{13}C NMR nonequivalence of the methyl carbons belonging to an isopropyl group attached to branched alkanes. Roberts and co-workers,[8] Lindeman and Adams,[9] and Carman and co-workers[10] have reported differences in ^{13}C NMR chemical shifts for methyl carbons in terminal isopropyl groups. Table I lists the branched alkanes studied by these investigators and presents the geminal nonequivalence observed by them. As discussed in the review by Jennings,[7] each of the compounds exhibiting geminal nonequivalence falls in either of two classes. They are either chiral or, if achiral, lack a plane of symmetry that bisects the CH_3–CH–CH_3 angle of the isopropyl group.

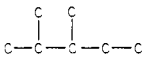
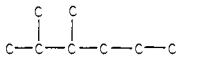
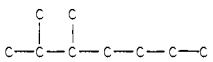
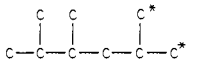
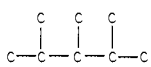
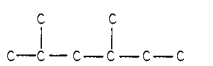
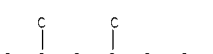
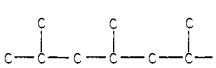
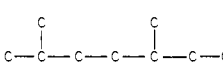
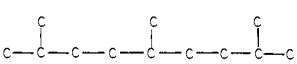
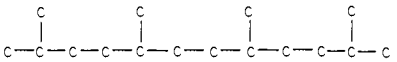
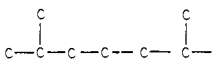
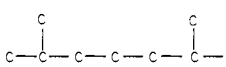
We have calculated the ^{13}C NMR chemical shift difference expected for the isopropyl methyl carbons in all but one of the branched alkanes listed in Table I. The γ-gauche effect method, which we previously demonstrated[11] can be utilized to predict the stereosequence-dependent ^{13}C NMR chemical shifts in vinyl homo- and copolymers and their model compounds, was used to calculate the methyl carbon chemical shifts.

As an illustration, consider 2,4-dimethylhexane (2,4-DMH), shown in Figure 1. The isopropyl methyl carbons, arbitrarily designated as side-chain (sc) and backbone (bb), are shielded[11] by their gauche arrangements with their γ substituent, the asymmetric C_4 methine carbon. The probabilities for these gauche

(1) Drysdale, J. J.; Phillips, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 319.
(2) Nair, P. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1957**, *79*, 4565.
(3) Shoolery, J. N.; Crawford, B., Jr. *J. Mol. Spectrosc.* **1957**, *1*, 270.
(4) Waugh, J. S.; Cotton, F. A. *J. Phys. Chem.* **1961**, *65*, 562.
(5) Gutowsky, H. S. *J. Chem. Phys.* **1962**, *37*, 2196.
(6) van Gorkom, M.; Hall, G. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 14.
(7) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.
(8) Kroschwitz, J. I.; Winokur, M.; Reid, H. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 5927.
(9) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(10) Carman, C. J.; Tarpley, A. R., Jr.; Goldstein, J. H. *Macromolecules* **1973**, *6*, 719.
(11) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.

0002-7863/84/1506-1157$01.50/0

Table I. Nonequivalent ^{13}C NMR Chemical Shifts for the Isopropyl Methyl Carbons in Branched Alkanes

alkane	Δδ obsd[a]	Δδ calcd
	2.2, 2.3	1.5
	2.2	1.5
	2.2	1.5
	2.2 (1.6*)	1.7 (2.4*)
	3.3	
	1.0 (1.9, 1.1, 0.9)[b]	1.6, 1.1, 0.9
	1.0	1.1
	1.1	1.4
	0.2	0.2
	0.2	0.2
	0.2	0.2
	0.0	0.0
	0.1	0.04
	0.0	0.0
	0.0	0.0

[a] Observed[8-10] between ambient temperature and 48 °C. [b] Observed[15] at −120, 25, and 90 °C in the present study.

arrangements are given by $(P_t + P_g^+)$ and $(P_g^+ + P_g^-)$ for C^{sc} and C^{bb}, respectively, where P_t, P_g^+, and P_g^- are the probabilities of finding the C_2–C_3 bond in rotational states t, g^+, and g^-.

From Mark's[12] rotational isomeric states (RIS) model for ethylene–propylene copolymers we determine[13] that $P_t = 0.380$, $P_g^+ = 0.014$, and $P_g^- = 0.606$.[14] Hence, C_4 is γ-gauche to C^{sc} with probability 0.394 and to C^{bb} with probability 0.620. We expect the ^{13}C chemical shift difference Δδ between C^{bb} and C^{sc} to be $(0.620 - 0.394)\gamma = 0.226\gamma$, where γ is the upfield shift produced by a gauche arrangement of the γ substituent relative to the trans (t) arrangement.

From our studies[11] of hydrocarbon vinyl polymers and their model compounds, it appears that $\gamma = -5$ is appropriate to the isopropyl methyl carbons in 2,4-DMH. Thus, $\Delta\delta = (0.226)(5) = 1.1$, with C^{bb} upfield from C^{sc}. Lindeman and Adams[9] observed $\Delta\delta = 1$, while we measure[15] 1.1 ppm at room temperature.

