[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electron Distribution in Molecules. III. The Proton Magnetic Spectra of Simple Organic Groups[1]

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Complex proton magnetic resonance spectra have been observed with a high resolution r.f. spectrometer in a large number of simple organic liquids. The components of the resonance absorption have characteristic positions which depend upon the electronic environment of the protons. The "chemical shifts" observed in the resonance positions of the various proton-containing groups are generally in good qualitative accord with the accepted concepts describing the electronic structures of the molecules. A graphical summary is given of the spectra, which appear to be of promise in structural and qualitative analysis, although there are limiting and complicating factors.

Introduction

The magnetic resonance absorption of a nucleus is influenced by its electronic environment. A difference in the electron distribution about a nucleus in different molecules produces a "chemical shift"[2] in the location of the resonance; this leads to complex resonance lines in a compound with structurally non-equivalent nuclei. In the first paper[3] of this series, the fluorine resonance shifts in substituted fluorobenzenes were related to the influence of the substituents upon the electron distribution in the benzene ring. In the second paper[4] the fluorine and proton resonance shifts in the halomethanes provided information about the ionic character of the C–H bonds and the double bond character of the C–X bonds. This article reports the proton resonance shifts in a number of simple organic compounds.

At the time this investigation was started, the primary purpose was the relation of the results to the chemical behavior of the more common organic functional groups. Qualitative theories based upon electronic effects have long been used by organic chemists to predict chemical reactivity.[5] The course of any reaction depends in principle upon the normal electronic states of the reactants and the various electronic interactions in the transition state. The chemical shifts in the nuclear magnetic resonances are a qualitative measure of electronic differences in the normal state of molecules and as such should be related to chemical reactivity. In addition, during the course of these measurements it became clear that the proton spectrum of a molecule was distinctive enough to be of value in structural analysis,[2] even though the proton resonance shifts are very small. Therefore, the research was extended to include a greater variety of proton types, and the emphasis was changed from observing particular groups to viewing and assigning the spectrum as a whole. The results obtained constitute a reasonably complete determination of the proton spectra of the simpler hydrogen-containing organic groups.

Experimental

The measurements were made with a high resolution spectrometer[6] using a permanent magnet with an adjustable field strength of about 4172 gauss. Maximum resolution was the order of one milligauss. The chemical shifts were obtained at a fixed radiofrequency and are reported with respect to the proton resonance in pure H_2O. The chemical shift parameter δ is defined as $10^6 \times (H_r - H_c)/H_r$, where H_r is the resonant magnetic field for the water reference and H_c is the field for the proton resonance in the group under observation. In practice, we measured the field difference between the resonance in the compound and in 95% sulfuric acid. The sample was placed in one part of a split r.f. coil[6] and the sulfuric acid in the other. The corrections for the slight field difference at the two positions and for the conversion to the H_2O reference were determined simultaneously by measuring H_2O with respect to the acid.

The observations were made at room temperature on pure liquid samples, except for methylamine and naphthalene. Melting point glass capillaries were used as sample tubes. The tubes have an internal diameter of about 1 mm. and were filled to a height of 4 to 5 mm., the height of the r.f. coil, so the sample volume was about 0.003 cm.^{3} The samples were obtained from commercial sources or from the various organic laboratories at the University of Illinois. Purity was generally high, although small amounts of impurities do not usually interfere with the measurements. The chemical shift is apparently independent of concentration in solution except in those cases where chemical exchange is important[7] or where there is strong hydrogen bonding.[8] The measurements on methylamine and naphthalene were made in solution. Solutions must be of relatively high concentration to give detectable absorption, or larger samples must be used. However, increasing the sample size reduces the resolution because of greater field inhomogeneities. Solids cannot be used since ordinarily the magnetic dipole interactions broaden[2] very greatly the absorption line and prevent the measurement of the small proton resonance shifts.

Figure 1 is a typical oscilloscope display of the proton resonances in a sample and the reference, as a function of applied magnetic field. The most intense line, on the right, is from the 95% H_2SO_4 reference. The sample was *o*-toluidine, $NH_2C_6H_4CH_3$, and the other three lines in the spectrum, from left to right, correspond to CH_3, NH_2 and the four protons on the benzene ring. The four benzene protons are not equivalent; but the shifts are small and unresolved. However, the line from the benzene protons is somewhat broadened, which gives it a peak intensity only slightly greater than that of the CH_3 group. In many cases, assignment of the resonances to particular groups could be accomplished in a similar manner from the observed intensities. The proton spectrum in Fig. 2 is that of benzylamine, $C_6H_5CH_2NH_2$. The intense line at the right is from the five protons on the benzene ring; but the two lines from CH_2 and NH_2 have comparable intensities. In such cases the assignment could be made generally by comparing the resonance shifts with the shifts observed for the same group in other molecules, *e.g.*, $C_2H_5NH_2$ and CH_3CH_2OH.

