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Computer - Program

Mailed: MAR 2 - 1961

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E cumenical  
L etters from  
L aboratories  
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N - M - R  
No. 29

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# BP RESEARCH CENTRE

PETROLEUM DIVISION  
SUNBURY-ON-THAMES  
ENGLAND

Mellon Institute,  
4400, Fifth Avenue,  
Pittsburgh 13, Pa.,  
U.S.A.

Dear Dr. Bothner-By,

In order to improve the base line stability of our Varian 40 Mc spectrometer, we have installed a transistor stabilised power supply for the heaters of the R/F unit. A conventional series stabiliser (Fig. 1) was designed and constructed having the following characteristics:-

Input: 115v from existing constant voltage transformer.  
Output: variable from 10-15v  $\pm$  0.1v at 1.5 amps. Ripple < 0.1v.

The unit will handle variations of input of -20% to +10% and is able to withstand a surge of 4 amps.

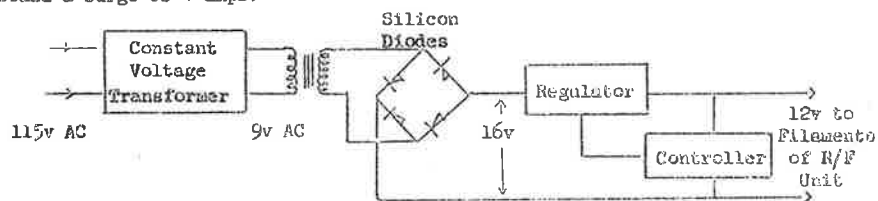


Figure I

The unit has given satisfactory service over 6 months and has produced a marked improvement in baseline stability.

A crystal frequency standard which monitors the output of our Hewlett Packard A/F oscillator has also been designed and built. The system is shown schematically in Fig. II. The output from a 3 k/c crystal controlled oscillator is divided into 1 k/c, 200 cps and 100 cps pulses which can be connected to the Y axis of a small oscilloscope. The output of the A/F oscillator is fed onto the Y axis and the X time base is switched off. When the frequency of the A/F oscillator is near a simple fraction of the standard frequency a series of "bouncing balls" is presented on the oscilloscope which become stationary when the exact



fractional relationship is reached. For example, if 1 k/c is the basic standard frequency, 200, 400, 600 and 800 cps outputs from the A/F oscillator all produce five "bouncing balls" since these frequencies are simple multiples of  $1/5 \times 1000$  cps. Thus on the 1 k/c range from the simple fractions  $1/5$ ,  $1/3$  and  $1/4$  we have the following convenient spot calibrations 800, 750, 666  $2/3$ , 600, 500, 400, 333  $1/3$ , 250, 200 cps and other intermediate frequencies where the number of balls is not excessively large. Similar spot calibrations are found in the 200 and 100 cps ranges.

We find that this system is suitable for most routine work where extrapolation from the A/F side bands is used and it has the advantages that the output of the A/F oscillator is continuously monitored during the running of a spectrum and that the whole unit can be incorporated into the dual-purpose console.