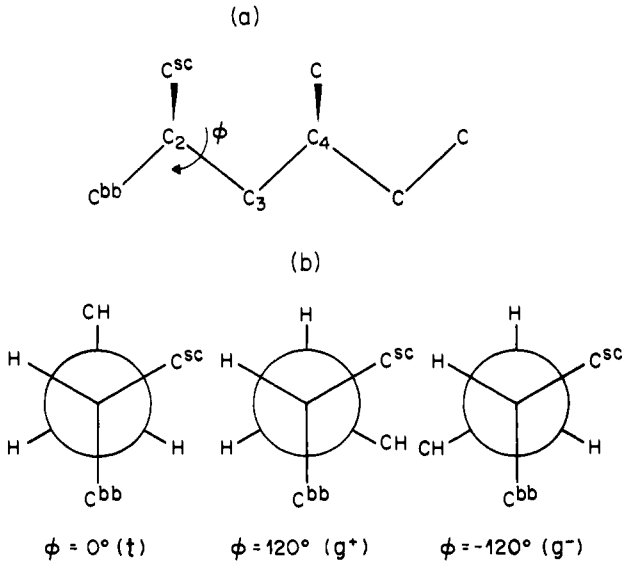


Figure 1. (a) 2,4-DMH in the all trans planar, zigzag conformation. (b) Newman projections illustrating rotational states about the C_2–C_3 bond of 2,4-DMH.

In addition we have found Δδ for 2,4-DMH to decrease from 1.9 to 0.9 as the temperature was increased from −120 to 90 °C. From the change in C_2–C_3 bond conformation probabilities produced by this 210 °C temperature change, we calculate $\Delta\delta = 1.6$ at −120 °C and 0.9 at 90 °C for a net decrease of 0.7 ppm. It therefore seems reasonable to conclude that the chemical shift nonequivalence observed for the isopropyl methyl carbons in 2,4-DMH has its origin in the conformationally sensitive γ-gauche effect.

Using Mark's[12] RIS model for those branched alkanes whose isopropyl groups are separated by at least one methylene carbon from the next substituted carbon and the RIS model developed by Asakura et al.[16] for head-to-head polypropylene to treat 2,3-dimethylpentane,[17] we have calculated Δδ's for all but one of the branched alkanes listed in Table I. The calculated values of Δδ are listed in the final column of the table.

The agreement between the observed and calculated nonequivalent ^{13}C chemical shifts is quite good, including the prediction that separation of the isopropyl group from the next substituted carbon by four or more methylene carbons removes the nonequivalence. On the basis of this comparison and the temperature-dependent nonequivalence observed and calculated for 2,4-DMH, we conclude that the conformationally sensitive γ-gauche effect is primarily responsible for the chemical shift nonequivalence observed for the isopropyl methyl groups in branched alkanes.

Registry No. 2,3-Dimethylpentane, 565-59-3; 2,3-dimethylhexane, 584-94-1; 2,3-dimethylheptane, 3074-71-3; 2,3,5-trimethylhexane, 1069-53-0; 2,3,4-trimethylpentane, 565-75-3; 2,4-dimethylhexane, 589-43-5; 2,4-dimethylheptane, 2213-23-2; 2,4,6-trimethylheptane, 2613-61-8; 2,5-dimethylheptane, 2216-30-0; 2,5,5-trimethylnonane, 49557-09-7; 2,5,8,11-tetramethyldodecane, 51324-39-1; 2,6-dimethylheptane, 1072-05-5; 2,6-dimethyloctane, 2051-30-1; 2,7-dimethyloctane, 1072-16-8; 2,8-dimethylnonane, 17302-30-6.

(12) Mark, J. E. *J. Chem. Phys.* **1972**, *57*, 2541.
(13) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969.
(14) From the Newman projections presented in Figure 1b., the φ = t and g^- conformations would appear to be equally populated. However, it is well-known[13] that rotational state probabilities for the bonds in linear chain molecules are dependent on the conformations, or rotational states, of neighboring bonds. The presence of an asymmetric center at C_4 produces intramolecular interactions depending simultaneously on φ and neighboring bond rotations which render the populations of φ = t and g^- states unequal.
(15) ^{13}C NMR spectra of neat 2,4-DMH were recorded at 50.3 MHz on a Varian XL-200 spectrometer.
(16) Asakura, T.; Ando, I.; Nishioka, A. *Makromol. Chem.* **1976**, *177*, 1493.
(17) In 2,3-dimethylpentane the isopropyl methyl groups are γ-gauche to both C_4 and the methyl carbon on C_3 when the C_2–C_3 bond is in a gauche (g^+ or g^-) conformation. On the basis of studies by Cantow et al.,[18] we assign the shielding produced by two simultaneous γ-gauche interactions a value of −8 ppm relative to the shielding produced by a single γ-gauche interaction, as occurs in the trans (t) conformation about the C_2–C_3 bond.
(18) Gronski, W.; Hasenhindl, A.; Limbach, H. H.; Möller, M.; Cantow, H.-J. *Polym. Bull.* **1981**, *6*, 93. Gronski, W.; Möller, M.; Cantow, H.-J. *Ibid.* **1982**, *8*, 503.