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Monthly Ecumenical Letters from Laboratories Of N - M - R

No. 17

[Contribution from the Noyes Chemical Laboratory, University of Illinois and the Department of Chemistry, Fordham University]

THE DETERMINATION OF DOUBLE-BOND CHARACTER IN CYCLIC SYSTEMS. V. PROTON CHEMICAL SHIFTS IN CHELATED DERIVATIVES OF BENZENE, NAPHTHALENE AND PHENANTHRENE.[1,2]

A. L. Porte,[3] H. S. Gutowsky,[3] and I. Moyer Hunsberger[4]

The OH proton chemical shifts are measured for phenol, β-naphthol, 9-phenanthrol, and for chelated o-substituted derivatives of each containing an aldehyde, methyl ketone and methyl ester group. The large amounts ($\Delta\delta$) by which the shifts to lower applied fields are greater in the chelated derivatives than in the parent phenols are measures of the strengths of the intramolecular hydrogen bonds and are proportional to the bond multiplicity of the ring bonds between the carbon atoms holding the chelated substituents. The $\Delta\delta$ values are also proportional to $\Delta\nu$ (C = O) values determined earlier from infrared spectra of the same compounds. Mechanisms responsible for the proton chemical shifts are discussed.

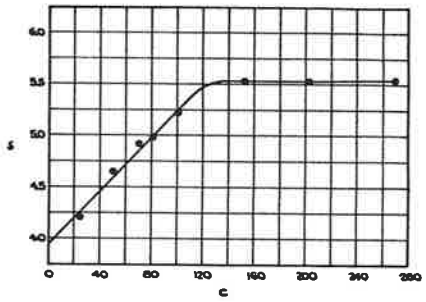


Fig. 1. The hydroxyl proton chemical shift (δ), in p.p.m. downfield from cyclohexane, in phenol as a function of the concentration (c) of phenol in carbon tetrachloride, in g./l. of solution.

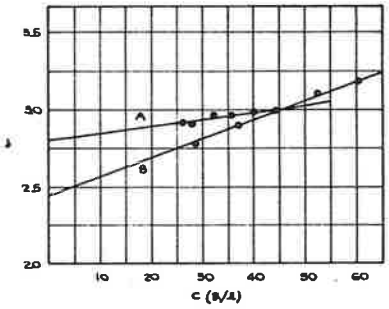


Fig. 2. The hydroxyl proton chemical shifts (δ), in p.p.m. downfield from cyclohexane, in β-naphthol (A) and phenol (B) as a function of concentration in benzene solution (C), in g./l. of solution.

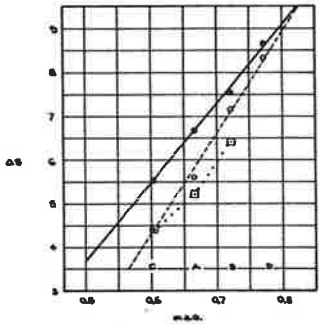


Fig. 3. Δδ values, in p.p.m., of chelated aldehydes (---), chelated ketones (—) and chelated esters (....) as functions of mobile bond order (m.b.o.) of the C = C bond spanned by the chelated system. A larger Δδ value corresponds to a larger downfield shift and stronger hydrogen bonding. The compounds included are 1,2-disubstituted benzenes (A), 1,2-disubstituted naphthalenes (B), 2,3-disubstituted naphthalenes (C), and 9,10-disubstituted phenanthrenes (D).

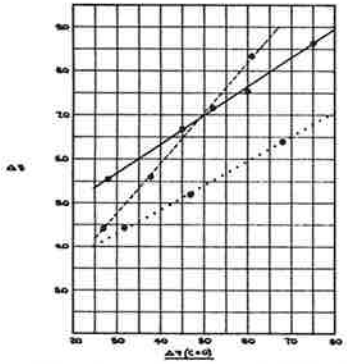


Fig. 4. Δδ values, in p.p.m., of chelated aldehydes (---), chelated ketones (—) and chelated esters (....) as functions of the corresponding Δν (C = O) values. A larger Δδ value corresponds to a larger downfield shift and stronger hydrogen bonding. The compounds included are listed in Table I.

Table I

The OH proton chemical shifts (p.p.m.) of phenol, β-naphthol, 9-phenanthrol, and some of their chelated o-substituted derivatives, in infinitely dilute solution in carbon tetrachloride. The shifts are downfield from and relative to cyclohexane.