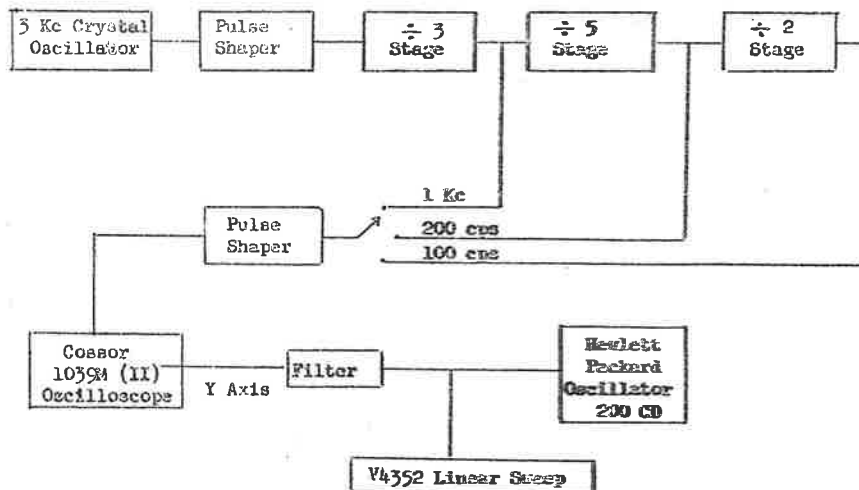


Figure II

Crystal Frequency Standard

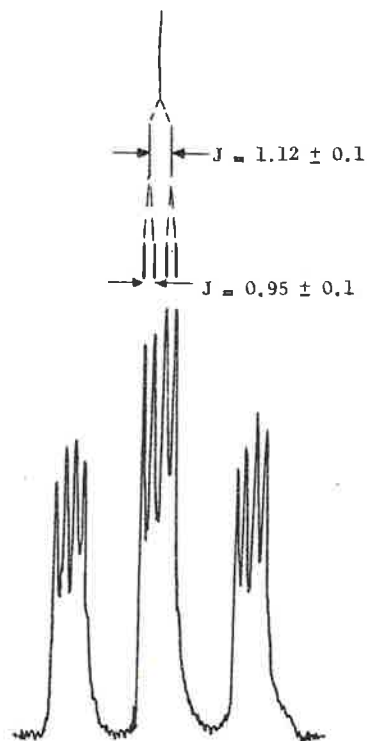
In conclusion, we have made a set of x, y and z gradient coils (MELLONMR No. 18, p.4) and have found them very satisfactory. We have tried controlling the curvature with a simple spiral coil which worked quite well but we have since tried a modified concentric coil method (MELLONMR No. 25, p.1) which has a similar effect without markedly disturbing the x, y and z settings.

With these simple coils we can usually obtain a resolution of 1 in  $10^6$  in a matter of minutes. The field trimmer has not been used since the installation of the coils and the magnet is roughly cycled only when it is switched on. The consequent saving in time has been remarkable.

Yours sincerely,

*S.A. Knight*  
S.A. Knight  
*R.L. Mackie*  
R.L. Mackie





Allylic Methyl Group of trans-  
thiono Phosdrin (with 10.0 c/s  
side-bands)

RESEARCH LABORATORIES

GENERAL MOTORS CORPORATION

February 7, 1961

Drs. A. A. Bothner - By and B. L. Shapiro  
M. E. L. L. O. N. M. R.  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Drs. Bothner - By and Shapiro:

I am happy at long last to pay my subscription fee to your valued newsletter.

The contribution of our laboratory consists of two parts. The first is a compilation of the diamagnetic susceptibilities of some 1000 compounds, a copy of which is enclosed herewith. We use this table in making susceptibility corrections to our NMR line positions relative to an external standard. Since the International Critical Tables contain only about 400 susceptibility values for organics and does not include any data taken later than 1925, I made a literature survey to bring the survey up to 1958. Because it would be inconvenient for you to publish this 25 page report in your newsletter, I invite those desiring a copy to address requests to me. It is our intention to submit the data to the Handbook of Chemistry and Physics to bring their tables up to date, if they so desire.

*unreproduced  
18.3.61*

Our second contribution is in the form of two tables of NMR line positions at 40 mc. The tables are based on data taken at General Motors Research Laboratories by Mr. D. H. Woodward and represent a summary of spectra of over 100 organic liquids.

The tables are fairly self-explanatory. Table I is a tabulation of average NMR peak positions relative to external water and uncorrected for susceptibility. In Table II, uncorrected and corrected line positions are compared. The correction used is the theoretical Lorentz sphere correction of  $\frac{2\gamma}{3}$  rather than the empirical term 2.60 of Bothner-By and Glick as  $\frac{2\gamma}{3}$  quoted by Hood and Reilly (*J. Chem. Phys.* 27, 1126, 1957). Range in both tables is the range of values covered by the raw line position data.




We greatly appreciate receiving M. E. L. L. O. N. M. R. and find it very useful.

