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Ecumenical
Letters from
Laboratories
of
N - M - R
No. 39

Author Index

MacLean	Protonated Aromatics	1
Tiers	τ-Table Errata	2
Page	Benzamides, Benzenesulfonamides	3
Shoolery	A-60 Cells	6
Shapiro	A-60 Cells	7
McLauchlan	Double Irradiation	7
Smith	Sidebands for V4210A	9
Fraenkel	Anilinium Salts	10
King	HR-60 Alterations	11
von Philipsborn	Cyclohexadienones	12
Malinowski	Chart Calibration	13
Freymann	A.M.P.E.R.E.	14
Agahigian	Hydroxyethylpyrrolidine	14
Robertson	3,4-Dehydroprolines	15
Bothner-By	Misc.	16

A monthly collection of informal private letters from laboratories of nmr.
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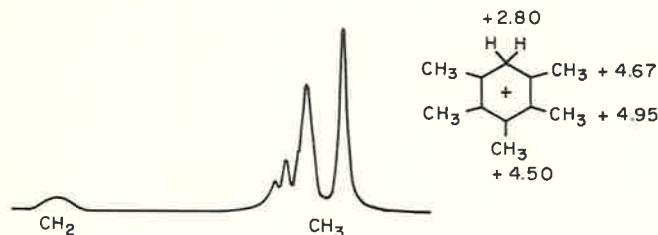
Amsterdam, 4th December 1961

- 2 -

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

Dear Dr. Bothner-By,

We have lately been engaged in the study of the kinetics of proton transfer reactions in solutions of aromatic hydrocarbons in hydrogen fluoride. We are now able to record the spectra of the proton complexes in absence of exchange. Thus spectra can be measured that show interesting details. For instance, in the proton complex of pentamethylbenzene there is a long-range π coupling between the CH_2 group and the para methyl group ($J = 3.4$ cps) over five carbon atoms. The meta methyl resonance is sharp and single, whereas that of the ortho methyl group is broadened ($J_{\text{CH}_2-\text{CH}_3} \sim 1$ cps). The CH_2 resonance is likewise broadened because it couples both to the para and ortho methyl groups.



Spectrum of the proton complex of pentamethylbenzene at 40 Mc/s.
 Solvent: $\text{HF} + \text{BF}_3$. Chemical shifts in ppm from benzene.

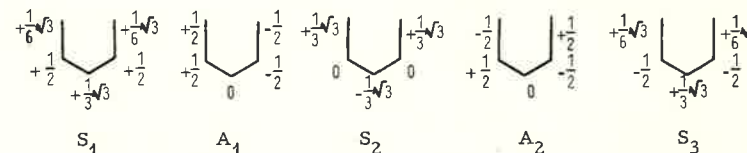
Similarly the methyl resonance of 9-methylantracene protonated in the meso position is split into a triplet ($J = 1.5$ cps). These couplings can be explained with the Fermi contact interaction using molecular orbital theory^{1, 2}. The following formula is obtained

$$J_{\mu\nu} = -0.033 \frac{Q_{\mu r} Q_{\nu s}}{E_T - E_0} c_{jr} c_{js} c_{ir} c_{is};$$

$Q_{\mu r}$ is the hyperfine interaction between hydrogen atom μ and a π -electron on carbon atom r . c_{jr} is the coefficient of the atomic orbital on carbon atom r in the j^{th} molecular orbital. The summa-

tion in the second-order perturbation energy is restricted to the lowest triplet state of appropriate symmetry.

The coefficients of the atomic orbitals in the Hückel approximation are given below. The symbols S and A refer to symmetric and antisymmetric MO's.



We only take into account the triplet state $S_1^1 A_1^2 S_2^1$ for which one estimates in SCF approximation (including configuration interaction) $\Delta E = 3.0$ eV. Reliable estimates for the Q values are: $Q(\text{CH}_3) = 28$ Gauss and $Q(\text{CH}_2) = 60$ Gauss. The following coupling constants of the CH_2 group with the methyl groups are calculated: $J_{(\text{para})} = 2.0$ cps, $J_{(\text{ortho})} = -1.0$ cps and $J_{(\text{meta})} = 0.0$ cps.

The absolute values of J and also the alternating character around the ring is adequately predicted. The main reasons why the couplings are large are the high value of $Q(\text{CH}_2)$, the existence of two conjugation paths over two ortho atoms and the low excitation energy.

It is of interest³ to compare these results with those calculated with an "effective excitation energy"². With $\Delta E_{\text{eff}} = 3$ eV, we calculate the values $J = +1.0, +1.2$ and $+1.6$ cps, respectively. This result is unsatisfactory, especially as regards the alternating trend in the magnitude of the coupling constant.

Yours sincerely,

C. MacLean

C. MacLean

E. L. Mackor

E. L. Mackor

References:

1. M. Karplus, J. Chem. Phys. **33**, 1842 (1960).
2. H. M. McConnell, J. Mol. Spectroscopy **1**, 11 (1957).
3. A. D. McLachlan, J. Chem. Phys. **32**, 1263 (1960).

CENTRAL RESEARCH DEPARTMENT

Minnesota Mining & Mfg. Co.

St. Paul 19, Minnesota

ERRATA: Tables of τ -values for a Variety of Organic Structures.
George Van Dyke Tiers, March 28, 1958.

τ of Line	Corrections to be made
2.11	Delete line.
Third 2.62	Change " C_6H_5CH " to " C_6H_5CH ". Insert "nq" in Mult.
Below 2.64	Insert " $C_6H_5CH=CHCOCH_3$ 2.64 - 5."
2.85	Change to "2.89".
2.89	Delete present line.
3.00	Change to "(cis)".
3.38	Change to "(trans)".
Below 3.40	Insert " $C_6H_5CH=CHCOCH_3$ 3.40 nq 5."
Below 3.56	Insert " $CHCl=CHCl$ (cis) 3.57 - 5."
Below 3.62	Insert " $CHCl=CHCl$ (trans) 3.63 - 5."
3.87	Change "Dimethyl" to "Diethyl", add "olef. H".
4.74	Add C, to read " $CH\equiv CMe=CH_2$ ".
First 6.38	Change to "6.369".
6.45	Delete line.
First 7.88	Change to " $MeCONCH_2CH_2$ (all H!)"
First 7.94	Change to " $Me_2C=CHCOMe$ (MeCO & Me cis to CO) 7.94 - 5."
Third 8.07	Change "10." to "6.".
8.08	Change to " $C_6H_5COC(CO_2H)CH_2CH_2$ ".
First 8.14	Change to " $Me_2C=CHCOMe$ (Me trans to CO) 8.12 d 5."
Second 8.33	Change to " $CCl_2CH_2CH=CH_2$ "
Second 8.51	Change to " $CCl_2CH_2CMeCH=CH_2$ ".
First 8.64	Change to "(Bridge CH_2)".