Phenol	3.93
Methyl Salicylate	9.14
Salicylaldehyde	9.55
o-Hydroxyacetophenone	10.63
β-Naphthol	4.3
Methyl 2-hydroxy-1-naphthoate	10.72
2-Hydroxy-1-naphthaldehyde	11.48
2-Hydroxy-1-acetonaphthone	11.85
Methyl 3-hydroxy-2-naphthoate	8.74
3-Hydroxy-2-naphthaldehyde	8.74
3-Hydroxy-2-acetonaphthone	9.85
9-Phenanthrol	4.61
10-Hydroxy-9-phenanthrenecarboxaldehyde	12.95
Methyl 10-hydroxy-9-phenanthryl ketone	13.25

Table II

OH stretching frequencies and hydroxyl proton chemical shifts in phenol, β-naphthol and 9-phenanthrol

	ν (OH) (cm^{-1})	Chemical shift (p.p.m.)
Phenol	3628	3.93
β-Naphthol	3618	4.30
9-Phenanthrol	3605	4.61

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

RATE PROCESSES AND NMR SPECTRA. III. PROTON EXCHANGE AND HYDROLYSIS OF AMIDES[1]

A. Saika[2]

The chemical exchange of the NH protons in pure liquid N-methylformamide (NMF) and N-methylacetamide (NMA) and the hydrolysis of the compounds in acid solution have been studied by high resolution proton magnetic resonance methods. The activation energy required for exchange among the NH protons is found to be 14 ± 2 kcal mole^{-1} for both NMF and NMA. The rate constants of the acid hydrolysis were determined at three different temperatures, giving activation energies of 13 ± 3 and 15 ± 3 kcal mole^{-1} for the hydrolysis of NMF and NMA respectively. The relationship between the proton exchange and the acid hydrolysis is discussed, and it is proposed that the N-protonated form of the amides is that which undergoes the acid hydrolysis.

TABLE I

TEMPERATURE DEPENDENCE OF $1/\tau\delta\omega$

N-methylformamide			N-methylacetamide		
T	$\delta\omega_e$*	$1/\tau\delta\omega$	T	$\delta\omega_e$*	$1/\tau\delta\omega$
°K	radian sec^{-1}	radian^{-1}	°K	radian sec^{-1}	radian^{-1}
301.5	30.0	0.00	302	29.5	0.00
368	28.1	0.13	410	28.5	0.09
373	28.3	0.11	413	28.2	0.11
379	27.1	0.17	418	28.3	0.10
383	25.7	0.21	422	27.6	0.15
386	24.6	0.26	426	27.4	0.15
390	23.6	0.27	431	26.7	0.19
393	21.0	0.34	435	26.0	0.22
395	19.2	0.37	441	25.4	0.24
395.5	18.7	0.38	445	24.1	0.28
			449	20.5	0.37
			449.5	20.2	0.37
			451.5	17.0	0.43

* $\delta\omega_e$ = doublet splitting (A. B-B.)

TABLE II

SUMMARY OF RESULTS FOR THE NH PROTON EXCHANGE IN N-METHYLFORMAMIDE AND N-METHYLACETAMIDE

	T_2[a]	$\delta\omega_{cp}$	$\delta\omega$	T_c[b]	E_a	ν_o
	sec.	radian sec^{-1}	radian sec^{-1}	°K	kcal mole^{-1}	sec^{-1}
NMF	0.13 ± 0.01	30.0 ± 0.2	30.2 ± 0.2	404 ± 1	14 ± 2	10^7 to 10^{10}
NMA	0.16 ± 0.01	29.5 ± 0.2	29.6 ± 0.2	461 ± 1	14 ± 2	10^6 to 10^8

[a] T_2 is defined as $2/\Delta\omega_{1/2}$, where $\Delta\omega_{1/2}$ is the width of each component of the doublet at half-maximum.

[b] T_c is the temperature at which the doublet coalesces to a single line.