Yours truly,

*George W. Smith*



George W. Smith  
Physics Department

Table I 40 Mcps Proton High Resolution NMR Line Positions (H<sub>2</sub>O at 0)

Chemical Group	Average Resonance Position (Cps)	Range (Cps)	Number of Spectra Averaged
CH <sub>3</sub> O-	64.2 ± 1.4	61 to 66	6
CH <sub>3</sub> -C(=O)-	126.7 ± 6.9	118 to 134	5
CH <sub>3</sub> - 	125.4 ± 3.9	116 to 132	9
CH <sub>3</sub> -CH <sub>2</sub> -C(=O)- CH <sub>3</sub> -CH-C(=O)-	161.1 ± 4.5	145 to 174	32
CH <sub>3</sub> -C(=O)-O-	154.2 ± 4.9	144 to 164	12
CH <sub>3</sub> -C(=O)-H	140.0 ± 4.4	135 to 148	5
-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> - CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> - Cyclic CH <sub>2</sub>	142.1 ± 4.1	132 to 157	30
C-CH <sub>2</sub> -C(=O)-	106.8 ± 2.7	100 to 113	14
-C(=O)-CH <sub>2</sub> -C(=O)-	69.0 ± 2.0	67 to 71	2
-CH <sub>2</sub> -OH -CH <sub>2</sub> -O-C(=O)- HO-CH <sub>2</sub> - 	37.5 ± 3.9 36.0 ± 2.0	27 to 46 34 to 38	23 2
-CH <sub>2</sub> -NH <sub>x</sub>  *	94.0 ± 2.0 -71.8 ± 10.2	91 to 96 -98 to -53	3 20
-OH (Alcohol and Glycol)	-5.0 ± 11.3	-22 to +27	12
-C(=O)-OH	-284.3 ± 9.6	-293 to -270	3
-C(=O)-H	-170.7 ± 7.6	-189 to -164	6
-NH <sub>x</sub>	76.7 ± 1.6	75 to 79	3
-CH-OH	56.0 ± 1.0	55 to 57	2

\*For wide lines or groups of lines, average position used in each spectrum.

Table II Comparison of Average Line Positions for Spectra Corrected and Uncorrected for Susceptibility (H<sub>2</sub>O at 0)

Chemical Group	Average Line Position (25°C Correction) (Cps)	Range (Cps)	Uncorrected Position (Cps)	Range (Cps)	Number of Spectra Averaged
CH <sub>3</sub> O	55 ± 5	50 to 60	65 ± 0	65	2
CH <sub>3</sub> -C(=O)-	115 ± 7	105 to 129	129 ± 5	118 to 134	4
CH <sub>3</sub> - 	122 ± 3	119 to 128	127 ± 3	120 to 130	7
CH <sub>3</sub> -CH <sub>2</sub> -C(=O) CH <sub>3</sub> -CH-C(=O) CH <sub>3</sub> -O-	156 ± 6 146 ± 2	144 to 166 144 to 149	164 ± 6 157 ± 5	150 to 174 150 to 164	13 4
CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> - CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> - Cyclic CH <sub>2</sub>	137 ± 3	130 to 143	146 ± 5	137 to 157	9
C-CH <sub>2</sub> -C(=O)-	99 ± 3	96 to 102	107 ± 1	106 to 107	2
-C(=O)-CH <sub>2</sub> -C(=O)-	59 ± 4	55 to 62	69 ± 2	67 to 71	2
-CH <sub>2</sub> -O-C(=O)-	29 ± 1	28 to 30	38 ± 2	35 to 41	3
-CH <sub>2</sub> -NH <sub>x</sub>  *	87 ± 2	85 to 89	94 ± 2	91 to 95	3
-76 ± 9	-103 to -59	-71 ± 14	-98 to -54	16	
-7 ± 14	-20 to +21	-3 ± 15	-18 to +27	4	
-183 ± 10	-199 to -172	-172 ± 8	-189 to -165	5	
74 ± 4	69 to 79	77 ± 2	75 to 79	3	

Lincoln College,  
Oxford.

10th February, 1961.