End of tables, last two footnotes: delete incorrect term "probable error" and remove parentheses from "(standard deviation)".

George Van Dyke Tiers
December 21, 1961

Battelle Memorial Institute

5 0 5 K I N G A V E N U E C O L U M B U S , O H I O

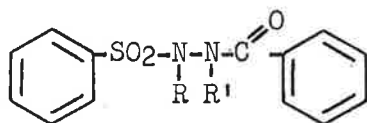
December 22, 1961

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

Dear Dr. Bothner-By:

We hope that this contribution will make your Saint Stephen's Day deadline. If not, maybe you can include it in the issue you will be mailing about Saint Agatha's Day.

Some time ago, we were asked if NMR could be used to establish the position of the alkyl substituent in compounds with the general structure:



where R = H, R' = alkyl
R = alkyl, R' = H

A preliminary examination of the so-called parent compound (I), i.e., R = R' = H, indicated the two N-H groups to be quite different (two doublets at 579 and 538 cps from TMS at 60 Mc./sec.) so that initially no particular problems were anticipated and it was believed that a simple correlation involving the -N-alkyl resonance positions would yield the required information.

However, upon taking the spectra of ϕ -SO₂-NH-NCH₃-C(=O)- ϕ (II) and ϕ SO₂-NCH₃-NH-C(=O)- ϕ (III)--both known compounds--we found that the spectra indicated the -N-CH₃ groups to be virtually identical--both absorbing at 199 cps. It was obvious, therefore, that a correlation involving the N-alkyl resonance frequencies of the benzenesulfonyl benzhydrazides with the position of alkyl substitution might not be dependable.

However, a more critical examination of the phenyl proton resonance indicated the phenyl resonance of II to be surprisingly simple when compared with that of III. Further comparison of these patterns with those of benzamide and benzenesulfonamide and all of the possible N-methyl derivatives of these two compounds strongly suggests that a resonance hybrid involving the -NH-C(=O)- ϕ fragment contributes considerably to the complexity of III's aromatic resonance.

Battelle Memorial Institute

Dr. A. A. Bothner-By

Page 2

December 22, 1961

With the exception of ϕ -C(=O)-N(CH₃)₂ (IV), all of the benzamides and benzenesulfonamides examined gave phenyl resonances typical of a benzene ring which is mono-substituted with an electronegative group. The phenyl resonance of IV, however, appeared as a single line. At this point, it must be concluded that the presence of the second N-methyl group in IV is responsible for the simplification of this compound's NMR pattern.

On going from VI (N-methyl benzamide) to IV, it is not difficult to visualize that the second N-methyl group will sterically hinder the benzene ring from becoming coplanar with the carbonyl group and thus prevent resonance involving the benzene ring from taking place. It is also worth noting that the inductive power of the carbonyl group must be quite small--otherwise the "ortho" positions of the attached ring would have been deshielded and the phenyl resonance of IV would have been split.

The splitting noted in all of the benzenesulfonamides is undoubtedly caused chiefly by the highly inductive -SO₂- group--with resonance playing, at most, only a minor role in the splitting of the aromatic resonances, again because of the lack of coplanarity of the phenyl ring. This conclusion is supported by the constant frequency of the para proton observed for the benzenesulfonamide series.

Upon applying the observations made for the benzamides and benzenesulfonamides to the spectra and structure of the compounds in question, one can logically explain the simplification noted in the aromatic spectral region of II as arising from the blocking of resonance by complete substitution of the nitrogen adjacent to the carbonyl. On the other hand, alkyl substitution on the -SO₂-N- nitrogen (as in III) does not result in any substantial change in the aromatic spectral region of compounds like III as compared with that of the parent compound, I. One would predict this on the basis of the benzene sulfonamide series. It is, therefore, only necessary to examine the aromatic region of mono-alkylated benzenesulfonylbenzhydrazides in order to determine on which nitrogen atom the alkylation has taken place. N,N'-Disubstituted compounds give the same kind of phenyl resonance pattern as II. However, these are easily detected with the aid of an integrated spectrum.

The ortho and para resonance frequencies of the compounds in question are contained in the appended table. The values reported here were obtained using very dilute CDCl₃ solutions. The same trends, although more pronounced because of solvent effects, were observed using dioxane as a solvent.

We are still somewhat puzzled by the shift to higher field of the -SO₂- ring's ortho protons observed for the last two compounds listed in the table. We have considered the possibility that the 480 and 476 cps

Battelle Memorial Institute

Dr. A. A. Bothner-By

Page 3

December 22, 1961

components noted for I and III were arising from the ortho protons of the $-C(=O)-\phi$ ring instead of as assigned in the table; however, we have ruled this out on the basis of the spectra of $\phi SO_2NHN(CH_3)_2$ and $\phi SO_2NHNHC(=O)-CH_3$ -- both of which show the ortho aromatic protons to be absorbing in the 470-472 cps range.

We enjoy receiving MELLONMR and very much hope that it can be continued. If sending 150 copies of a communication to be included in MELLONMR will help, we shall certainly comply with your request.

Sincerely yours,

Thomas F. Page Jr.

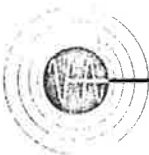
Robert J. Jakobsen

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

TFP:RJJ/bqb

PHENYL RESONANCE FREQUENCIES IN CPS FROM INTERNAL $Si(CH_3)_4$

Compound	$\phi-SO_2-$		$\phi-C(=O)-$	
	Ortho H's	Para H	Ortho H's	Para H
ϕSO_2NH_2	477	456		
ϕSO_2NHCH_3	473	456		
$\phi C(=O)-NH_2$			469	451
$\phi C(=O)-NHCH_3$			466	448
$\phi C(=O)-N(CH_3)_2$			443	443
$\phi SO_2NHNHC(=O)-\phi$	480	453	~460	451
$\phi SO_2N(CH_3)NHC(=O)-\phi$	476	455	458	448
$\phi SO_2NHN(CH_3)C(=O)-\phi$	455	443	443	443
$\phi SO_2N(CH_3)N(CH_3)C(=O)-\phi$	451	440	440	440



411 HANSEN WAY * PALO ALTO, CALIFORNIA * DAVENPORT 6-1000

November 28, 1961

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

Dear Barry,

Since your letter of August 28, 1961, which appeared in MELLONMR #35 was circulated, it has become more and more apparent that several factors bearing on your comments about sample tubes should be brought to light. I would therefore appreciate it if you would circulate the following comments in the next MELLONMR issue.