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(1) Supported in part by ONR.

(2) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951); prior publications are cited there.

(3) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

(4) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(5) See for example, R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950. . Also, a bibliography is given in reference 3.

(6) H. S. Gutowsky, L. H. Meyer and R. E. McClure, *Rev. Sci. Instruments*, **24**, August (1953).

(7) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, in press (1953).

(8) J. T. Arnold and M. E. Packard, *ibid.*, **19**, 1608 (1951).

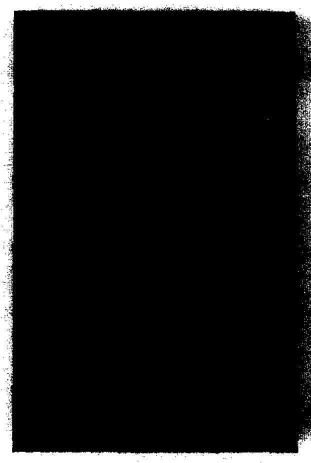

Fig. 1.—Oscilloscope photograph of the proton magnetic resonance spectrum in *o*-toluidine, $NH_2C_6H_4CH_3$, displayed simultaneously with the reference resonance in 95% sulfuric acid. From left to right the absorption lines are from protons in CH_3, NH_2, C_6H_4 and in the reference. The total sweep in applied magnetic field is 100 milligauss, decreasing from left to right.

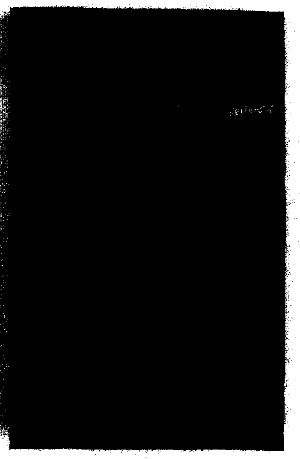

Fig. 2.—Oscilloscope photograph of the proton magnetic resonance spectrum in benzylamine, $C_6H_5CH_2NH_2$. From left to right the absorption lines are from protons in the NH_2, CH_2 and C_6H_5 groups. The total sweep in applied magnetic field is 50 milligauss, decreasing from left to right.

Mention should be made of the fine structure produced in some of the resonances by the indirect interaction of structurally non-equivalent magnetic nuclei.[9] The appearance of the multiplet structure is usually predictable and rarely causes difficulty in the measurements. In some cases the multiplets are useful in locating the relative position of groups in a molecule. The splittings, when found in these compounds, ranged from 0.5 to 2 milligauss. There were cases in which the resolved fine structure or unresolved broadening obscured an adjacent resonance. Fortunately, the fine structure splittings can always be distinguished from chemically shifted resonances by observations at two field strengths; the fine structure separations, in gauss, are independent of the applied magnetic field while the chemical shifts, in gauss, are directly proportional to the field.

Results

The chemical shift δ-values with respect to the proton resonance in H_2O are listed in Table I for a number of organic compounds. The different sections in the table give the δ-values for particular types of proton-containing groups in the compounds. The average chemical shift, $\bar{\delta}$, for the particular proton type in the compounds listed is given with the section heading. The probable error for each of the individual δ-values is no more than ±0.03 δ-unit. In some of the sections there are entries for only one or a few compounds; for these proton types the $\bar{\delta}$-values will be subject to revision when more data are available. In some cases the incomplete resolution of absorption lines corresponding to two different proton types prevented their individual assignment; in such cases the compounds are listed without δ-values.

Figure 3 is a graphical presentation of the proton magnetic resonance spectra in the simple organic groups. The horizontal lines give the experimental range of the δ-values for each group in the compounds investigated. The vertical lines are the average δ-values, $\bar{\delta}$, for each group. The numbers in parentheses following the structural classifications give the number of compounds observed of each type. In cases where only a few compounds have been investigated, the range of absorption will no doubt be extended when additional compounds are measured.