Dr. A. Bothner-By,  
Assistant Director of Research,  
Mellon Institute,  
4400 Fifth Avenue,  
Pittsburgh 13,  
PA, USA.

Dear Aksel,

I am writing about some work which Dr. W. G. Paterson has started to do in my laboratory.

One problem is concerned with the study of the exchange kinetics of protons between benzyl alcohol and water in dioxane/water mixtures. In non-buffered solutions the exchange time is found to give erratic variations with concentration, because of the difficulty of preventing changes of pH caused by the glass tubes.

In buffered solutions, reproducible results are obtained, but the results depend on the nature of the buffer salts. For example, the slope of the graph obtained by plotting the product of the concentrations of benzyl alcohols and water against exchange time is negative with a buffer solution of pH 6.99 using  $\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4 + \text{NaCl}$ , but is positive at the same pH when using a buffer of citric acid and  $\text{Na}_2\text{HPO}_4$ .

As the pH is lowered, using the citrate buffer, the exchange rate increases and a pronounced curvature in the above graph appears and finally resolves itself into two distinct linear portions when the pH has reached 3.

Alkaline solutions also show much more rapid exchange rates than neutral solutions but accurate measurements are more difficult than in the acid solutions due again to interactions with the glass. We are obtaining quantitative results for the rate constants and are hoping to study them for a set of alcohols with substituents in the benzene ring. I am afraid we have not got enough results yet however, to see any interesting trends.

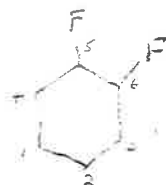
The calculation of the exchange rate requires interpolation tables from the equations given by Takeda and Stejskal, J.A.C.S., 82, 25, (1960). In case these tables would be of value to other people, I enclose a copy of some calculated values which are very helpful in obtaining values of  $\sigma$ .

Dr. Paterson is also analysing the A<sub>2</sub>B<sub>2</sub>X<sub>2</sub> case of o-difluorobenzene. The analysis of the spectrum is fairly well advanced but we have not yet got satisfactorily accurate detailed results. If the substituents in the benzene ring are numbered as below

we find that the chemical shift between H<sub>1</sub>H<sub>2</sub> is about two to three  $\frac{\text{c/s}}{\text{s}}$ , we find that  $J_{15} + J_{16} + J_{35} + J_{36} = 220/\text{s}$ , that  $J_{15}^4 + J_{35} + J_{36} + J_{12} + J_{14}$  all have the same sign and  $J_{16}$  is probably of the opposite sign.

With best regards,

Yours sincerely,



Reference: M. Takeda and E. O. Stejskal JACS 82, 25 (1960).

$\delta\omega_{1/2}$

Calculated values of  $\delta\omega_{1/2}/\delta\omega$  as a function of  $T_2\delta\omega$  and  $T_2\delta\omega$

$T_2\delta\omega$	$T_2\delta\omega = 9$	$T_2\delta\omega = 10$	$T_2\delta\omega = 12$	$T_2\delta\omega = 16$	$T_2\delta\omega = 20$
0	.222	.200	.167	.125	.100
0.5	.349	.327	.294	.252	.227
1.0	.486	.464	.431	.390	.365
1.5	.641	.621	.590	.551	.528
2.0	.816	.798	.772	.740	.720
2.222	.895	.879	.856	.828	.811
2.5	.991	.978	.959	.935	.922
3.0	1.142	1.132	1.118	1.101	1.092

$\delta\omega_{1/2}$  = width of observed signal at half-maximum when the doublet has become a broad singlet. (angular frequency units)  
 $\delta\omega$  = magnitude of spin-spin interaction. (angular frequency units)  
 $\bar{T}_2$  = average lifetime of the nucleus (before exchange) which produces the doublet.  
 $T_2$  = spin-spin relaxation time.