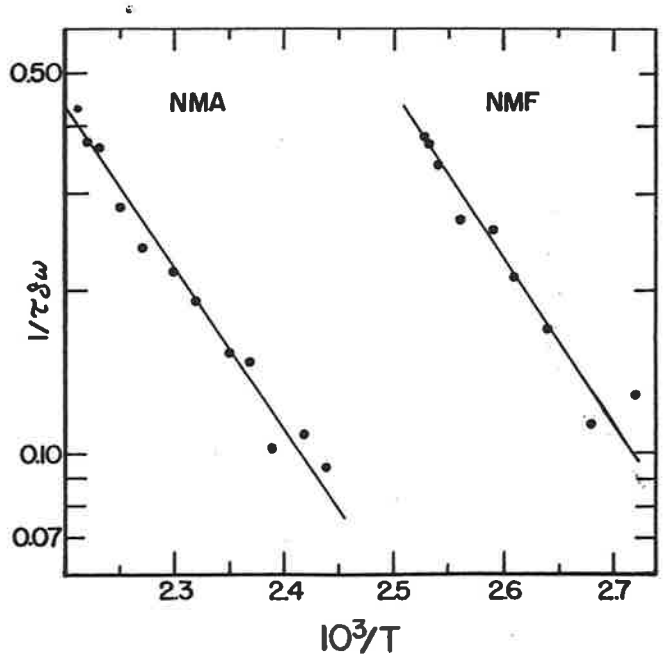


Fig. 1. Temperature dependence of the NH proton exchange rate in pure liquid N-methyl formamide (NMF) and N-methylacetamide (NMA). The exchange rate is proportional to $1/\tau\delta\omega$, the $\log_{10}$ of which is plotted versus the reciprocal temperature, $10^3/T$. The least squares straight lines give activation energies for the exchange of 14 ± 2 kcal mole^{-1} for both NMF and NMA.

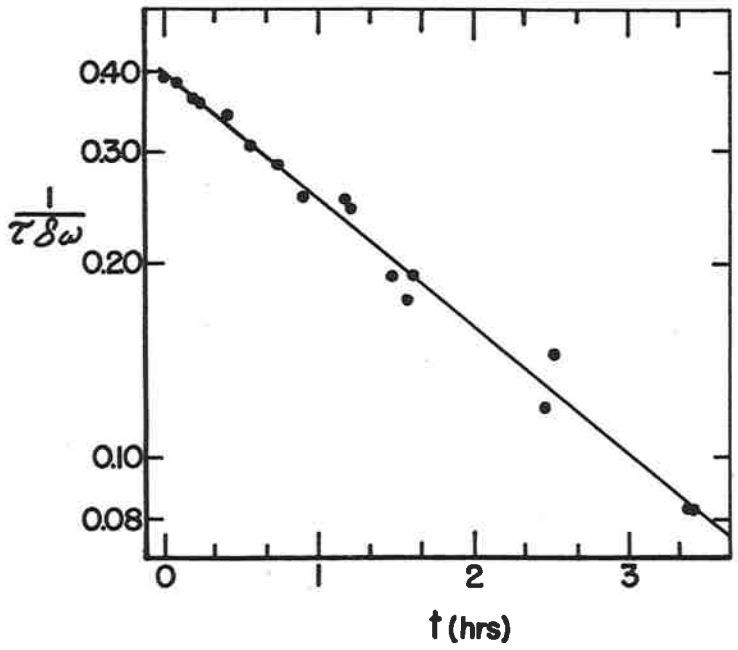


Fig. 2. The rate of acidic hydrolysis of N-methylformamide as determined from measurements of the H_3O^+ concentration via its effect upon the NH proton exchange rate. $[H_3O^+]$ is proportional to $1/\tau\delta\omega$, the $\log_{10}$ of which is plotted against time. The slope of the least squares straight line gives a pseudo first order rate constant for the hydrolysis of 1.26×10^{-4} sec^{-1}.

SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

TELEPHONE OLYMPIC 3-2100

A DIVISION OF
SHELL OIL COMPANY

February 3, 1960

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

It has been some time since I have written to you and I feel that I must be about due for a contribution to MELLONMR. I hope you will continue to include a bibliography in each issue, because I find this very valuable -- particularly in calling my attention to some of the foreign papers that I might otherwise miss.

Jerry Swalen and I have recently devised an improved technique for analyzing NMR spectra, that is very suitable for use with a digital computer. An outline that may be useful is given here prior to publication.

Our analysis starts by either assuming or deriving some approximate values for the NMR parameters (chemical shifts and coupling constants). If the internal evidence in the spectrum is inadequate then fairly good guesses may be made knowing what these parameters are for molecules of related structure.

At least a partial assignment of the lines is usually possible following the approximate analysis. Assuming that a sufficient number of lines has been assigned, the energy levels $(\lambda_i)_{exp}$ may be derived as follows. A schematic energy level diagram for the system is constructed showing the assigned transitions (see attached Figure). The lowest level is tentatively assigned the value zero. The positions of the other levels (starting with the highest) with respect to this zero can be found by adding up the frequencies of the appropriate transitions connecting the levels. If more than one path is available, either a simple average can be used or a least squares treatment can be made. Of course, the more transitions that can be initially assigned, the more reliable will be the values for the experimental energy levels. The experimental energy level matrix (diagonal) Λ_{exp} is then derived from these levels by noting that $\sum_i (\lambda_i)_{exp} = 0$.