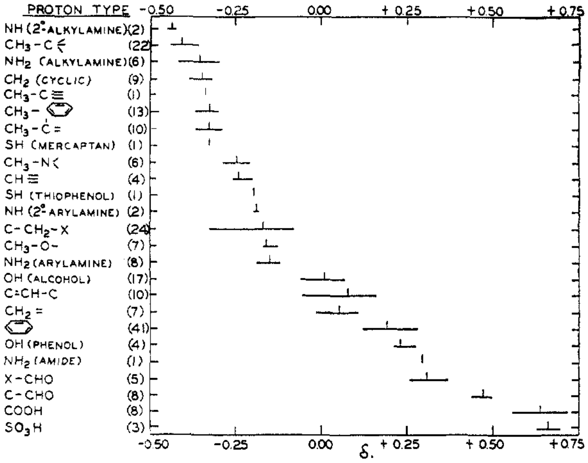

Fig. 3.—The proton magnetic resonance absorption spectra in simple organic groups. The horizontal lines indicate the range of absorption observed for each group; the vertical lines are the average values. The number in parentheses after the group designation is the number of different compounds in which the absorption of the given group was observed. The zero of the scale is the proton resonance in water.

Discussion

Within the limits of our present understanding of the factors determining the proton δ-values, the observations reported here are qualitatively in good accord with the current electronic theories of the chemical behavior of the groups. In the paper giving the resonance shifts in the halomethanes,[4] it was found that the proton δ-values become increasingly positive with increasing ionic character of the C–H bond. And the same rule should apply[4] to protons in other bonds such as SH, OH or NH. However, in a more complex manner, the resonance shifts depend also upon the species of atom to which the proton is bonded, as shown by the results on the hydrides.[2] Therefore, a direct, simple comparison cannot be made of the δ-values for an OH proton and, for example, an SH proton. Before discussing the proton classes individually, several intercomparisons will be given.

Fuson has noted[10] that the methyl group reactivity increases in the sequence CH_3–CH_3, CH_3–C_6H_5, CH_3COCH_3 and CH_3–NO_2. The proton δ-values in Table I 1, n, m and r, corresponding to the methyl groups in these compounds are −0.41, −0.34, −0.33 and −0.13, respectively. The correlation shows that the reactivity of the methyl group is directly proportional to the ionic character of the C–H bonds in the group. In the same tabulation[10] of

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(9) H. S. Gutowsky, D. W. McCall and C. P. Slichter, THIS JOURNAL, **21**, 279 (1953).

(10) Reference 5, p. 7.