The considerations which led to the recommendation of the present precision sample tube for the A-60 were neither the desire to sell a more expensive tube nor to insist on a tube of greater precision than actually needed for the application at hand. Instead, the dominant consideration is the high filling factor of the receiver coil, needed for optimum sensitivity of the instrument, and achieved by very close tolerances and a very thin and consequently fragile receiver coil support tube. In order to avoid the disaster of breaking this part of the probe structure by inserting a sample tube in a cocked position, the decision was made to provide a high-precision spinner bearing of sufficient length to prevent cocking the tube enough to break the insert. At the same time, it was found that the small spinner which could be accommodated in the limited gap of the A-60 operated much better with precision tubes than with tubes which were as much as several thousandths off of the correct size.

The only way to provide a sufficiently straight tube with a sufficiently precise diameter is to shrink the glass on a mandrel and grind down to the correct diameter. The precision grinding results in the cost difference between these recommended A-60 cells and the "semi-precision cells" which are simply shrunk on a mandrel. Since the semi-precision cells can range in diameter from .191" to .197", it is necessary to use extreme caution in inserting or removing any tube smaller than .194". Varian cannot be responsible for probe breakage resulting from the use of undersized or insufficiently straight tubes.

The maximum diameter tube which can be accommodated by the A-60 probe is .196". Therefore, there is a possibility that if the glass used in manufacturing the semi-precision cells is running on the large side, a large proportion of the

MARIAM
associates

Dr. B. L. Shapiro
Mellon Institute
Pittsburgh, Pennsylvania

- 2 -

November 28, 1961

cells could be too big to be inserted in the probe. I have contacted the Wilmad Glass Company, manufacturers of these semi-precision tubes, and have been told by them that they cannot accept for return any semi-precision tubes which do not fit the A-60. However, they will quote on tubes with the diameter selected to fall between .193 to .196 inches, and in the hands of a careful operator, these tubes should be relatively satisfactory for most work.

It is worth noting that the precision A-60 tubes have a cross-sectional area which is 8% larger than the semi-precision tubes. It appears that slightly less trimming of resolution is required in changing from one sample to another if precision cells are used, possibly due to small irregularities in the thickness of the glass if the grinding operation is omitted. However, for many applications these considerations are unimportant and the semi-precision tubes can be used with complete success.

If, as in some laboratories, inexperienced personnel are permitted to operate the A-60, the more expensive precision cells might be the most economical in the long run if expensive and time-consuming repairs to the probe can thereby be avoided.

Sincerely yours,

James N. Shoolery

James N. Shoolery

JNS:jl

39-6

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

28 December 1961

KAMcI/D&T



Department of Scientific and Industrial Research NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

Telegrams: Physics, Teddington Telephone: Teddington Lock 3222, ext. 199

Please address any reply to
THE DIRECTOR
and quote: BP.5/6/01
Your reference:

BASIC PHYSICS DIVISION

24th November, 1961.

Dear Dr. Bothner-By,

May I become the third member of the NPL group to contribute to your invaluable newsletter?

Concerning Sample Tubes for Use in the A-60

The above letter from Jim Shoolery is certainly a most timely and satisfying discussion of the reasons behind Varian's advocacy of the super-quality A-60 sample tubes which they supply. In our previous comments on the tube problem (MELLONMR 35, 9), it was, of course, not our intention to encourage the use of tubes of dangerous geometries. As we tried to make clear, our use of the less expensive Wilmad tubes was dictated primarily by economic considerations, for we were prepared - for routine applications - to be extra careful and to sacrifice just a little from the performance in order to use \$1.25 tubes rather than \$3.80 tubes.

Anyhow, all of this is useless history, at least as far as we are concerned, since we have just been informed that the new price for the high quality Varian A-60 sample tubes is \$55 per package of 25 tubes. Thus, the cost is \$2.20 per tube and we feel that this cost, while still high, (high, not unreasonable!), is within reach when all the other factors are considered. Thus, we will be using the Varian A-60 tubes exclusively when our present supply of the cheaper Wilmad tubes is exhausted.

B. L. Shapiro

Ye Associate Editor

I should like to report a novel use of the double-irradiation technique as recently applied to a proton system by Dr. R.J. Abraham, Dr. R. Freeman, Mr. L.D. Hall and myself. In the problems discussed below the chemical shifts between the two nuclei to be decoupled are small and so both the strong radiofrequency field used for decoupling and the weaker one used to display the spectrum are both sideband responses, the former obtained by modulation of the spectrometer oscillator and the latter by modulation of the magnetic field. In this way the smallest of the modulation frequencies can be chosen so that the complete spectrum can be scanned without the unused sidebands overlapping the spectrum.

The problems arose during an investigation into the conformations of some 1,2-isopropylidene derivatives in solution⁽¹⁾. These compounds normally give spectra which are readily assigned and in which the J_{23} coupling is near zero so that protons H_2 and H_3 show doublet absorption patterns. These two protons have very similar chemical shifts but in general their peaks are recognised without trouble since J_{12} and J_{34} , whilst similar, are not equal. However in some spectra, e.g. those of 3,6-anhydro-1,2-O-isopropylidene-5-O-togyl- α -D-glucofuranose (I) and 3,6-anhydro-1,2-O-isopropylidene- α -D-glucofuranose (II), the splittings observed in the H_2 and H_3 doublets



are precisely equal and it is impossible to differentiate between the two protons by normal means.

Clearly one of these protons is coupled to H_1 which gives a doublet (3.5 cps splitting) well removed from other lines. When H_1 is irradiated strongly and the difference in modulation frequencies is set equal to the chemical shift between H_1 and the low field doublet and H_1 and the high field doublet in turn, it is the low field doublet which collapses, thus identifying H_2 . In neither instance was there any effect on the high field doublet.

/The

39-7

NATIONAL PHYSICAL LABORATORY

- 2 -

Dr. A.A. Bothner-By

24th November, 1961.

The relevant parts of the spectra are shown in the figure with the normal spectrum above the decoupled one in each example, and with an indication of the collapse of the H_2 doublet.

This work has been submitted for publication in the Journal of the Chemical Society.