With the approximate NMR parameters an approximate Hamiltonian matrix H is next calculated for the system and diagonalized on a computer to find its eigenvectors and eigenvalues. This process can be symbolized by

$$UHU^{-1} = \Lambda$$

a similarity transformation, where Λ is the diagonal matrix of the eigenvalues λ_i and U is a unitary matrix, the columns of which are the eigenvectors corresponding to these various eigenvalues. In general, at this stage, Λ will not be identical with Λ_{exp} because H is only approximate. However, an improved H can now be obtained by carrying out the transformation

$$U^{-1}\Lambda_{exp}U = H$$

The diagonal elements $H_{nn} = \sum_i U_{ni}^2(\lambda_i)_{exp}$ of this matrix are sufficient to solve for improved values[1] of the NMR parameters. The process can be repeated until Λ is consistent with Λ_{exp} (e.g. by a least squares criterion).

At any stage of the iteration the intensities may be calculated from the eigenvectors in the usual way and the assignment corrected, if necessary.

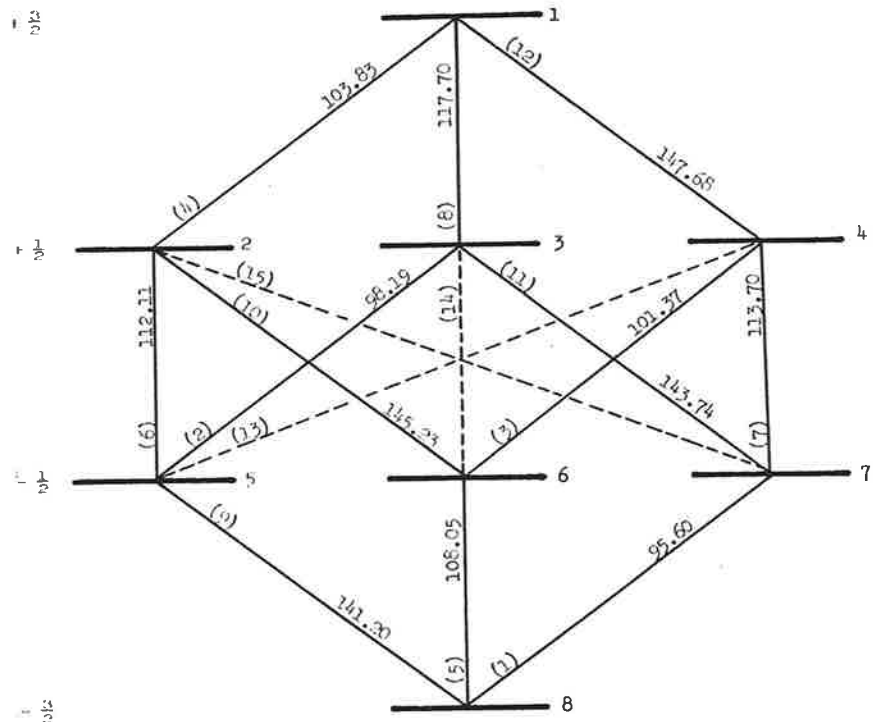
This scheme has been used with great success for the accurate analysis of systems of three spins ABC (J. Chem. Phys., in press), as well as of four spins and five spins of various symmetries.

We hope this description of our method may be of use to other NMR spectroscopists.

Sincerely yours,

Charles A. Reilly

CAR:jel
encl.



SCHEMATIC NMR ENERGY LEVEL DIAGRAM FOR STYRENE OXIDE

Dashed Lines = Combination Transitions (not observed)

Lincoln College,
Oxford,
England.

10th. February, 1960

Dr. A. Bothner-By,
Mellon Institute,
4400, Fifth Avenue,
Pittsburg, 13,
Pennsylvania
U. S. A.

Dear Aksel,

I am writing, rather late I am afraid, to tell you about some of the work which has been going on in high resolution n-m-r here at Oxford. Mr. Bishop has been studying the chemical shifts and coupling constants in a number of substituted olefines and the results are shown in the accompanying table. Most of the spectra were of the ABC type and we were able to solve these with the aid of the Oxford computor. It is noteworthy that the cis coupling constant is abnormally large when a benzene ring is attached to the olefine.

Mr. Bishop has also studied the AB_2C case and has applied it to an analysis of the spectrum of meta dinitrobenzene. We were fortunate to have the collaboration of Dr. R. Abraham who had considered independently the AB_2X case and had applied it to the spectrum of meta dinitrobenzene obtained at 60 Mc. From this analysis the chemical shifts and coupling constants can be obtained, but not their relative signs. At 30 Mc. the spectrum is an AB_2C case and we have found that it is possible clearly to distinguish the signs of the two larger coupling constants. We find that in this case the two larger coupling constants have the same sign, which is presumably positive.