TABLE I

PROTON CHEMICAL SHIFTS IN SIMPLE ORGANIC GROUPS

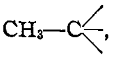
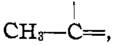
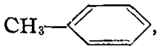
Compound	δ
H_2O	0.00
a. OH (alcohol), $\bar{\delta} = +0.01$	
CH_3OH	+ .01
C_2H_5OH	+ .05
n-C_3H_7OH	+ .05
i-C_3H_7OH	− .01
n-C_4H_9OH	.00
i-C_4H_9OH	− .02
s-C_4H_9OH	− .03
t-C_4H_9OH	− .06
n-$C_5H_{11}OH$	− .01
Cyclohexanol	+ .05
$C_6H_5CH_2OH$	+ .03
1-Ethyne, 1-hydroxycyclohexane	.00
Allyl alcohol	+ .06
Methylbutynol	− .03
Methylpentynol	− .05
Ethylene glycol	+ .06
Glycerol	+ .07
b. OH (phenol), $\bar{\delta} = +0.23$	
C_6H_5OH	+ .27
o-Cresol	. . .
m-Cresol	+ .23
p-Cresol	+ .21
o-F-Phenol	. . .
m-F-Phenol	. . .
p-F-Phenol	. . .
p-Cl-phenol	. . .
Methyl salicylate	+ .21
p-CH_3O-phenol	. . .
c. COOH, $\bar{\delta} = +0.64$	
$HCOOH$	+ .56
CH_3COOH	+ .63
C_2H_5COOH	+ .72
n-C_3H_7COOH	+ .71
i-C_3H_7COOH	+ .67
CF_3COOH	+ .60
CF_2HCOOH	+ .67
Acrylic acid	+ .56
d. SO_3H, $\bar{\delta} = +0.66$	
$HOSO_3H$	+ .63
$ClSO_3H$	+ .65
CH_3SO_3H	+ .70
e. SH (mercaptan), $\bar{\delta} = -0.33$	
n-C_4H_9SH	. . .
$C_6H_5CH_2SH$	− .33
$HOCH_2CH_2SH$	. . .
f. SH (thiophenol), $\bar{\delta} = -0.20$	
C_6H_5SH	− .20
g. NH (2°-alkylamine), $\bar{\delta} = -0.44$	
$(C_2H_5)_2NH$	. . .
$(C_6H_5CH_2)_2NH$	− .45
Morpholine	− .43
h. NH (2°-arylamine), $\bar{\delta} = -0.20$	
$C_6H_5NH(CH_3)$	− .20
$C_6H_5NH(C_2H_5)$	− .19
i. NH_2 (alkylamine), $\bar{\delta} = -0.36$	
$C_2H_5NH_2$	−0.42
i-$C_3H_7NH_2$	. . .
n-$C_4H_9NH_2$	. . .
i-$C_4H_9NH_2$	− .36
s-$C_4H_9NH_2$	− .33
n-$C_7H_{15}NH_2$	. . .
$C_6H_5CH_2NH_2$	− .36
Allylamine	− .38
Ethylenediamine	− .31
j. NH_2 (arylamine), $\bar{\delta} = -0.15$	
$C_6H_5NH_2$	− .15
o-Toluidine	− .19
m-Toluidine	− .17
p-Phenetidine	− .13
m-Cl-Aniline	− .12
p-F-Aniline	− .13
2,6-Dimethylaniline	− .16
2,3-Dimethylaniline	− .17
k. NH_2 (amide), $\bar{\delta} = +0.29$	
$HCONH_2$	+ .29
l. , $\bar{\delta} = -0.41$	
C_2H_5OH	− .40
$(C_2H_5)_2O$	− .41
C_2H_5CHO	− .43
C_2H_5COOH	− .42
$C_2H_5NH_2$[a]	− .42
$(C_2H_5)_2NH$	− .42
$(C_2H_5)_3N$	− .43
$C_6H_5NH(C_2H_5)$	− .44
$C_2H_5NO_2$	− .40
$C_6H_5C_2H_5$	− .41
$HCOOC_2H_5$	− .41
$CH_3COOC_2H_5$	− .42
$(C_2H_5)_2NCOCl$	− .39
i-C_3H_7OH	− .40
i-C_3H_7CHO	− .40
i-C_3H_7COOH	− .41
i-$C_3H_7NH_2$	− .41
i-$C_3H_7NO_2$	− .41
C_6H_5-*i*-C_3H_7	− .42
t-C_4H_9OH	− .41
C_6H_5-*t*-C_4H_9	− .42
Methylbutynol	− .36
m.  $CH_3-\overset{\vert}{C}=$, $\bar{\delta} = -0.33$	
Crotonaldehyde	− .37
Tiglaldehyde	− .36 − .29
CH_3COOH	− .32
CH_3COOCH_3	− .32
$CH_3COOC_2H_5$	− .34
CH_3CHO	− .34
CH_3COCl	− .29
$(CH_3CO)_2O$	− .31
$(CH_3)_2CO$	− .33
n. , $\bar{\delta} = -0.33$	
$C_6H_5CH_3$	− .34
o-Xylene	− .34

TABLE I (*Continued*)