Calculated values of  $\delta\omega_e/\delta\omega$  as a function of  $T_2\delta\omega$  and  $T_2\delta\omega$

$T_2\delta\omega$	$T_2\delta\omega = 9$	$T_2\delta\omega = 10$	$T_2\delta\omega = 12$	$T_2\delta\omega = 16$	$T_2\delta\omega = 20$
0	.999	.999	.999	.999	1.000
0.050	.977	.979	.981	.983	.985
.100	.931	.934	.939	.945	.948
.1429	.870	.875	.883	.892	.897
.1666	.826	.832	.842	.853	.859
.200	.747	.757	.770	.785	.794
.231	.654	.666	.684	.705	.716
.250	.580	.596	.618	.644	.662
.286	.385	.412	.450	.492	.515
.300	.258	.302	.355	.410	.438

$\delta\omega_e$  = doublet separation (angular frequency units).

20th February 1961

PHYSIKALISCHES INSTITUT  
DER UNIVERSITÄT BASEL /Switzerland  
KLINGELBERGSTRASSE 82 TELEFON 430422  
VORSTEHER: PROF. DR. P. HUBER

Dr. B.L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13 Pennsylvania USA

Dear Dr. Shapiro,

We have been working for some time on the problem of substitution effects in proton magnetic resonance spectra of substituted benzene. As there are no chemical shift data of monosubstituted benzene available we had to get the answer using the principle of additivity. This possibility is well known, but, as far as I know, has never been examined with enough accuracy in subst. benzene. There are several ways of testing, the simplest is the following: we analyse the  $A_2B_2$ -spectra of 3 paradisubst. benzene-molecules  $C_6H_4XY$ ,  $C_6H_4YZ$ ,  $C_6H_4XZ$  (X,Y,Z being any substituent). If the substitution effects are additive, then it is obvious, that the chemical shift  $\delta_{AB}$  in the first molecule is equal to the difference between the chemical shifts of the second and third molecule.

$$\delta_{AB}^{XY} = \delta_{AB}^{XZ} - \delta_{AB}^{YZ}$$

We tested this relation and found excellent additivity in 18 of 24 substances. We used concentrations of 5 Mol % in hexane. The departures from additivity were below 0,10 p.p.m. in all 24 cases studied. Besides, we were able to show that departures from additivity always occur in molecules with non additive dipole-moments (additional mesomeric moments).

As it is impossible to separate the substitution effects in paradisubst. benzene, we started to study metadisubst. benzene. Again, there is a very simple test of additivity: The chemical shift of the four ringprotons in para-di-X-benzene is equal to the arithmetic mean of the shift values for the 2- and 5-protons in 1,3-di-X-benzene. All the four substituents studied this way (Br, Cl,  $OCH_3$ ,  $CO_2CH_3$ ) showed additivity within the probable errors.

It was now possible to separate the individual substitution

effects in paradisubst. benzene by substitution of the values measured in metadisubst. benzenes. Finally we got the following table of substitution effects:

Substitution effects in meta- and para-disubst. benzene  
(relative to 5 Mol-% benzene in hexane)  
Concentration: 5 Mol % in hexane. Unit:  $10^{-8}$  Ho.

Subst.	S <sub>ortho</sub>	S <sub>meta</sub>	S <sub>para</sub>
NH <sub>2</sub>	+68	+22	
OH	+50	+16	
OCH <sub>3</sub>	+42	+10	+33
F	+25	+1	
CH <sub>3</sub>	+17	+13	+17
Cl	-5	+6	+13
Br	-22	+11	+6
CN	-35	-13	
J	-41	+22	
CO <sub>2</sub> CH <sub>3</sub>	-74	-10	-20
NO <sub>2</sub>	-98	-21	

accuracy  $\pm 5$ . Positive sign means shift to high field. All the shifts have been measured relative to an external reference of  $CHCl_3$ , corrected for susceptibility difference and for the difference in shift between  $CHCl_3$  and 5 Mol % benzene in hexane.

As I already pointed out, new substitution effects are found whenever dipole moments of substituents are non additive. So we measured quite different S-values in o-disubst. benzene, where mesomeric and steric effects as well as mutually induced dipole moments are important. As a general rule the S-values in these substances depart from those of the Table mentioned above especially in ortho position to the "disturbed" substituent, whereas "farther off" the values are close to the normal S-values.