We are studying a number of solutions in which specific interactions occur between the solute and solvent. One of these systems has been studied by Mr. Hatton and is concerned with the interaction between amides and solvents. For example, addition of various solvents to dimethyl formamide causes relative changes in the chemical shifts of the two methyl resonances. In particular, aromatic substances cause the chemical shift of both methyl resonances to shift to high fields relative to an internal reference, but the low field resonance shifts by a greater amount than the high field resonance with the result that the two lies cross over at a certain concentration and separate again so that the one which had been at lower applied fields is now at higher fields. We believe that these changes can be interpreted in terms of rather specific interaction between the aromatic ring and the amide, but this work is so far incomplete. We find that naphthalene compounds produce very large effects. We hope to study these shifts as a function of temperature in different solvents and hence to obtain still further information about them. Mr. Hatton has also studied the chemical shifts of the acetylenic hydrogen of substituted acetylenes in a wide variety of solvents. Chemical shifts occur which can be attributed to some form of association, like hydrogen bonding, and the behaviour is very similar to that found with mixtures of chloroform. A greater variety of systems can be studied, however, because the nature of the acetylenic hydrogen can also be varied.

I should like to say how very much I appreciate receiving your Newsletter and I certainly find it of great interest. The bibliography is especially valuable.

Yours ever, Rex

c/s at 29.9200 Mc/s.

	J_{gem}	J_{cis}	J_{trans}	chemical shift: C-B	B-A	Notes.
CH_2:CH.OCOMe	1.3	6.7	13.9	9.4	73.1	C A B
CH_2:CH.Br	-1.9	7.3	15.1	4.1	14.9	B A C
vinyl phthalimide	0.0	9.9	16.4	18.0	25.2	C A B
CH_2:CH.C_6H_5	1.1	11.0	17.8	15.6	29.1	C A B
CH_2:CH.$C_6H_2(Me)_3$	2.3	11.6	18.0	7.9	35.1	B A C
CHO.CH:CH.C_6H_5			15.9		36.5	J_{BX}= 5.7 J_{AX}= 1.6
C_6H_5.CH:CH.COOMe			15.9		36.6	
C_6H_5.CH:CH.COCl			15.9		35.6	
NO_2.CH:CH.C_6H_5			14.0		10.8	
Br.CH:CH.C_6H_5			14.5		12.8	
CH_3CO.CH:CH.C_6H_5			16.3		23.4	
C_6H_5CH:CH.COOH			15.8		34.8	
C_6H_5CH:CH.COOH		12.3			27.7	
o-(CN)C_6H_4.CH:CH.COOH			15.8		30.2	
o-(CN)C_6H_4.CH:CH.COOH		12.3			26.6	

Laboratorium
für physikalische Chemie
Eidg. Technische Hochschule
Zürich

ZÜRICH, February 18, 1960
Universitätstrasse

Dr. A.A. Bothner-By
Assistant Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.
U.S.A.

Dear Dr. Bothner-By:

Thank you for your letter of February 15. You certainly may reproduce our preprint on the "Group Contributions to the Chemical Shift" if you find it suitable for the M.E.L.L.O.N.M.R. There is just one remark of warning we like to add. The content of this paper consists of a mathematically best representation in the sense of least squares of several hundert chemical shifts according to a more or less dubios scheme and nothing more. Very often this scheme gives astonishingly good predictions of chemical shifts, but we have now some evidence that the class of substances included in our calculations were too narrow to claim a general validity of this scheme. The following esters were not included in the input material:

CH_3-CO-O-$C\underline{H}_2$-CH_2-CH_3 exp.: $T = 3{,}20 \pm 0{,}01$
pred.: $T = T_0+T_2+T_{20} = 3{,}158$

CH_3-CO-O-$C\underline{H}$-$(CH_3)_2$ exp.: $T = 2{,}35 \pm 0{,}01$
pred.: $T = T_0+2T_1+T_{20} = 2{,}906$

The first example shows a fair agreement while the second case is a typical example for a whole class of compounds which were too weakly represented in the input data and therefore are not well described. Some of the results are difficult to interpret in a physically meaningful manner, compare e.g. the values of T_{10}, T_{11}, T_{12} with that of T_{17}, T_{18}, T_{19}.