	Compound	δ
	m-Xylene	− .33
	p-Xylene	− .33
	Mesitylene	− .34
	o-Cresol	− .37
	m-Cresol	− .32
	p-Cresol	− .34
	o-Toluidine	− .35
	m-Toluidine	− .31
	2,6-Dimethylaniline	− .30
	2,3-Dimethylaniline	− .31 − .35
o.	CH_3—C≡, $\bar{\delta} = -0.34$	
	CH_3CN	− .34
p.	CH_3—N$<$, $\bar{\delta} = -0.25$	
	CH_3NH_2[a]	− .24
	$C_6H_5NH(CH_3)$	− .29
	$C_6H_5N(CH_3)_2$	− .27
	$HCON(CH_3)_2$	− .24
	$(CH_3)_2NCOCl$	− .22
	$(CH_3)_2NSO_2Cl$	− .21
q.	CH_3—O—, $\bar{\delta} = -0.16$	
	CH_3OH	− .17
	$C_6H_5OCH_3$	− .17
	p-CH_3O-phenol	− .15
	$HCOOCH_3$	− .15
	CH_3COOCH_3	− .16
	$C_2H_5COOCH_3$	− .13
	Methyl salicylate	− .17
r.	CH_3X[d]	
	CH_3NO_2	− .13
	CH_3SO_3H	− .18
	$(CH_3)_2SO_4$	− .12
	CH_3F	− .23
	CH_3Cl	− .23
	CH_3Br	− .21
	CH_3I	− .18
s.	CH_2 (cyclic), $\delta = -0.35$	
	Cyclohexane	− .39
	Cyclohexanol	− .38
	Cyclohexanone	− .32
	Cyclohexene	− .36
	Cyclohexyl fluoride	− .39
	Cyclohexyl chloride	− .33
	Cyclohexyl bromide	− .33
	1-Ethyne, 1-hydroxycyclohexane	− .32
	Cyclopentanone	− .32
t.	C—CH_2—X, $\bar{\delta} = -0.17$	
	C_2H_5OH	− .16
	$(C_2H_5)_2O$	− .15
	$HCOOC_2H_5$	− .13
	$CH_3COOC_2H_5$	− .13
	$C_6H_5CH_2OH$	− .08
	Allyl alcohol	− .09
	$(ClCH_2CH_2)_2O$	− .11 − .11
	Ethylene glycol	− .12
	Glycerol	− .09
	1,4-Dioxane	− .12
	Ethylene oxide	− .25
	Morpholine	−0.11 − .23
	$C_2H_5NH_2$	− .27
	$(C_2H_5)_2NH$	− .30
	$(C_2H_5)_3N$	− .33
	$C_6H_5CH_2NH_2$	− .17
	$(C_6H_5CH_2)_2NH$	− .20
	Allylamine	− .17
	$(C_2H_5)_2NCOCl$	− .16
	Ethylenediamine	− .21
	$C_2H_5NO_2$	− .11
	$C_6H_5CH_2SH$	− .16
u.	CH_2=, $\bar{\delta} = +0.05$	
	Pentene-1	− .02
	Acrylonitrile	+ .07
	Acrolein	+ .10
	Acrylic acid	+ .06
	$C_6H_5CH{=}CH_2$	+ .04
	Allyl alcohol	+ .06
	Allylamine	+ .06
v.	CH≡, $\bar{\delta} = -0.24$	
	$C_6H_5C{\equiv}CH$	− .25
	1-Ethyne, 1-hydroxycyclohexane	− .20
	Methylbutynol	− .26
	Methylpentynol	− .26
	Hexyne-1	...
	Heptyne-1	...
w.	C=CH—C, $\bar{\delta} = +0.08$	
	Acrylonitrile	+ .07
	Acrolein	+ .10
	Acrylic acid	+ .06
	$C_6H_5CH{=}CH_2$	− .05
	Allyl alcohol	+ .06
	Allylamine	+ .06
	Cyclohexene	+ .06
	Crotonaldehyde	+ .16 + .16
	Tiglaldehyde	+ .16
x.	Aromatic (benzene ring), $\bar{\delta} = +0.19$	
	Benzene	+ .18
	$C_6H_5CH_3$	+ .19
	$C_6H_5C_2H_5$	+ .21
	C_6H_5-*n*-C_3H_7	+ .22
	C_6H_5-*i*-C_3H_7	+ .21
	C_6H_5-*n*-C_4H_9	+ .21
	C_6H_5-*s*-C_4H_9	+ .20
	C_6H_5-*t*-C_4H_9	+ .20
	$C_6H_5CH_2OH$	+ .22
	$C_6H_5CH_2SH$	+ .22
	$C_6H_5CH_2NH_2$	+ .18
	$(C_6H_5CH_2)_2NH$	+ .17
	C_6H_5CHO	+ .26
	$C_6H_5CH{=}CH_2$	+ .16
	$C_6H_5C{\equiv}CH$	+ .15
	C_6H_5OH	+ .19
	C_6H_5SH	+ .18
	$C_6H_5NH_2$	+ .18
	$C_6H_5NH(CH_3)$	+ .18
	$C_6H_5NH(C_2H_5)$	+ .18
	$C_6H_5N(CH_3)_2$	+ .18
	$C_6H_5NO_2$	+ .28
	C_6H_5F	+ .18

TABLE I (*Continued*)

Compound	δ	Compound	δ
C_6H_5Cl	+ .19	Quinoline	$+0.18_{(5)}$ $+ .28_{(1)}$ $+ .36_{(1)}$
C_6H_5Br	+ .26	Isoquinoline	$+ .18_{(5)}$ $+ .30_{(1)}$ $+ .39_{(1)}$
C_6H_5I	+ .27	y. X—CHO, $\bar{\delta} = +0.31$	
$C_6H_5OCH_3$	+ .17	HCOOH	+ .29
o-Xylene	+ .16	$HCOOCH_3$	+ .31
m-Xylene	+ .17	$HCOOC_2H_5$	+ .26
p-Xylene	+ .15	$HCONH_2$	+ .37
o-Cresol	+ .16	$HCON(CH_3)_2$	+ .34
m-Cresol	+ .16	z. C—CHO, $\bar{\delta} = +0.47$	
p-Cresol	+ .15	CH_3CHO	+ .45
o-Toluidine	+ .18	C_2H_5CHO	+ .50
m-Toluidine	+ .12 + .19	*n*-C_3H_7CHO	+ .48
p-CH_3O-phenol	+ .20	*i*-C_3H_7CHO	+ .50
p-Phenetidine	+ .17	C_6H_5CHO	+ .49
m-Cl-aniline	+ .21	Acrolein	+ .46
Methyl salicylate	+ .17	Crotonaldehyde	+ .44
Mesitylene	+ .14	Tiglaldehyde	+ .46
x′. Other aromatic compounds			
Naphthalene[b]	+ .29		
Pyridine	$+ .19_{(3)}$[c] $+ .35_{(2)}$		