We were of course interested to see whether our substitution effects did work in monosubst. benzene as well. Again we found that as far as it could be tested (ortho position of substituents  $NO_2$ , Br,  $OCH_3$ ,  $CH_3$ ) the S-values seemed to give reasonable shifts in monosubst. benzene as well.

The next step was to study the nature of the substitution effects. We found correlations of S-values with Hammett parameters. As one would predict from chemical knowledge,  $S_{ortho}$  and  $S_{para}$  are found to be functions of the Hammett-parameter  $\sigma_p$ .

$$S_{ortho} = -117 \cdot \sigma_p$$

$$S_{para} = -49 \cdot \sigma_p + 10 \quad (\text{Unit: } 10^{-8} \text{ Ho})$$

In o-position the anisotropy of the CN-group causes an additional shift to high fields. Besides, the halogens show systematic additional shifts to high field. So far, we do not know why. In meta-position the substitution effects are small but seem to be proportional to  $\sigma_p$  as well.

$$S_{meta} = -30 \cdot \sigma_p + 6$$

Again the halogens deviate from the average behaviour.

Our results allow a test of the electrostatic theory of substitution effects<sup>1)</sup> which predicts the following relative magnitudes of the effects:  $S_{ortho} : S_{meta} : S_{para} \sim 9:3:2$ . We find  $\sim 9:2,3:3,0$ . Supposing the electrostatic theory as well as our  $\sigma_{Hammett}$ -correlations to be true, one would predict the electric dipol moments of the substituents to be linear functions of their Hammett parameter  $\sigma_p$ . Actually we find that this is approximately true as long as the resonance contribution  $\sigma_r$  to  $\sigma_p$  is relatively unimportant. This explains why for the substituent  $\text{NO}_2$  the electrostatic theory predicts reasonable effects, whereas for F and  $\text{N}(\text{CH}_3)_2$ <sup>2)</sup> there are obvious mistakes.

More details of this work will be published shortly.

Yours sincerely,

P. Diehl

P. Diehl

Literature:

- 1) A.D. Buckingham, Can. J. Chem., 38, 300, 1960
- 2) R. R. Fraser, Can. J. Chem., 38, 2226, 1960.

UNIVERSITY OF WASHINGTON  
DEPARTMENT OF CHEMISTRY  
SEATTLE 5

February 23, 1961

KENNETH B. WIBERG

Dr. A. A. Bothner-By  
Mellon Institute  
Pittsburgh, Pennsylvania

Dear Aksel:

I have enclosed a print out of our current version of your program, in case you might be interested in our modifications. The programs have been written for operation with the FORTRAN monitor system (i.e. all input on tape unit 5, all output on tape unit 6, no rewind or backspacing on either tape unit). All parts are tied together as subroutines rather than being handled as a chain job with the programs on tape. This cuts down the amount of tape handling considerably. Also, the table of frequencies and intensities is condensed, which cuts down on printing time and on the amount of paper produced as output. Finally, it uses the SHARE subroutine HDIAG (MI-HDI3) which appears to be better than the subroutine EIGEN in that we have never observed a "NO GOOD" on checking eigen<sup>2</sup> with matrix<sup>2</sup>, whereas EIGEN often gives such an indication.

Two versions of our subroutine PLOT are included. The first provide a sorted list of frequencies and intensities, and gives the calculated spectrum with summed intensities in the form of a table. The second version gives the sorted list, and then produces a plot of the summed intensities. Examples of the results obtained with the two PLOT subroutines is enclosed.

If any of the readers of MELLONMR should like to have a listing of the above programs, I would be happy to send it to them.

Sincerely,

KBW:jp

Enclosure



# Battelle Memorial Institute

5 0 5 KING AVENUE COLUMBUS 1, OHIO

February 20, 1961

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

Dear Dr. Bothner-By:

Please excuse our delay in contributing to your excellent newsletter. We have experienced the usual magnet difficulties and had a little trouble installing our integrating system. However, everything is now in working order.

We are presently working on a variety of problems of which the determination of the stereochemical configuration of various oxime isomers is a good example.