We will soon start some new calculations with more input data and a somewhat improved scheme but the trouble is that we still have too few reliable data of chemical shifts. The situation would of course improve very much if people could make up their minds and publish more data from their piles of nmr spectra.

Hans Primas
Rolf Arndt
Richard Ernst
Peter Bommer

We would like to emphasize how much we like your nmr-bibliography. The inclusion of papers only loosly related to nmr-spectroscopy is most useful, so we save ourselves the trouble of browsing through the whole chemical literature.

International Meeting of Molecular Spectroscopy
Bologna, September 1959

Group Contributions to the Chemical Shift in Proton Magnetic Resonance of Organic Compounds

by H. Primas, R. Arndt, R. Ernst
(Swiss Federal Institute of Technology, Zurich)

The lack of sufficient data is often most disturbing in structure determination of organic compounds with the aid of nuclear magnetic resonance. In spite of the wealth of empirical material now available there is frequently no sufficient information allowing an estimation of the shielding parameters for a wide variety of compounds. Until now there is no quantum mechanical treatment of the chemical shift which is successful enough for practical applications. Therefore, we have tried an approach of estimating the tau-values of G.V.D. Tiers 1) on a pure empirical basis.

These tau-values are not necessarily identical with the chemical shifts of an isolated molecule but are defined as the shifts in a sufficiently diluted solution with tetramethylsilane as an internal standard 2). The simplest empirical scheme that can be stated is the additive and linear one. Of course, there are no sound theoretical reasons to believe that such an approach may be successful; we just think it is worthwhile to try it.

1) G.V.D. Tiers, J. Phys. Chem. 62, 1151 (1958)

2) Tiers defines:

$$\tau = 10.000 + 10^6 \cdot \frac{H_{obs} - H_{SiMe_4}}{H_{SiMe_4}}$$

We do not agree with Tiers that it is desirable or convenient to introduce a new scale. It seems that benzene soon is generally accepted as zero in nmr-measurements. We therefore prefer to refer the tau-values to benzene as zero and define:

$$T = 7.266 + 10^6 \frac{H_{obs} - H_{SiMe_4}}{H_{SiMe_4}}$$

According to the precision measurements of Tiers 1) as have the relation:

$$\tau = T + 2.734$$

which was used throughout this paper.

3) Of course, there is empirical evidence for the additivity of the chemical shift. This was demonstrated with fewer data e.g. by H.S.Gutowsky, D.W.McCall, B.R.McGarvey, L.H.Meyer, J. Am. Chem. Soc. 74, 4809 (1952), and J.N. Shoolery, Varian Technical Information Bulletin 2, No. 3 (1959).

We are using the following model:

The tau-values of a certain molecule is assumed to be composed additively of contributions T_j:

$$T = T_0 + \sum c_j T_j$$

where c_j is the number of the occurence of the characteristics that correspond to the T_j under consideration. For a first trial we used the following system 4).

Our calculation of T-values is restricted to protons attached directly to a C-atom. The whole C-atom skeleton is numbered, starting with this C-atom as number 1. Each figure gives the number of chemical bonds to the proton under consideration. For reasons of simplicity we confined our scheme to compounds that contain no rings. Further, with the exception of ethers, esters and acid anhydrides molecules with a heteroatomic skeleton were excluded. We considered the skeleton only up to position 4 and substituents only up to position 3. According to our present scheme the skeleton is described by the following four substituents attached to the carbon-atom number 1.

No.	skeleton substituent	characteristic contribution
1	$-C^2$	T_1
2	$-C^2-C^3$	T_2
3	$-C^2(C^3)(C^3)$	T_3
4	$-C^2(-C^3)(C^3)(C^3)$	T_4

A C-atom in position 4 as well as all other groups are considered as ordinary substituents. Those we used in this work are given in Table I. We have to add the following explanations to this table:

a) All tau-values of aldehydes, ketones, esters, ethers, acid anhydrides, and acid halides are assumed to be composed from contributions of the substituents =O, -O-CO-R, methoxy-, ethoxy-, etc.

b) For lack of data acids are not included in our scheme!

c) Double and triple bonds are numbered as usually.

Examples are given in the appendix.

Using values measured by G.V.D. Tiers 5) and supplemented by our own measurements 6) we set up a sufficiently over-determined system of linear

4) The study of a more complete scheme is now in progress

5) G.V.D. Tiers, "Tables of τ-values for a Variety of Organic Compounds" (1958, unpublished). This table is the first extensive collection of reliable shielding values that seems to make data processing worthwhile. We are grateful to Dr. Tiers for making these important data available.