[a] H_2O solution. [b] In CCl_4 Solution. [c] Subscript numbers in parentheses indicate the intensity ratio of the absorptions. [d] X is a group for which the C–X bond is not a C–C bond.

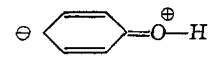
electronic and chemical properties, the compounds CH_3OH, C_6H_5OH and CH_3CO_2H are listed in order of increasing acid strength. The δ-values of the protons in the OH groups are +0.01, +0.27 and +0.63, respectively, indicating the expected relation between acid strength and the ionic character of the OH bond.

A less simple case is that of protons attached to aliphatic, olefinic and acetylenic carbon atoms. In these compounds the δ-values are about −0.4, +0.05 and −0.25, respectively. One might have felt that the proton δ-value for the acetylenic group, HC≡C, should be even more positive than that for the olefinic group, CH_2=C, instead of between it and the aliphatic group, CH_3–C. But on going from an aliphatic to an acetylenic group, large changes in bond hybridization are involved as well as changes in ionic character of the bonds. Bond hybridization differences are a probable cause of the complex dependence of the proton shifts upon the atomic species to which the proton is bonded,[2] and could very well account for the apparently anomalous behavior of the acetylenic proton.

In the following sections the δ-values are discussed in more or less detail for the particular classes of protons.

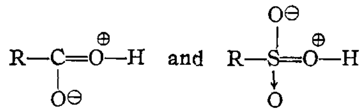
a. OH (**Alcohol**).—The δ-values for the alcoholic OH protons are in the range ±0.07, agreeing with the neutral character of the OH group and emphasizing its similarity to water, for which $\delta \equiv 0.00$. The range in δ is small for the number of compounds measured; the differences arise no doubt from such factors as hydrogen bonding[8] and substituent effects[3] of the group attached to the OH. Similar measurements on five simple alcohols have been reported[11] by the magnetic resonance laboratory at Stanford. They measured the chemical shifts of the CH_3 and CH_2 groups with respect to the hydroxyl resonance in each alcohol, and insofar as their measurements overlap those in Table I, the agreement is very good.

b. OH (**Phenol**).—The phenolic OH protons have large positive δ-values, +0.21 to +0.27, compared to those of the alcoholic OH groups. The introductory discussion related this difference to the acidic nature of the phenols. In terms of electronic structure, the phenols have resonance forms of the type



which increase the ionic character of the OH bond, and thereby increase δ. As shown in Fig. 3 the absorption region of the phenolic OH protons is overlapped by absorption of aromatic protons, and the resonances are resolved only in some cases; this is evidenced by the incomplete entries in Table Ib.

c. CO_2H and d. SO_3H.—The protons in these two groups are comparable in that they have the most positive δ-values, +0.56 to +0.72, observed in this survey. The acidic nature and the ionic character of the OH bonds in the pure acids arise from resonance forms of the types



$$\mathrm{R{-}\underset{O^{\ominus}}{\underset{|}{C}}{=}\overset{\oplus}{O}{-}H} \quad \text{and} \quad \mathrm{R{-}\overset{O^{\ominus}}{\overset{|}{\underset{\overset{\downarrow}{O}}{S}}}{=}\overset{\oplus}{O}{-}H}$$

which are stabilized by the symmetry of the anion. No correlation has been found between the δ-values of the acids and their ionization constants in solution. The lack of correlation is not too surprising since dissociation in solution depends also upon solvation energies and entropies of ionization,[3] factors which do not influence the δ-values in the pure acids.

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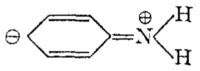
(11) J. T. Arnold, S. S. Dharmatti and M. E. Packard, *J. Chem. Phys.*, **19**, 507 (1951).

