

PROTON CHEMICAL SHIFT-CHARGE DENSITY CORRELATIONS IN SUBSTITUTED ALKYL DERIVATIVES.

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Attempts have been made in recent years to correlate proton chemical shifts and charge densities in different series of compounds.¹ Mono substituted methanes and ethanes, owing to their relatively simple electronic structure, seem to yield more useful information on the electronic mechanism involved in determining the proton chemical shift.^{2,3,4,5,6} In these compounds correlations between C¹³ and H¹ chemical shifts and substituent electronegativity were observed,²⁻⁵ although several limitations were found to be present. It is commonly accepted that beside electron density changes around the proton due to the electronegativity of substituents, other factors, namely magnetic anisotropy^{3,4} and electrostatic field effects,⁷ are important. Recently⁶ it has been observed that good correlations between ¹³C and ¹H chemical shifts and substituent electronegativity for methyl and ethyl derivatives can be found, if corrections to the experimental shifts are allowed for lone pair dipole moments in substituent groups.

We present now a series of correlations involving proton chemical shifts for mono and polysubstituted aliphatic hydrocarbon derivatives and positive charge densities on hydrogen determined by a MO-LCAO method proposed by Del Re.⁸ The method provides charge densities which are consistent with the dipole moments of the molecules examined and they seem to have the properties required by real charges.^{8,9}

The compounds examined here, the relative proton chemical shifts and proton charge densities are listed in the Table. Charge densities (q_H) for several compounds were computed by means of the parameters given by Del Re.⁸ In other cases we have evaluated the MO-LCAO parameters by employing known values of dipole moments: the parameters obtained were made consistent with those of other substituents belonging to the same row or group of the periodic system. The plot of the chemical shifts in δ units against q_H , reported in the Figure, clearly shows that a linear relationship exists for substituted aliphatic compounds limited to substituents of the same row of the periodic system. This holds for mono- and polysubstituted methanes and branched aliphatic derivatives. This fact should lead to the conclusion that, in substituted aliphatic compounds, the proton chemical shift is mainly determined by the electronic charge on the hydrogen atom. Nevertheless an explanation should be found for the fact that charge densities

TABLE *

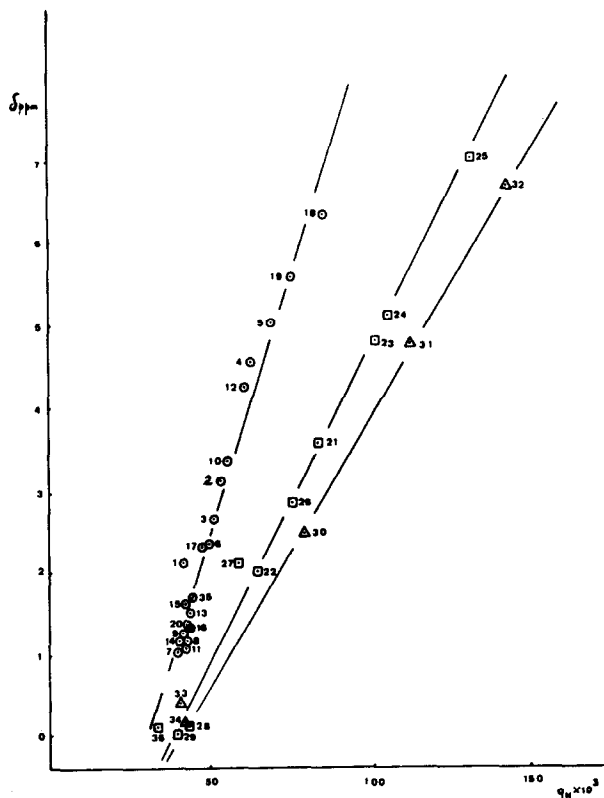
n°	Compound	δ^{\dagger}	q_H	n°	Compound	δ^{\dagger}	q_H
1	$(CH_3)_3N$	2,11	0,041	19	CH_2F_2	5,62 ^b	0,075
2	$(CH_3)_2O$	3,17	0,053	20	\underline{CH}_3CH_2F	1,35	0,042
3	CH_3CCl_3	2,64	0,051	21	$\underline{CH}_2(SET)_2$	3,59	0,083
4	$\underline{CH}_2(OEt)_2$	4,56	0,062	22	$(CH_3)_2S$	2,00	0,064
5	$\underline{CH}(OEt)_3$	5,03	0,069	23	$\underline{CH}(SET)_3$	4,83	0,101
6	\underline{CH}_3NH_2	2,34 ^a	0,049	24	CH_2Cl_2	5,13	0,105
7	$\underline{CH}_3CH_2NH_2$	1,08 ^a	0,040	25	$CHCl_3$	7,08	0,131
8	\underline{CH}_3CH_2SH	1,18 ^a	0,042	26	CH_3Cl	2,85	0,075
9	\underline{CH}_3CH_2OH	1,21 ^a	0,041	27	\underline{CH}_3SH	2,09 ^c	0,058
10	\underline{CH}_3OH	3,37 ^a	0,055	28	$(CH_3)_4Si$	0,00	0,039
11	$(\underline{CH}_3CH_2)_2S$	1,11 ^a	0,042	29	$(\underline{CH}_3)_3SiCH_2Cl$	0,12 ^b	0,043
12	CH_3F	4,26 ^b	0,060	30	CH_3Br	2,47	0,079
13	$(\underline{CH}_3)_2CHCl$	1,51	0,043	31	CH_2Br_2	4,78	0,112
14	$(\underline{CH}_3CH_2)_2O$	1,14	0,040	32	$CHBr_3$	6,72	0,142
15	$(\underline{CH}_3)_3CCl$	1,59	0,042	33	$(CH_3)_3As$	0,40 ^d	0,040
16	\underline{CH}_3CH_2Cl	1,32	0,043	34	$(CH_3)_4Ge$	0,127 ^d	0,042
17	$(\underline{CH}_3)_2NH$	2,31	0,047	35	CH_3CH_2Br	1,68	0,044
18	CHF_3	6,38 ^b	0,085	36	$(CH_3)_3SiH$	0,08 ^d	0,033