6) We thank Messrs. P. Bommer and H.R.Loosli for carrying out these measurements.

equations. This system was solved by the method of least squares of C.F.Gauss on the electronic computer ERMETH. The result obtained in this way was an estimation of the mean values of the T_j and their standard deviations. The findings are summarized in Table I (Appendix).

The standard deviation of the tau-values calculated with our scheme is 0.22 (284 samples). By judging this result it should be emphasized that the tau-values we used are the results of a rough analysis of the nmr-spectra only and are not necessarily identical with the exact chemical shifts. As a typical example, C.V.D. Tiers 5) gives for the CH-proton in Isobutane T = 5.71, while an exact analysis carried out by J.S.Waugh and F.W.Dobbs 7) resulted in a chemical shift of T = 5.53. Our present scheme gives T = 5.59. Table II (Appendix) summarizes the distribution of the errors.

The deviations of some 93% of the sample can be fitted in a normal distribution with a standard deviation of 0.17. This value can be considered as due to normal random events (measuring errors etc.). The difference of 0.05 to the total standard deviation of 0.22 is essentially caused by the inadequacy of our model. It may be of interest to list explicitely the compounds with deviations larger than allowed by a normal distribution. These are given in Table III (Appendix).

With only two exceptions all the poor values are arising from halogen compounds. This is certainly not a computational error, for there are a lot of correctly represented halogen compounds. It is of considerable interest to notice that the tau-values of ketones, esters, aldehydes, and ethers may be composed of contributions of =O, OMe, -OEt, etc. The evidence is given in Table IV (Appendix).

We found no significant difference of the contributions of the =O - group to the shift of chemically different oxygen compounds (acids not included!). In the least-square analysis we excluded all compounds with conjugated double or triple bonds, α,β-unsaturated ketones, and esters. But now we can show that some conjugated systems are well represented in our scheme (cf. Table V, Appendix).

We had not enough data for the discussion of α,β-unsaturated acids. Further it may be that e.g. a chlorine-atom in β-position to a double bond may show an extraordinary contribution, so that the question of conjugated systems cannot be considered as settled.

At present the accuracy of the proposed scheme is not sufficient to allow a profitable discussion of such points as cis-trans or other types of steric isomerism. But we hope that the elimination of several obvious weaknesses in the present system can result in an essential improvement of the mean square error. To this end more accurate analyses are urgently needed, too. The extension of this work to ring compounds is in progress.

7) J.S. Waugh, F.W. Dobbs, The Ten Spin System of Isobutane (1959, preprint).

Acknowledgments

We would like to express our thanks to Professor Hs. H. Günthard for his advice and encouragement, as well as to the staff of the Institute of Applied Mathematics, ETH, for the calculations on the ERMETH.

The supports given by the Swiss National Foundations for the Advancement of Science, and Hoffmann-LaRoche, Inc., are gratefully acknowledged.

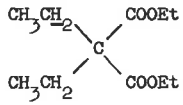
A p p e n d i x

For illustration we are giving some typical example for estimation of chemical shifts.

1) $CH_3CO\text{-}COCH_3$

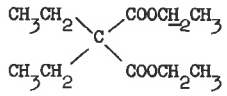
$T = T_o + T_2 + T_5 + T_{12} + T_{13} = 5.1o$

value measured by Tiers $T = 5.o4$

2) 

$T = T_o + T_1 + T_4 + T_5 + 2T_{13} + 2T_{16} = 5.689$

value measured by Tiers $T = 5.43$

3) 

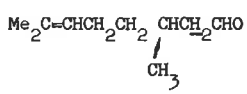
$T = T_o + T_1 + T_{2o} = 3.154$

value by Tiers $T = 3.12$

4) $HC\text{-}CCH_2Br$

$T = T_o + T_2 + T_{1o} + T_{28} = 3.4oo$

value measured by Tiers $T = 3.45$

5) 