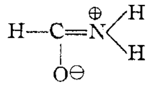
e. SH (Mercaptan) and f. SH (Thiophenol).—SH group protons were measured only in benzyl mercaptan, −0.33, and in thiophenol, −0.20. In pure liquid H_2S the δ-value is −0.36.[2] These values are lower than those for the OH groups in alcohols and phenols, but the difference probably involves bond hybridization as well as ionic character effects. The more positive value for thiophenol, compared to the mercaptan, no doubt arises in the same way as in the phenols compared to the alcohols, discussed in (b). The smaller difference between the sulfur compounds, compared to the oxygen, reflects the decreasing ability of the larger atoms to form double bonds.[12]

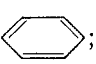
g. to j. NH_2 (1° and 2° Alkyl and Aryl Amines).—The 1° alkyl and aryl amines have $\bar{\delta}$-values of −0.36 and −0.15, respectively, while the 2° amine $\bar{\delta}$-values are −0.44 and about −0.20. In pure liquid NH_3 the δ-value is −0.43.[2] The δ-values of the aryl amines, both 1° and 2°, are around 0.23 more positive than in the alkyl amines, which fact is consistent with the relative basicities of the compounds. The difference may be attributed to resonance forms of the type

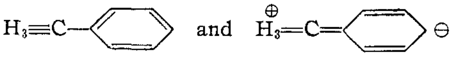


These forms are similar to those discussed for the phenols, and it is of interest to note that the difference in δ-values between the alcohols and phenols is the same as the difference between the alkyl and aryl amines. There are too few data for comparison of 1° with 2° amines.

k. NH_2 (Amide).—The only compound of this type investigated is formamide, for which the NH_2 proton δ-value is +0.29. This large positive value, compared to the amines, conforms with the loss of basic character of the NH_2 group in formamide. It also illustrates the influence of the carbonyl group, which is suggested by resonance forms such as



l. CH_3—C$<$; m. CH_3—C=; n. CH_3—**; and o. CH_3—C≡.**—Among the CH_3 group protons, those in which the CH_3 group is bonded to an aliphatic carbon, class l, have the lowest $\bar{\delta}$-value, −0.41, and also the smallest range of δ-values, −0.36 to −0.44, considering the number of compounds measured. The small range indicates the similarity of the CH_3 groups in the various compounds, as might well have been anticipated from their similar chemical behavior. The three classes, m, n and o, in which the methyl group is attached to various multiple bonded carbon atoms, do not differ significantly among themselves in their δ-values. However, $\bar{\delta}$ for these three classes is −0.33, definitely more positive than the −0.41 for the aliphatic compounds. The difference may be considered as verification of the importance of hyperconjugation, the resonance forms of which increase the ionic character of the C–H bonds in the CH_3 group



p. CH_3—N$<$; q. CH_3—O—; and r. CH_3X.—The relatively large shifts toward more positive δ-values for the CH_3 groups in these compounds may be attributed at least partially to inductive effects of the N, O and X atoms. The electronegativities vary in order O > N > C, which accounts qualitatively for the $\bar{\delta}$-values of −0.16, −0.25 and −0.41 for protons in methyl groups attached to O, N and aliphatic carbon, classes q, p, and l, respectively. The chemical shifts for the methyl halides are included in Table Ir; they have been discussed in detail elsewhere,[4,13] demonstrating that in these compounds the δ-values are influenced by resonance effects as well as by inductive effects. For instance, the δ-value in CH_3NO_2 is relatively positive, −0.13, compared to the δ-value of −0.24 observed in the CH_3—N$<$ compounds, class p. However, this result is consistent with the difference in the sign of the resonance effects in the NH_2 and NO_2 groups.

s. CH_2 (Cyclic) and t. C–CH_2–X.—These two classes of methylene groups have δ-values much the same as the CH_3 groups. The $\bar{\delta}$-value for the cyclic methylene groups is −0.35, slightly more positive than the −0.41 value of CH_3 groups attached to aliphatic carbon, class l. But it should be noted that the measurements are limited to five- and six-membered rings. Class t which contains all other methylene groups measured includes δ-values ranging from −0.11 to −0.33. The same factors apply here as for the CH_3 groups in classes p, q and r.

u. CH_2=; v. CH≡; and w. C=CH—C.—In the introductory discussion, the large differences between δ-values of protons attached to carbons having multiple bonds and those attached to aliphatic carbon were ascribed to differences in bond hybridization as well as to changes in ionic character of the C–H bond. The intermediate position of the acetylenic C–H δ-values is particularly striking in view of the known acidic behavior of this proton type. The range of δ-values for the C=CH–C group, w, overlaps that of the CH_2= group.

x. Benzene and Other Cyclic Aromatic Compounds.—Protons on the benzene ring have a $\bar{\delta}$-value of +0.20. This rather positive value is somewhat higher than the $\bar{\delta}$-values of +0.05 in CH_2=, class u, and of +0.10 in C=CH—C, class w; again, the differences probably are associated with the nature of the bond hybrids. It was hoped that the resonances from the structurally non-equivalent protons on the ring could be resolved to give a more direct measure of substituent effects than in the previous work on substituted fluorobenzenes.[3] To date this resolution has not been

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[12] K. S. Pitzer, This Journal, **70**, 2140 (1948).