It is well known that the proton magnetic resonance spectrum of cyclohexanone oxime shows three separate methylene resonances; while the spectra of compounds like cyclohexyl amine and cyclohexanone exhibit only two. The third methylene absorption in cyclohexanone oxime arises because of the hindered rotation of the =NOH group about the carbon-nitrogen double bond.

From a consideration of the bond angles involved it can be seen that the oxime oxygen can lie very close to one of the methylene groups adjacent to the -C=N- bond as shown in Figure I. This close approach of

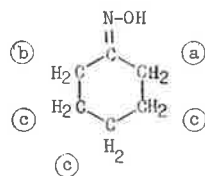


Figure I

the oxygen should deshield the protons denoted as "(a)" in Figure I and cause their resonance to fall at a lower magnetic field than those denoted

# Battelle Memorial Institute

Dr. A. Bothner-By

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as "(b)". Both "(a)" and "(b)" are expected to be, and are, found at lower fields than the six protons denoted as "(c)" because of their proximity to the double bond.

To substantiate this argument we have examined the spectrum of 2,2-dimethyl cyclohexanone oxime. Steric considerations as well as the mechanism of oxime formation from the ketone and hydroxylamine, would suggest that the oxime is "anti" to the two methyl groups in this compound, as shown in Figure II. The methylene protons denoted as "(a)" in

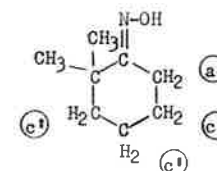


Figure II

Figure II would therefore, be expected to experience very much the same electric field effect as the corresponding methylene protons in cyclohexanone oxime and, as a result, should require about the same magnetic field to bring them into resonance. In addition, no methylene absorption corresponding to the "(b)" protons in cyclohexanone oxime should be observed. A comparison of the spectra of the two compounds indicates this to be the case.

Isophorone oxime exists as two geometrical isomers; one melting near 102° C and the other melting near 78° C. The two possible structures for this compound are shown in Figure III. From the relationship found

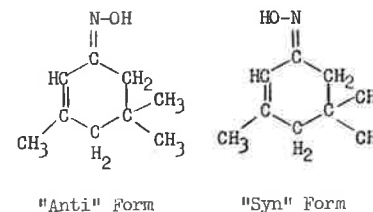


Figure III

Dr. A. Bothner-By

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between cyclohexanone oxime and 2,2-dimethyl cyclohexanone oxime, it is now possible to assign the high-melting and low-melting isomers of isophorone oxime to their respective structures.

The NMR spectrum of the "anti" form should show a methylene absorption at almost the same spectral position as the "in field"<sup>1</sup> methylene protons of cyclohexanone oxime and 2,2-dimethyl cyclohexanone oxime. On going from the "anti" isomer to the "syn" isomer this "in field" methylene absorption should disappear from the spectrum, and a new peak corresponding to the "out of field" methylene of cyclohexanone oxime should appear. At the same time, the olefinic hydrogen, which is not being influenced by the electrical field of the =N-OH group in the "anti" form, should move in the "syn" form to a spectral position which corresponds to less shielding. The remainder of the spectrum should remain almost unchanged.

It was found that the spectrum of the high-melting isomer of isophorone oxime corresponded to the "anti" configuration and the low-melting isomer corresponded to the "syn" structure.

Table I contains a summary of the chemical shift data obtained for the compounds discussed. All samples were run as dilute solutions in  $\text{CCl}_4$  and referred internally to  $\text{Si}(\text{CH}_3)_4$ .

TABLE I. CHEMICAL SHIFT DATA OF OXIMES<sup>(a)</sup>

Environment	Cyclohexanone	2,2-Dimethyl Cyclohexanone		Isophorone	
		Cyclohexanone	Anti	Syn	Syn
"In field" $\text{CH}_2$	7.55	7.52	7.66	--	--
"Out of field" $\text{CH}_2$	7.84	--	--	7.95	--
Insulated $\text{CH}_2$ 's	6.38	6.44	--	--	--
Olefinic H	--	--	4.12	3.45	--
-C=C- $\text{CH}_2$ -	--	--	8.07	8.07	--
-C=C( $\text{CH}_3$ )-C	--	--	8.18	8.18	--
( $\text{CH}_3$ ) <sub>2</sub> C	--	8.87	9.01	9.01	--
=NOH <sup>(b)</sup>	0.61	0.25	0.19	0.22	--

(a) Dimensionless units relative to  $\text{Si}(\text{CH}_3)_4 = 10.00$ .

