Tetrahedron Letters No. 33, pp 3421 - 3424, 1972. Pergamon Press. Printed in Great Britain.

NMR SPECTRA OF MONOSUBSTITUTED ALKANES. II

ISOPROPYL DERIVATIVES

Gerd Schrumpf

Organisch-Chemisches Institut der Universität, Göttingen, Germany

(Received in UK 3 July 1972; accepted for publication 12 July 1972)

We are interested in the problem of how substitution of a saturated hydrocarbon molecule by an electronegative substituent affects the nmr shielding and coupling parameters (1, 2). We are currently investigating the monoderivatives of the higher straight-chain paraffins, the nmr spectra of which were previously much too complicated for analysis. For purposes of comparison, precise nmr data of the lower members of the alkyl monoderivatives are needed.

In this study the spectra of several isopropyl derivatives were remeasured and the A_6B spin systems analyzed by the method of least squares (3). The spectra of the compounds were recorded at several different concentrations in benzene as a solvent. The concentration dependence of the chemical shifts were fitted to a quadratic equation and this was used to extrapolate to the shift values of the neat liquid and to infinite dilution in benzene. The results are listed in table 1 .

From the upfield and the downfield doublets of the satellite spectra of the methyl group protons, the one-bond ^{13}CH coupling constants were obtained. The midpoint of the two spectra, which corresponds to the chemical shift of the methyl protons directly bound to the ^{13}C atom in the molecule CH_3-CHX-$^{13}CH_3$, was displaced towards higher field by about 0.2 to 0.3 Hz. An isotope shift of this magnitude and sign on ^{13}C substitution is in accord with earlier findings in paraffinic hydrocarbons (4) and their derivatives (2, 5). Long-range coupling between the protons of the methyl groups splits the doublets of the satellite spectra into quartets. Because of second order effects, the low field band of the upfield satellite is resolved best indicating absolute values of $^4J_{HH}$ of approximately 0.1 to 0.2 Hz.

At the base of each of the two methyl doublet lines two weaker absorptions were detected. We excluded the possibility of spinning side bands and signals due to impurities. The weak lines are the inner satellites of the methyl proton resonances indicating either geminal ^{13}CCH or vicinal $^{13}CCCH$ coupling. The observed values agree well with the magnitude of both types of coupling reported for related compounds (4, 6, 7). The sign of the geminal $^2J(^{13}CCH)$ in aliphatic compounds was found to be negative, while the sign of ^3J ($^{13}CCCH$) is positive relative to positive $^1J(^{13}CH)$. Since the sign was not determined in the present study the question remains open whether we observed the geminal or the

Table 1

Chemical shifts and ^{13}CH coupling constants of isopropyl derivatives CH_3-CHX-CH_3

X	c[a]	(CH_3)[b]	(CH)[b]	$J(^{13}CH_3)$[c]	Δ iso[d]	$J(^{13}C...H)$[e]
Cl	100	-582.18	-315.37	127.64	-0.28	±4.4
	0	-600.56	-341.53			
Br	100	-563.31	-305.43	127.73	-0.20	±4.5
	0	-584.54	-336.48			
J	100	-543.02	-299.78	127.83	-0.17	±4.7
	0	-568.39	-335.53			
$COCH_3$	100	-627.71	-473.50	-	-	-
	0	-630.84	-507.56			
CN	100	-609.27	-462.45	-	-	-
	0	-650.11	-534.85			

[a] Concentration in benzene in mole percent ; extrapolated values.

[b] Values in Hz at 100 MHz relative to internal benzene on the δ-scale ; absolute uncertainity is ± 0.15 Hz originating mainly from errors in the concentration measurements.

[c] Uncertainity ± 0.15 Hz.

[d] Isotope shift of the methyl protons directly bound to a ^{13}C atom ; negative values indicate upfield shifts which are accurate to 0.10 Hz.

[e] $^2J(^{13}CCH)$ or $^3J(^{13}CCCH)$: no sign determined ; accurate to 0.15 Hz .

---

vicinal ^{13}C . . . H coupling constant.