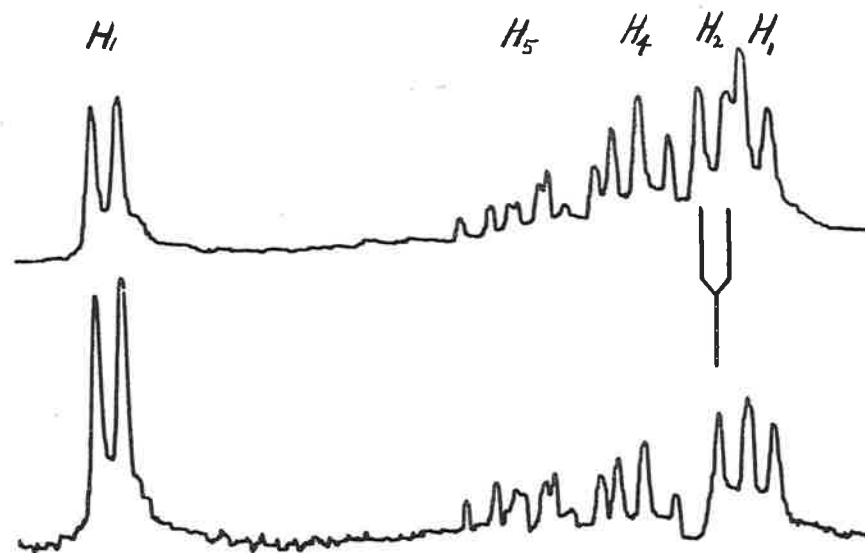
Yours sincerely,



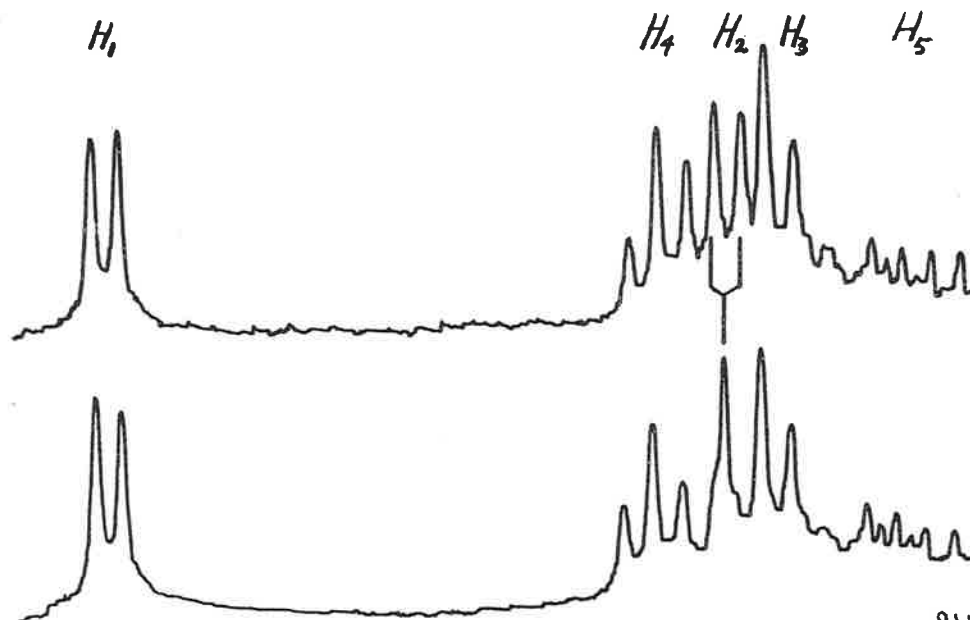
K.A. McLauchlan
Basic Physics Division

(1) R.J. Abraham, K.A. McLauchlan, L.D. Hall and L. Hough. Submitted to Chem. and Ind.

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



I.



II.

29-8

November 16, 1961 - 2

RESEARCH LABORATORIES

GENERAL MOTORS CORPORATION

November 16, 1961

Redated: December 4, 1961

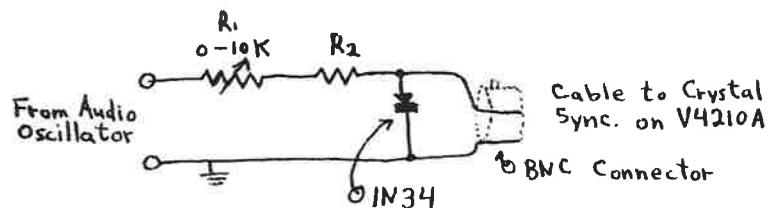
Dr. A. A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburg 13, Pennsylvania

Dear Dr. Bothner-By:

Thank you for your letter of November 7. I am sorry to be so tardy about submitting a letter to MELLONMR. I had been intending to submit this contribution earlier, but because of other projects, it was put off.

Mr. B. W. Joseph and I have constructed and tested a simple device for producing NMR sidebands with the Varian Model V4210A Variable Frequency RF Unit. We felt that it might be of interest to MELLONMR readers since no provision for sidebands was made for this unit by Varian Associates. No circuitry changes are necessary with our simple device.

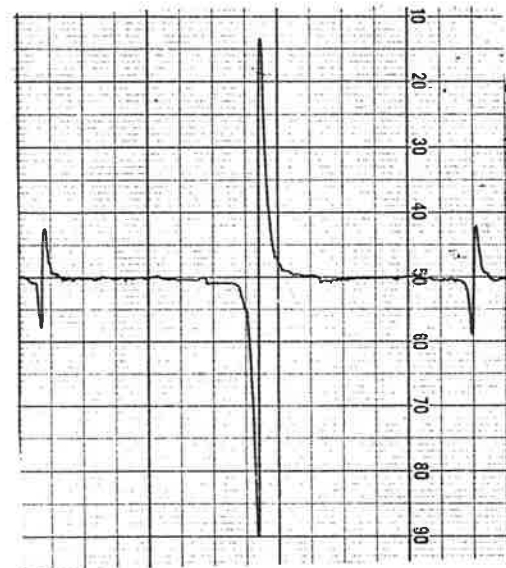
The circuit for the modulator is as follows:



Input to the modulator unit is from an audio oscillator such as a Hewlett-Packard 200CD. The output is plugged into the Crystal Sync. BNC connector on the front of the V4210A RF Unit. Frequency modulation of the rf is produced, and one is able to observe sidebands at frequencies of about 100 cps to 11 K cps which should be sufficient for most purposes. Certainly one can obtain a good calibration of his field scan at any magnetic field strength with the unit. 11 K cps represents the maximum frequency for which we could see sidebands with the above design.