(b) The =NOH proton resonance is very concentration dependent.

<sup>1</sup> The term "in field" will be used to denote protons which are being affected by the electrical field of the oxime hydroxyl. The term "out of field" will be used to refer to environments which are adjacent to the C-H bond but which do not lie in the electrical field of the =NOH group.

Dr. A. Bothner-By

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From the chemical shifts observed, it was found that at 60 Mc./sec. a methylene group adjacent to an oxime function is shifted about 17 cps to lower field when placed in the electrical field of the oxime oxygen. However, under the same conditions, an olefinic proton is shifted about 40 cps to lower field. This is a good reflection of the relative ease with which electrons can be removed from a double bond as compared to a single bond due to the much closer approach of the double bond's pi electron cloud to the oxygen atom of the =NOH group.

We are also studying other oxime isomers to determine the magnitudes of shifts which can be expected for the resonances of different proton-containing functional groups due to different stereochemical arrangements relative to the oxime group. Our ultimate goal for this study is the interpretation of nuclear magnetic resonance spectra of steroids containing oxime groups.

Congratulations once again for the fine work you are doing with MELLOMR.

Yours truly,

Thomas F. Page, Jr.

Robert J. Jakobsen

Thomas F. Page, Jr. and  
Robert J. Jakobsen

TFP/tJJ:bq

WASHINGTON UNIVERSITY  
SAINT LOUIS

February 14, 1961

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raised by Cotton and Klapper (MELLONMR No. 28, p. 10) is safely avoided as the error goes as  $(H_1/\nu_m)^2$  and  $H_1$ 's of the order of 0.1 mg are usually quite satisfactory.

For my own satisfaction and confirmation of this technique, would you please send me (when it is convenient) your series of standard samples so that I may make a detailed quantitative comparison.

Sincerely,

*Thomas R. Hughes*

Thomas R. Hughes

TRH:bw

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

Dear Dr. Bothner-By:

I would first like to present a simple modification of Varian's TWL insert that enables one to extend high resolution studies below  $-60^{\circ}\text{C}$ , the rated lower limit of the THR insert. It consists of a piece of tubing having the same i.d. as the THR insert to the top of which is affixed a ball joint that mates with the Varian insert cap. Three drops of glass around the bottom outside of the modification assist in maintaining the array concentric. Some holes placed just above the borrowed teflon-beryllium-copper bushing permit the cold gas to enter, and a slot in the ball joint permits convenient entry of the 'running' thermocouple. Finally a spring was used to seat the modification firmly and it derived its thrust from the bottom of the spliner insert.

Obviously there is a considerable loss in signal to noise due to the larger receiver coil; however, this is not always a limiting consideration. The resolution achieved at 56.4 mc/s was quite satisfactory, or more specifically the first line of the  $\text{CH}_2$  group in acidified ethanol clearly showed second order splitting.

Secondly I offer a comment on the measurement of chemical shifts. A variety of techniques are in use, but I have not heard mentioned one that I find quite satisfactory. A  $\nu_m$ , greater than the span of the spectrum, is applied with sufficient amplitude to generate three complete spectra of roughly the same heights. This spectrum in triplet is then swept once up and then once down-field. Six pieces of information are then available for each peak, rapid passage effects are averaged out, and the precision measure has consistently run to  $\pm 0.2$  to  $\pm 0.3$  cps for reasonably narrow lines. This technique has obvious advantages as far as complex structures are concerned; no settings need be changed during the course of the run; and finally if one is performing low temperature studies, one's hands and attention are freer to see that all is running well. Finally, the point

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