Previously chemical shifts and coupling constants of isopropyl derivatives were obtained at 40 MHz (8, 9. 10) and at 60 MHz (11, 12) by first order analysis of the spectra. A set of coupling data was derived from an A_6B type analysis using analytical expressions for the transition energies (13) . The coupling constants measured in this investigation are larger than those given in the literature but the general dependence on the nature of the substituent is the same in both sets of data (table 2) . The coupling constants of isopropyl compounds are compared to those between the methine proton and the methyl protons of 2-substituted butanes (2) , to the average coupling constant between the protons of the two methylene groups of n-propyl derivatives (1) and to the coupling constant of ethyl

Table 2

Vicinal coupling constants ${}^{vic}J_1$ of isopropyl derivatives and some simple alkyl compounds[a]

X	isopropyl			sec-butyl	n-propyl	ethyl
	b	c	d	e	f	g
OH	6.16[h]	6.2	6.05	6.13[i]	6.45[j]	6.97[k]
Cl	6.48	6.4	6.31	6.54	6.60	7.23
Br	6.58	6.5	6.40	6.67	6.67	7.33
J	6.76	6.6	6.43	6.82	6.80	7.45
$COCH_3$	6.95	-	6.95[l]	-	7.25	7.40[m]
CN	7.03	-	-	-	7.04	7.61

[a] All values in Hz. [b] This work ; accuracy 0.015 Hz. [c] Ref. 13. [d] Ref. 11

[e] Ref. 2. [f] Ref. 14. [g] Ref. 14 [h] Unpublished results. [i] Ref. 15.

[j] $n\text{-}C_3H_7\text{-}O\text{-}n\text{-}C_2H_7$ [k] Ref. 11. [l] Ref. 16. [m] Ref. 17.

compounds (14). The coupling constants of isopropyl, sec-butyl, and n-propyl derivatives are very similar, although the latter is a different type of coupling fragment. The ethyl couplings are larger than these by about 0.7 Hz. There is a linear relationship between the vicinal coupling constants of isopropyl and ethyl derivatives.

The chemical shifts of the halogen derivatives for the neat liquids and the infinitely dilute solutions in benzene are compared to those measured in cyclohexane (8) and in carbon tetrachloride solution (12) shown in table 3. The absolute shifts in cyclohexane and CCl_4 solutions and the neat compound are in close agrement but differ from that in the benzene solution where a considerable ASIS (18) is observed. The solvent effect produced by benzene seems to influence both types of protons in the isopropyl derivatives in a way similar to the reaction field in CCl_4 solution, because the internal shifts in benzene solution are close to those in CCl_4 solution.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft.

Table 3

Internal chemical shifts and solvent shifts of isopropyl derivatives

X		Internal shifts				Solvent shifts		
		a	b	c	d	e	f	g
Cl	CH_3	2. 71	2. 59	2. 67	2. 59	-0. 08	-0. 01	0. 33
	CH					0. 04	0. 03	0. 44
Br	CH_3	2. 55	2. 48	2. 58	2. 48	-0. 05	0. 01	0. 38
	CH					0. 02	-0. 02	0. 45
J	CH_3	2. 45	2. 35	2. 43	2. 33	-0. 01	0. 00	0. 41
	CH					0. 09	0. 02	0. 53

[a] All chemical shift values are in ppm, shifts to higher field being positive. The numbers are rounded off to the nearest hundredth ppm. Cyclohexane, ref. 8.

[b] CCl_4, ref. 12. [c] Neat, this work. [d] Benzene, this work. [e] $\nu (CCl_4 - C_6H_{12})$.

[f] $\nu (\text{neat} - C_6H_{12})$. [g] $\nu (\text{benzene} - C_6H_{12})$.

References

1. G. Schrumpf, J. Magnet. Resonance 6, 243 (1972)
2. G. Schrumpf, unpublished results
3. S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964)
4. R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. A 269, 385 (1962)
5. G. Schrumpf and W. A. Klein, unpublished results
6. H. Sackmann and E. Dreeskamp, Z. physik. Chem. (Frankfurt/M.) 34, 261 (1962)
7. G. J. Karabatsos and C. E. Orzech, J. Amer. Chem. Soc. 87, 560 (1965)
8. A. A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc. 80, 1728 (1958)
9. G. V. Tiers, cited by F. A. Bovey, NMR Data Tables for Organic Compounds, Vol. 1, Interscience Publishers, New York 1967
10. D. E. Webster, J. Chem. Soc. 1960, 5132
11. R. E. Glick and A. A. Bothner-By, J. Chem. Phys. 25, 362 (1956)
12. J. R. Cavanaugh and B. P. Dailey, J. Chem. Phys. 34, 1099 (1961)
13. J. Ranft, Annal. Physik 10, 1 (1963)
14. S. Ebersole, S. Castellano and A. A. Bothner-By, J. Phys. Chem. 68, 3430 (1964)
15. L. M. Jackman and N. S. Bowman, J. Amer. Chem. Soc. 88, 5565 (1966)
16. L. M. Jackman and D. P. Kelly, J. Chem. Soc. (B) 1970, 102
17. D. H. Sardella, J. Molec. Spectr. 31, 70 (1969)
18. P. Laszlo, Progr. N. M. R. Spectr. 3, 231 (1967)