The resistors serve to isolate the audio oscillator from the rf unit and one is made variable to allow optimum sideband strength to be achieved. R_2 has a value of several hundred ohms. Several precautions must be indicated. When the unit is connected to the Crystal Sync. connector the central rf frequency will be shifted a small amount so that it is necessary to retune for resonance. Adjustments of R_1 and the audio oscillator level can also shift the frequency of V4210A.

We close this note with an example. This is the D_2O line in 20% D_2O in H_2O (+0.5 mole $MnSO_4$ per liter) with 5 K cps sidebands. The signal is overmodulated.



Yours truly,

George W. Smith

George W. Smith
Physics Department

GWS:el

39-9

THE OHIO STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY
55 WEST 18TH AVENUE
COLUMBUS 10, OHIO

December 20, 1961

Dr. Aksel A. Bothner-By
Mellon Institute
4400 5th Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel,

The NMR equipment here is working well. In addition to all the usual control features, we have insulated all exposed metal parts with aluminized styrofoam and built a box around the entire magnet. This last feature seems to have done more good than all the others put together. We also have been manufacturing our own recorder pens for the varian G10: buy a Leroy Lettering Pen for \$1 and have your machinist solder a brass cylindrical reservoir to the top.

Along with others we have also been interested in the NMR spectra of anilinium salts. The highly complicated ring proton spectrum in aniline collapses to a single line when aniline is dissolved in strong acids. This had been found for salts of aniline *p*-toluidine and *p*-chloroaniline including the *N*-methyl and *N,N*-dimethyl derivatives. From the well spaced *N*-methyl proton multiplets and the line-shapes of the *N*-H bands, it is clear that *N*-H exchange is too slow to contribute to the coalescence of the ring hydrogen lines. Very similar effects are observed when these salts are dissolved in dimethyl sulfoxide, methanol, dioxane, and *N,N*-dimethylacetamide. From the NMR spectra it is found that these salts are not dissociated and *N*-H exchange is slow. Not all these salts show the same degree of coalescence for the ring hydrogen lines, the effect being least for iodides and most for the chlorides though even iodides show some collapse. The smallest effect of all is found for *N,N,N*-trimethylanilinium iodides. For instance in the ring hydrogen spectrum for *N,N,N*-trimethylanilinium iodide in dimethyl sulfoxide and dioxane is very similar to that of nitrobenzene, benzoic acid - any monosubstituted benzene with a strong electron withdrawing group.

It is evident that the effects observed here are due chiefly to the accompanying anions and only to a small extent to specific solute-solvent interactions. There seem to be two parts to the anion effect, the exchange of anions between anilinium cations and the process by which a small anion will average out the ring hydrogen shifts in the anilinium cation. The first effect has been observed from NMR spectra of *p*-chloroanilinium iodide and

THE OHIO STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY
55 WEST 18TH AVENUE
COLUMBUS 10, OHIO

Dr. Aksel A. Bothner-By

Page 2

chloride. The iodide dissolved in dimethylsulfoxide gives for the ring hydrogens a well defined quartet while the chloride yields a single line with small satellites; for solutions containing both salts in dimethylsulfoxide the ring hydrogen line shape is the average for the two salts and shows a degree of collapse intermediate between them.

The *p*-substituted anilinium salts were chosen for the simplicity of analysing the spectra. Similar results were found for ortho and meta substituted anilines.

It should also be pointed out that in aqueous solution the *N*-H exchange rate varies over a wide range, as already reported, and rate constants can be evaluated.

Recently in conjunction with Michael Cava, we have been looking at some derivatives of 1,5-dibenzcyclooctatetraene. This compound forms a tetrabromide with bromene. The tertiary hydrogens give two doublets. The chemical shift between these hydrogens is 0.49 ppm and the coupling $J = 9.75$ cps. The latter implies that the dihedral *H,H* angle must be close to 180°. The only Dreiding stereomodel which fits all these conditions is that of the skewed boat form.

Sincerely,

Gideon

Gideon Fraenkel

GF:ljc

39-10

IOWA STATE UNIVERSITY

of Science and Technology



AMES, IOWA

December 21, 1961

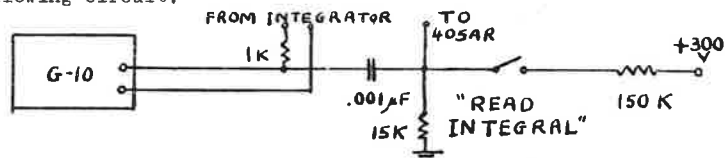
Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

In a year's use of our HR-60 for more or less routine proton spectra we have found that operation could be streamlined somewhat by a few simple modifications that may be of interest to readers of MELLONMR.

We insert audio sidebands in the normal way via the jacks on the V4352 Linear Sweep Unit, but the modulation switch now has three positions. That on the right applies modulation, the centre is off - isolating the oscillator from the 2 Kc/s. field modulation of the Varian integrator system - and the left-hand position, which is spring-loaded, actuates a relay across the 'RESET' button of a Hewlett-Packard 5210 electronic counter permanently connected to the oscillator. To measure the audio frequency this switch is moved to the left and released, no disturbance of other controls being necessary.

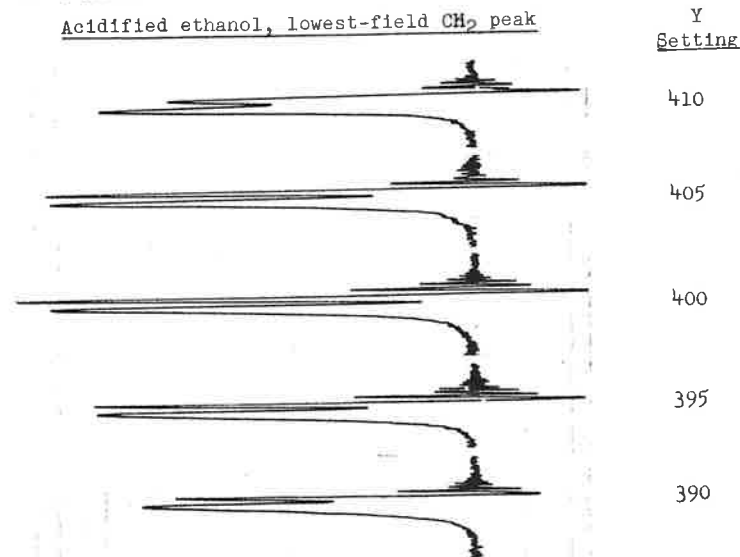
To facilitate integration, we have installed 'CANCEL INTEGRAL' and 'READ INTEGRAL' buttons in a panel on the console top. The first is connected to the corresponding terminals on the integrator and the second to the 'EXT. SAMPLE' jack of a H-P 405AR digital voltmeter (and to a G-10 recorder) by the following circuit:



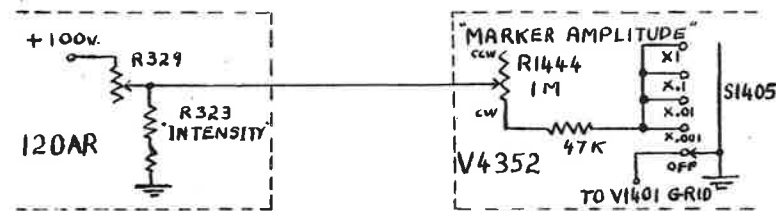
When the switch is closed, the voltmeter reads (and holds) the value of the integral while simultaneously a pip about $\frac{1}{2}$ mm. high appears on the G-10 trace. With practice, accurate

readings of short steps and even of inflections may be made without having to record changing figures on a moving chart.

Being blessed with a good magnet, we have found, as did Dr. Shapiro with the A-60 (MELLONMR #35), the Y shim coil control to be too coarse. Displacement from optimum by as little as 5/1000 of the range of the Helipot with which we have replaced it has a noticeable effect on the resolution:



Finally, to eliminate one movement and to avoid burning the 120AR oscilloscope face, we have connected four unused contacts on one wafer of the V4352 Sweep Field Coarse switch via the Marker Amplitude control (never used in our applications) to one end of the oscilloscope brightness control:



The oscilloscope is adjusted so that the spot is just visible with the sweep off; when it is turned on the spot is automatically brightened to an extent controllable by the former Marker Amplitude potentiometer.

The above modifications compensate to some extent for the lack of unified design inevitable in the development of the HR-60 and also make life easier for operators of less than average reach.

Sincerely yours,

Roy W. King
Roy W. King

39-11

Organisch-Chemisches Institut
der Universität Zürich
Zürich, Rämistrasse 76

December 18, 1961.

Dr. W. von Philipsborn
Dr. T. Mabry

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

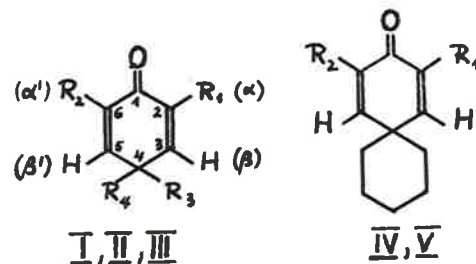
Dear Dr. Bothner-By:

For a long time we have gained invaluable information from your excellent Mellon Letter system. Now, to justify a subscription we would like to present some data on long-range coupling of protons in cyclic dienone systems which may be of considerable diagnostic and theoretical value.

We have observed that in (p-)cyclohexadienones which are unsymmetrically substituted in the α -positions the protons H_β and $H_{\beta'}$ show spin-spin coupling of the order of 3 c/s. For example, in compound III $H_{\beta'}$ gives a doublet ($J=2.9$ c/s) and H_β a quintuplet because of additional allylic coupling to the methylene group at C-2. The multiplicity and intensity ratio of the H_β signal show that $J_{H_\beta CH_2}$ is about half of $J_{H_\beta H_{\beta'}}$. The complete analysis of the spectrum proves that there is no coupling of the β -protons and the groups attached at C-4. The observed $H_{\beta}H_{\beta'}$ coupling is characteristic for this type of dienones. Thus in IV the β' -proton couples with $J=2.8$ c/s with the β -proton in addition to the larger coupling ($J=10$ c/s) with the α' -proton which appears as a doublet at higher field. The data of these and two other compounds are listed in the following table.

The fact that the β -protons in the symmetrically substituted dienone V produce only a singlet rules out coupling of these

protons with the protons on the saturated spiro ring in IV.



Compound	H_β	$H_{\beta'}$	$H_{\alpha'}$
I $R_1=R_3=CH_2-CH=CH_2$ $R_2=H$; $R_4=CH_3$	quint.; 3.57 $J_{\beta\beta'} = 3.0$ $J_{\beta CH_2} \sim 1.5$	quart.; 3.30 $J_{\alpha'\beta'} = 10.0$ $J_{\beta\beta'} = 3.0$	doubl.; 3.90 $J_{\alpha'\beta'} = 10.0$
II $R_1=R_3=CH_2C_6H_5$ $R_2=H$; $R_4=CH_3$	quint.; 3.80 $J_{\beta\beta'} = 3.0$ $J_{\beta CH_2} \sim 1.5$	quart.; 3.38 $J_{\alpha'\beta'} = 10.0$ $J_{\beta\beta'} = 3.0$	doubl.; 4.00 $J_{\alpha'\beta'} = 10.0$
III $R_1=R_3=CH_2-CH=CH_2$ $R_2=Br$; $R_4=CH_3$	quint.; 3.43 $J_{\beta\beta'} = 2.9$ $J_{\beta CH_2} \sim 1.5$	doubl.; 2.77 $J_{\beta\beta'} = 2.9$	---
IV $R_1=Br$; $R_2=H$	doubl.; 2.42 $J_{\beta\beta'} = 2.8$	quart.; 2.85 $J_{\alpha'\beta'} = 10.0$ $J_{\beta\beta'} = 2.8$	doubl.; 3.65 $J_{\alpha'\beta'} = 10.0$
V $R_1 = R_2 = Br$	singl.; 2.50		---

The spectra were obtained with a Varian A-60 instrument in CCl_4 - solutions. Chemical shifts are given in τ -units and J-values in c/s.

Furthermore there is good evidence that the two α -protons show a similar but smaller coupling* as could be shown in

* $J = 1.5 - 2$ c/s

39-12

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

10-alkyl-2-keto- $\Delta^{1,2,3,4}$ -hexahydro-naphthalenes. These spectra together with a detailed analysis of the cyclohexadienone spectra will be presented in a full paper *.

The smaller value for the $H_{\alpha}H_{\alpha'}$ coupling in the above mentioned compounds seems to eliminate coupling via the dienone bonds for the observed $H_{\beta}H_{\beta'}$ coupling in the (p-)cyclohexadienones. Other possible explanations for the phenomenon include long-range coupling through the tetrasubstituted carbon atom or a short-range mechanism by direct orbital overlap between the dienone double-bonds. If the latter mechanism is operating this would allow interesting conclusions regarding the dienone structure.

* J. Borgulya, R. Garner, G. Sassu, T. Mabry & W. von Philipsborn, in preparation.