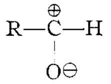
[13] Note added in proof.—There is an as yet unresolved discrepancy in the δ-values, −0.33 and −0.94, given for CH_4 in references 2 and 4, respectively. The data given in this article suggest an intermediate value. The zero of the δ_H values in reference 4 is accordingly uncertain, but the arguments and conclusions given there are unaffected.

achieved except in a few isolated cases, namely, *m*-toluidine and the heterocyclic aromatics. It appears that the natural line widths may exceed the chemical shifts of the ring protons, in gauss, at moderate magnetic fields and hence preclude their resolution.

The proton δ-values in the monosubstituted benzenes are in effect an average over the three types of protons on the ring, and should be a measure of any net substituent effect. Unfortunately, the observed range is relatively small. Nonetheless, it is of interest that the proton δ-values do correlate at least approximately with the average of the substituent effects measured in the *o*-, *m*- and *p*-monosubstituted fluorobenzenes.[3]

The δ-values for the four other cyclic aromatic compounds, naphthalene, pyridine, quinoline and isoquinoline, are listed principally to show the differences in their spectra. In naphthalene, the α- and β-protons were not resolved; moreover, the δ-value of +0.29 is higher than in any of the benzene compounds. The observations on the heterocyclic compounds demonstrate the strong influence of the nitrogen in the ring, and also show the rapid attenuation of the effects with increasing distance from the nitrogen.

y. X–CHO and z. C–CHO (Aldehydes).—The $\bar{\delta}$-values for the protons in these two classes are +0.31 and +0.47, respectively, the most positive values observed except for the acid protons. The two classes are similar to C=CH–C, class w, for which $\bar{\delta}$ is +0.08, except that doubly bonded oxygen replaces the carbon. The much more positive δ-values observed in the oxygen compounds emphasize the importance of the structural form



$$R{-}\overset{\oplus}{C}{-}H \quad \text{with } \underset{}{O^{\ominus}} \text{ on C}$$

This structure has a net positive change on the carbon atom of the carbonyl group, and hence increases the ionic character of the C–H bond, and the δ value.

Concluding Comments

The discussion above suggests the value of proton resonance shifts in the study of electron distribution in organic compounds. There are a number of good correlations of the δ-values with the chemical behavior and with the prevailing concepts of the electronic properties of the various structural groups. However, the effects of changes in bond hybridization are imperfectly understood at present and limit comparisons to similar types of compounds. Even within this limitation the results may prove useful as a quantitative evaluation of "group effects." For example, the changes in $\bar{\delta}$ for the proton resonance in the OH group, proceeding from alcohols to phenols to acids, are 0.22 and 0.41, which agree very well with the changes of 0.21 and 0.44 in $\bar{\delta}$ for the NH_2 group between alkyl amines, aryl amines and amides. Moreover, if an analysis of the bond hybridization effects can be made, the results presently considered *anomalous* will provide further information about the molecular electronic structures.

The application of the proton chemical shifts to problems in structural and quantitative analysis appears promising. There are several limiting and complicating factors, such as the small range of shifts, the overlapping of the absorption regions of different groups, the multiplet structure of some of the lines, the variations in natural line widths which influence the apparent intensities, and the necessity of using liquid samples to resolve the absorption. However, the general appearance of the proton spectrum can be predicted directly from the relative numbers of non-equivalent protons in a postulated structure. And no doubt such simplicity is one of the main advantages of this type of spectroscopy.

We are developing techniques for observing the proton shifts in compounds which are solids at room temperature. And, if successful, the research will be extended to such compounds. Also, there are a number of results obtained in this survey which are inconclusive, but which we hope to report on in more detail when a wider range of compounds and conditions have been investigated.

Acknowledgment.—We are indebted to the Research Corporation for financial assistance in obtaining the magnet. Also, we wish to thank a large fraction of our friends and colleagues for their interest and patience in supplying a drop of this or of that compound.

URBANA, ILLINOIS