Short Communication

Relation Between the Carbon Chemical Shifts and the *J*(CH) Spin-Spin Coupling Constants

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WHILE the ^{13}C chemical shifts are additive and can be calculated with high accuracy in aliphatic hydrocarbons,[1,2] the alicyclic and particularly the rigid bi- and polycyclic compounds present additional problems.[3 to 6] For example, chemical shifts of the bridgehead methyl carbons vary considerably in 1-substituted bi- and tricyclic hydrocarbons, even though the immediate neighbouring atom is the same and the strong 1,4-interactions are not operative due to the molecular geometry (see Table 1). The methyl shift in the only reported structurally similar aliphatic compound, 3-methyl-3-ethyl-*n*-pentane,[2] is 23·2 ppm from TMS. In this particular case the diamagnetic contribution to this shift due to the γ-effects of the three methyl groups must be about 9 ppm and therefore the 1-methyl groups listed in Table 1 should all be less shielded. In some cases, however, just the opposite is true and these methyl carbon shifts are actually scattered over more than 10 ppm. The α-effects are also not constant in these hydrocarbons, and an approximate linear relation exists between the α-effects and the methyl carbon chemical shifts (see Fig. 1). At the same time the β-effects are fairly constant, thereby showing that the differences in methyl carbon shieldings are caused by changes in the C—CH$_3$ bond itself and not by remote interactions. The spin–spin coupling constants are related to the hybridisation of the carbon orbitals and so can provide important information about this bond. Unfortunately both the ^{13}C and ^{1}H single resonance spectra consist of many overlapping multiplets and are too complicated for a successful interpretation. From the proton spectra of the 1-methyl derivatives only the *J*(CH$_3$) values, which are virtually identical, could be measured.

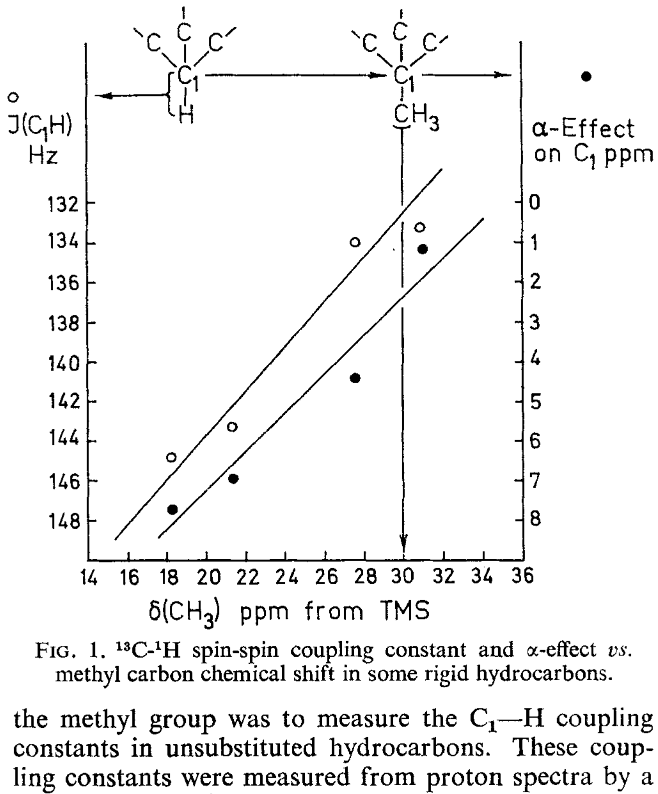

FIG. 1. ^{13}C-^{1}H spin-spin coupling constant and α-effect *vs.* methyl carbon chemical shift in some rigid hydrocarbons.

The only remaining possibility for characterising the hybridisation of the C$_1$ carbon orbital directed towards the methyl group was to measure the C$_1$—H coupling constants in unsubstituted hydrocarbons. These coupling constants were measured from proton spectra by a special ^{1}H—{^{13}C} double resonance technique which consists of alternately adding and subtracting proton spectra in a core memory during rapid 10 to 20 sec sweeps, once as single resonance and then with partial decoupling with a perturbing field of about 50 Hz amplitude, resonant with C$_1$ in the ^{13}C spectrum. The technique is similar to that described by Freeman,[7] but simpler and gives pure ^{13}C satellite spectra with other and possibly overlapping lines attenuated up to hundredfold.

TABLE 1. METHYL CARBON CHEMICAL SHIFTS AND ^{13}C-^{1}H COUPLING CONSTANTS IN SOME RIGID HYDROCARBONS

Compound	Methyl carbon chemical shift[a]	Substituent effects[b]			Spin-spin coupling constants $J(^{13}C—^1H)$, in Hz		
		α-	β-	γ-	$J(C_1H)$[c]	$J(CH_3)$	$J(CCH_3)$
1-Methylnorbornene[4]	18·3	7·7	7·1[d]	2·5[d]	144·8 ± 0·5		
1-Methylnorbornane[3]	21·4	6·9	6·8	1·1	143·2 ± 0·3	123·6 ± 0·2	4·6 ± 0·2
1-Methylbicyclo[3,2,1] octane	27·7	4·4	6·8[e]	0·1[e]	134·0 ± 0·5		
1-Methyladamantane[5]	31·1	1·3	6·6	0·3	133·5 ± 0·5	124·0 ± 0·2	4·6 ± 0·2

[a] In ppm; downfield from external tetramethylsilane.
[b] Paramagnetic shifts of the α, β and γ-carbons upon introduction of the methyl group into the unsubstituted compound.
[c] In the corresponding unsubstituted hydrocarbons.
[d] Effects on saturated carbon atoms.
[e] Mean values.

The same technique allows one to measure ^{13}C satellites and $^{13}C—^{1}H$ long-range coupling constants which are otherwise buried under the ^{12}CH main line in the ordinary single resonance proton spectra. For example, the coupling constants of methyl protons with the bridgehead carbon in 1-methylnorbornene and 1-methyladamantane were measured and found to be equal (4·6 ± 0·2 Hz). On the other hand, the $C_1—H$ coupling constants in unsubstituted hydrocarbons vary considerably and correlate with the chemical shifts of the methyl carbons in 1-methyl derivatives (see Fig. 1). The $C_1—H$ coupling constant in norbornadiene (146·4 ± 0·3 Hz) is even larger than in norbornene. A diamagnetic 17·5 ppm methyl shift could be estimated for the corresponding 1-methyl derivative.

It follows from the data given in Table 1 and Fig. 1 that hybridisation of the neighbouring saturated carbon atom is an important factor in determining the ^{13}C chemical shifts of the substituents.

REFERENCES

1. D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.* **86**, 2984 (1964).
2. L. P. Lindeman and J. Q. Adams, *Anal. Chem.* **43**, 1245 (1971).
3. E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova and A. Platé, *Org. Magn. Resonance* **2**, 581 (1970).
4. J. B. Grutzner, M. Jautelat, G. B. Dence, R. A. Smith and J. D. Roberts, *J. Amer. Chem. Soc.* **92**, 7107 (1970).
5. T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayuschkin and A. I. Tarasova, *Org. Magn. Resonance* **3**, 783 (1971).
6. E. Lippmaa, T. Pehk and J. Paasivirta, *Org. Magn. Resonance* **5**, 277 (1973).
7. R. Freeman, *J. Chem. Phys.* **43**, 3087 (1965).