$T = T_o + T_1 + T_3 + T_5 + T_{12} = 4.955$

value measured by Tiers $T = 5.o8$

6) $CF_2Cl\text{-}CHCl_2$

$T = T_o + T_1 + 2T_{23} + 2T_{25} + T_{26} = 1.313$

value measured by Tiers $T = 1.35$

Table I

		characteristic contribution	number of samples
---		T_o = 6,333	284
no skeleton substituent		no contribution	21
skeleton substituent no. 1		T_1 = - o.248	96
skeleton substituent no. 2		T_2 = - o.244	137
skeleton substituent no. 3		T_3 = - o.147	56
skeleton substituent no. 4		T_4 = - o.oo6	1o
substituent	position		
$-CR_3$	3	T_5 = + o.o38	11o
double bond	1	T_6 = - 3.8o2	21
	2	T_7 = - o.583	31
	3	T_8 = - o.2o3	7
triple bond	1	T_9 = - 1.o32	3
	2	T_{1o}= - o.694	4
= O	1	T_{11}= - 8.536 *)	7
	2	T_{12}= - 1.o21	21
	3	T_{13}= - o.oo4	11
$-OCH_3$	2	T_{14}= + o.373	6
$-OCH_2-CR_3$	2	T_{15}= + o.237	7
	3	T_{16}= - o.21o	6
-OH	1	T_{17}= - 2.467	8
	2	T_{18}= - o.o48	8
	3	T_{19}= - o.235	5
$-O-CO-CR_3$	1	T_{2o}= - 2.931	28
	2	T_{21}= - o.o41	11
	3	T_{22}= + o.o86	5
-F	2	T_{23}= - o.o89	9
	3	T_{24}= - o.131	9
-Cl	1	T_{25}= - 2.17o	29
	2	T_{26}= - o.254	19
	3	T_{27}= - o.177	12

Table I cont.

substituent	position	characteristic contribution	number of samples
-Br	1	T_{28} = - 1,995	24
	2	T_{29} = - o,363	16
	3	T_{3o} = - o,o23	7
-J	1	T_{31} = - 1,846	1o
	2	T_{32} = - o,388	5
$-NH_2$	2	T_{33} = - o,o94	3
$-O-CR_3$	1	T_{34} = + 1,434 **)	

It may be any group, including R = H.

*) By using this group the only allowed substituent in position 1 is T_{34}.

**) Has only to be used in combination with T_{11}.

Estimation of the characteristic contributions T_j origing in a least square analysis

(These values should not be considered as final. More accurate values will be published in Helvetica Chimica Acta)

Table II

deviation in ppm	percentage of the sample
o ... o,1o	45.o7 %
o.11 ... o.2o	28.87
o.21 ... o.3o	17.96
o.31 ... o.4o	2.82
o.41 ... o.5o	1.41
o.51 ... o.6o	1.o6
o.61 ... o.7o	o.7o
o.71 ... o.8o	1.41
o.81 ... o.9o	o
o.91 ... 1.oo	o.35
1.o1 ... 1.1o	o
1.11 ... 1.2o	o
1.21 ... 1.3o	o.35
o ... 1.3o	loo.oo %

Distribution of the errors of the input data

Table III

Compound	Error
$Me_2\underline{C}H\underline{C}H_2Cl$	- o.36
$(Br\underline{C}H_2)_2\underline{C}H_2$	+ o.38
$Br\underline{C}H_2\underline{C}H_2(CH_2)_8COOEt$	- o.41
$CH_2{=}\underline{C}(CH_3)O\underline{C}OCH_3$	- o.42
$CF_3(CF_2)_6\underline{C}(CH_3){=}\underline{C}H_2$	+ o.43
$CF_3(CF_2)_2\underline{C}OO\underline{C}H_3$	+ o.43
$(CH_3)_2\underline{C}{=}\underline{C}H\underline{C}O\underline{C}H_3$	- o.5o
$(CH_3)_2\underline{C}H\underline{C}H_2I$	- o.51
$(CH_3)_2\underline{C}H\underline{C}l$	+ o.53
$\underline{C}H_3I$	- o.62
$CH_3\underline{C}H\underline{B}r(CH_2)_5CH_3$	+ o.64
$\underline{C}H_2I_2$	- o.72
$\underline{C}H\underline{B}r{=}\underline{C}H\underline{B}r$, trans	- o.73
$CH_3\underline{C}Cl_3$	+ o.77
$(CH_3)_2\underline{C}H\underline{B}r$	+ o.77
$(CH_3)_2\underline{C}H\underline{I}$	+ o.96
$Cl_2{=}\underline{C}H\underline{C}l$	- 1.22

List of substances not well represented in our present scheme (a total of 284 samples was used)

Table IV

type of compound	number of samples	mean error	standard deviation
ester	17	- o.o5	o.16
ketone	6	- o.16	o.29
aldehyde	7	- o.o2	o.o2
acid halide	2	+ o.22	o.24
acid anhydride	1	- o.o5	-

Evidence for the similarity of the contribution of the CO-group in different oxygen compounds.

Table V

type of compound	number of samples	mean error	standard deviation
conjugated double bonds	2	- o.o5	o.o2
α,β -unsaturated ketones	4	- o.1o	o.33
α,β -unsaturated esters	6	+ o.o6	o.o3
total	12	+ o.1o	o.19

Representation of conjugated systems