Sincerely yours

W. von Philipsborn

W. von Philipsborn

T. Mabry

T. Mabry

Department of
Chemistry and Chemical Engineering

November 28, 1961

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

Dear Dr. Bothner-By:

Operators of DF-60 and HR-60 Varian Spectrometers do not have the advantage of calibrated chart paper (in contrast to A-60 operators). Consequently, many hours are spent in calculating chemical shifts and coupling constants. I wish to inform such unfortunate MELLONMR readers of a labor-and time-saving technique we have been using in our laboratory during the past six months.

Essentially, the method consists of using an adjustable scale. Our graphical scale is drawn on a piece of paper 30" x 30". The bottom of the paper is divided into ten equal divisions. Bold lines are drawn from these points to a common vertex at the top of the paper. Each division is further subdivided into twenty equally spaced, light lines coalescing at the vertex. The bold lines are marked 0 to 10, from left to right respectively, signifying τ values. Below each τ value are written the corresponding cps units (for example $\tau = 0$ corresponds to 600 cps, $\tau = 1$ corresponds to 540 cps, etc.). A series of lines one-half inch apart are drawn parallel to the base line. The purpose of the parallel lines is to help properly position the NMR spectrum.

Normally we obtain spectra on dilute solutions using CCl_4 or CCl_3 as solvents containing a trace amount of tetramethylsilane as an internal standard. With the wide-range oscillator an image of T.M.S. is superimposed at about 350 to 500 cps downfield (depending upon the type of compound). After the spectrum has been taken light pencil lines are drawn thru the major peaks perpendicular to the base line. The spectrum is then positioned on the graphical scale so that the T.M.S. peak lines up on the zero cps line and its image upon whatever frequency was used in calibration. Care must be taken to align the base line exactly parallel to the bottom of the graphical scale. τ values or cps relative to T.M.S. can be read directly from the graph for each peak.

Thanks for the copies of MELLONMR bulletins.

Sincerely,
Edmund R. Malinowski
Edmund R. Malinowski

ERM:mbb

39-13

LABORATOIRE DE SPECTROSCOPIE HERTZIENNE

ANNEXE DU
LABORATOIRE DE RECHERCHES PHYSIQUES A LA SORBONNE
1, RUE VICTOR COUSIN, PARIS-V.

RF/AM 545

PARIS, 1E 21 décembre 1961
Odfon : 24-13 POSTE 263

Dr Aksel A. BOTHNER-BY
Director of Research
MELLON INSTITUTE
4400 Fifth Avenue
PITTSBURGH 13 PA.

U.S.A.

Cher Dr Bothner-By,

En vous félicitant de votre heureuse initiative, la création des MELLONMR, je voudrais dans cette première lettre, associer votre idée originale à l'existence d'un groupement ayant des buts orientés dans la même direction, - mais de façon plus générale : Il s'agit du Groupement A.M.P.E.R.E., ceci étant l'abréviation de : Atomes et Molécules par Etude Radio Electrique. Ce Groupement est peut-être moins connu aux U.S.A. qu'en Europe et c'est pourquoi il me semble utile de faire part ici aux lecteurs des MELLONMR du but et de la réalisation de ce Groupement :

Le Groupement A.M.P.E.R.E. réunit les chercheurs utilisant d'une façon générale les ondes hertziennes en vue de travaux sur la structure atomique ou moléculaire, la Résonance Magnétique Nucléaire étant l'une des branches de son activité. Un Bulletin d'Informations paraît régulièrement et apporte les renseignements sur Congrès, publications et travaux des membres du Groupement, etc... Tous les ans depuis 1951 un Colloque réunit les chercheurs en une ville d'Europe différente : successivement à Paris, Grenoble (France), Paris, puis en 1956 Genève, 1957 Saint-Malo-Rennes (France), 1958 Paris, 1959 Londres, 1960 Pise, 1961 Leipzig.

Du 2 au 7 Juillet 1962 le Colloque A.M.P.E.R.E. se tiendra à Eindhoven (Pays Bas). Pour tous renseignements, les chercheurs des U.S.A. qui désireraient se rendre à ce Congrès où ils seront les bienvenus-pourront s'adresser à M. le Professeur G. Béné, Institut de Physique, Boulevard d'Yvoy à Genève (Suisse).

Si vous souhaitez des renseignements complémentaires, je vous les adresserai bien volontiers.

Recevez, cher Dr Bothner-By, l'expression de mes sentiments très cordiaux.

R. FLEHMANN
Professeur à la Faculté des Sciences
de Paris.

Olin

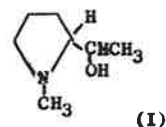
275 WINCHESTER AVENUE, NEW HAVEN 4, CONNECTICUT

December 21, 1961

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

Dear Aksel:

I was browsing through Dr. Cecile Naar-Colin's Mellon Newsletter when I ran across a piece of work done by Dr. R. J. Abraham. The subject was "Solvent Shift - Hydroxy Proline Spectra", No. 33 Mellon NMR, pp.23. This prompted my writing a much delayed note concerning some work that is being done at Olin Mathieson concerning a similar system. The problem, although chemical in nature, developed as a result of an NMR spectrum. The compound (I) was synthesized using a chemical method involving the reduction of the pyrrole.



The NMR spectrum was rationalized on the basis of two isomers being present. In further experiments, using a catalyst in the presence of hydrogen, the ratio of isomer was reversed. By means of chromatography, a small amount of the predominant isomer in the latter synthesis was separated. This is the state of the work as of now, and the program involves preparation of these isomers by the two methods and identification and analysis by NMR. The "τ" values of the NCH₃ and CH₃ are given:

	NCH ₃	CH ₃ Doublet
Isomer - I	7.52 τ	8.80, 8.91
Isomer - II	7.65 τ	8.84, 8.95

Sincerely,

Harry Agahigian
H. Agahigian

HA/djf

P.S. Cecile has started the boron program and is making the transition from the academic world to the industrial. In a few short months she has become an expert on boron NMR. It appears she will be quite busy once she gets going. We have our boron decoupler now, and this will be of help to her.

If possible, I'd like to be added to the mailing list; however, it would not be a hardship merely to read Cecile's Mellon NMR and occasionally contribute something.

39-14



The University of Sydney

SYDNEY, N.S.W.

IN REPLY PLEASE QUOTE: Department of Organic Chemistry

12th December, 1961.