* Where not specified chemical shifts were measured in our laboratory, by employing a Varian DP 60 spectrometer operating at 56.4 Mc.

† in ppm from TMS (negative values).

a Ref. 2. b Ref. 10. c Ref. 11. d Ref. 12.

correlate differently with proton chemical shifts when substituents belong to different rows of the periodic system. No doubt q_H in substituted aliphatic derivatives is a smoothly varying function of the position of the substituent in the periodic table since it follows parallelly the electronegativity of substituents as one goes across the periodic table and the same holds roughly for proton chemical shifts,^{5,6} but evidently the two quantities do not possess the same slope. The slopes of the linear correlations reported in the Figure should throw light on the



mechanism of transmission of substituent effects to the proton, and this mechanism seems to be the same within the same row of the periodic system. Since elements of the same row possess the same inner electron shell and elemental properties are mainly connected to the outer electron configuration, these slopes could reflect such a situation; this consequently should also mean that proton chemical shifts and charge densities have a different sensitivity to valence electron configuration.

Further elaboration of the data is required to clear up this point. A preliminary check on carbon charge densities (q_C), evaluated by the same method, seems to indicate that good fits can be obtained with C^{13} chemical shifts, and the product $q_C \cdot q_H$ is well related to J_{C-H}^{13} coupling constants.

A complete description of the results obtained will be reported soon.

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REFERENCES

- 1) T. Schaefer, W.G. Schneider, Can.J.Chem., **41**, 966 (1963); P.J. Black, R.D. Brown and M.L. Heffernan, Austr.J.Chem., **20**, 1305, 1325 (1967); J.M. Sichel and M.A. Whitehead, Theor.Chim.Acta, **2**, 35 (1966).
- 2) B.P. Dailey and J.N. Shoolery, J.Am.Chem.Soc., **77**, 3977 (1955).
- 3) J.R. Cavanaugh and B.P. Dailey, J.Chem.Phys., **34**, 1089 (1961).
- 4) H. Spiesecke and W.G. Schneider, J.Chem.Phys., **35**, 722 (1961).
- 5) F. Taddei, C. Zauli, contribution to "Nuclear Magnetic Resonance in Chemistry" Ed. B. Pesce - Academic Press Inc. - New York - 1965 - p. 179.
- 6) P. Bucci, J.Am.Chem.Soc., **90**, 252 (1968).
- 7) T.W. Marshall and J.A. Pople, Mol.Phys., **1**, 199 (1958).
- 8) G. Del Re, J.Chem.Soc., 1958, 4031.
- 9) G. Del Re, B. Pullman and T. Yonezawa, Biochim.and Biophysic. Acta, **75**, 153 (1963).
- 10) W. Brugel, "Nuclear Magnetic Resonance spectra and chemical structure" vol. I - Academic Press - New York - London, 1967.
- 11) D.W. Mathieson "Interpretation of organic spectra" - Academic Press Inc. - London, 1965.
- 12) M.L. Maddox, S.L. Stafford and H.D. Kaesz in "Advances in organometallic chemistry" Edited by F.G.A. Stone and R. West - Academic Press - New York - London, 1965 - vol. 3.