Dear Enthusiasts,

With this contribution I hope to get the University of Sydney on the mailing list for MELLONMR. The work was done when I was at NIH, Bethesda, where Bob Bradley and Ted Becker do a wonderful job in satisfying the demands of empirical organic chemists like myself. One of our chemical interests was 3,4-dehydroproline (I) and its derivatives. NMR was by far the quickest way of finding the position of the double bond in the ring, and whether it had shifted in the course of chemical reactions. In addition, some intriguing NMR effects are observed and some of these are briefly described below.

Various derivatives have been prepared using different protecting groups on the nitrogen and carboxyl functions. In several of these, the two olefinic protons appear as a singlet although the signals from the protons on C-2 and C-5 are complex multiplets. In the remaining derivatives the olefin band is a multiplet of at least 14 peaks. For 3,4-dehydroprolinamide (II) the olefin band is a singlet in deuteriochloroform but changes to the multiplet in deuterium oxide. In discussions with Aksel Bothner-By and Jim Shoolery the following interpretations have emerged:

(a) spectra with the 2 proton olefin singlet. The olefin protons have the same chemical shift. They split each other and both are split by the protons on C-2 and C-5. The result is a deceptively simple pattern for the olefin absorption. Bothner-By has made calculations on simpler structures (two olefin protons and one other proton all coupled to each other) which provide a good model. The model requires that the protons on C-2 and C-5 be complex multiplets and that small satellite signals be present at the base of the olefin singlet. Sure enough, tiny but reproducible peaks are observed at high gain in the dehydroproline series.

(b) spectra with the olefin multiplet. The multiplet is essentially an AB quartet in which each branch is split further into a quartet. Overlapping then reduces the number of observed peaks from 16 to 14. The primary AB quartet is due to the two olefin protons which have a slight chemical shift difference. The three protons on C-2 and C-5 then split each of the olefin protons with a coupling constant of the same magnitude.

In all cases, the complexity of the splitting pattern for the other ring protons demands that the C-2 and C-5 protons be coupled to each other as well as to the olefin protons.

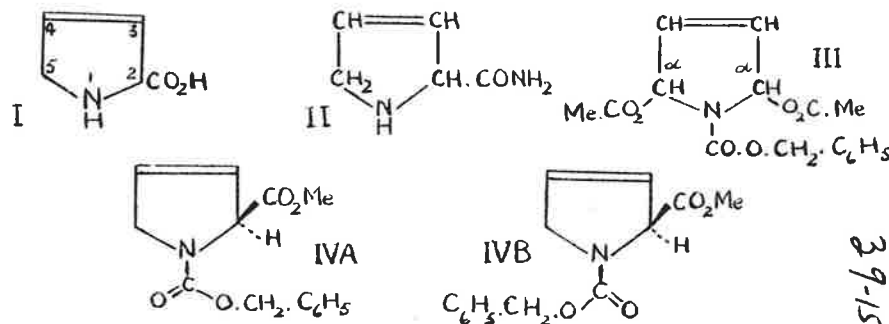
The interesting derivative III, which contains five different types of protons, gives a spectrum consisting of five sharp singlets of appropriate chemical shift and area. The protons on the α -carbon atoms do not split each other or the olefin protons. This is in contrast to the compounds discussed above although the dihedral angles between the ring protons must be practically the same in all cases.

In carbobenzoxydehydroproline methyl ester, the peak for the methyl of the ester group is a doublet of separation 9 cps in deuteriochloroform. This is not due to splitting (thank goodness - there are already enough problems in this series) because in acetonitrile the doublet separation changes to 5 cps. Two different conformations IVA and IVB must be present in equal amounts because of restricted rotation about the amide bond, as in dimethylformamide. In agreement with this explanation, the aromatic signal is also a doublet of separation 2 cps in both solvents. Vapour phase chromatography gives a single peak showing that the compound (an oil) is pure, and that the barrier to rotation has been exceeded at the temperature of the column (140°).

Finally as a news item from the Southern Hemisphere, CSIRO and Australian Universities have 5 A-60's and 3 DP-60's on order, so that those of you who have been plagued with Australian samples can expect relief shortly. Unfortunately this University is not amongst those mentioned in the last sentence, but we are campaigning hard for funds and are optimistic of success.

Yours sincerely,

A.V. Robertson.



39-15

A low muttering which threatens to grow into a definite rumble is beginning to arise from the recipients of "... please remember that the 'price' of a subscription..." letters, and distinguishable in this murmur are phrases such as "how come he doesn't take himself off the list?", "... parasite..." etc. Ye editor has hastily reviewed the situation and sure enough, nothing has been contributed from this corner since issue No. 26. Herewith hasty amends.

As mentioned in Alex Robertson's letter, we thought we might be able to explain the capricious appearance and disappearance of splitting patterns in the spectra of 3,4-dehydroproline spectra on this basis; suppose tight coupling (7 cps) and no chemical shift between the olefinic protons, and further suppose the protons of the $-CH_2N$ group are coupled with about +2 cps to the adjacent olefinic proton and about -2 cps to the remote olefinic proton (all reasonable for the geometry). Then by considerations similar to those developed by Abraham and Bernstein (Can. J. Chem. 39, 216 (1961)), the effective coupling between the olefinic protons and the $N-CH_2$ protons would be the average coupling, or 0 cps. If a chemical shift is introduced between the olefinic protons, then the averaging effects will disappear, and a rich splitting pattern will be observed. Calculations in the past few days using our FREQUENT III program have shown that we can indeed match the spectra for 3,4-dehydroprolinamide in chloroform (simple pattern) and in D_2O (complex pattern) changing only the chemical shift of one olefinic proton. Perfect matching has not been obtained yet - we will hope to provide the exact parameters next month.

Other activities at Mellon include a pursuit of the rotational isomer problem in alkylethylenes (cf. Mellonr 26, 9). Dr. H. Günther has prepared 4,4-dimethyl-3-t-butylpentene-1 (di-t-butylpropene), and 2,5,5-trimethyl-4-t-butylhexene-2 (1,1-dimethyl-3,3-di-t-butylpropene-1) and we have analyzed the spectra of these. The values for $J_{1,4}$ are 10.65 and 11.37 cps respectively, indicating a large proportion of 1,4 rotamer with olefinic and allylic proton trans-oriented. The long range coupling constants fall to -0.10 cps (trans) and -0.65 cps (cis) in the di-t-butylpropene, also. We have preprints of this work and will forward it to any who indicate the desire to see it.

We have also done some work (with Dr. Naar-Colin) on the 2,3-disubstituted butanes, very similar to that reported by F. A. L. Anet (Mellonnr No. 37). Articles by Anet and by us are due to appear in JACS shortly.

Work on programming continues. Mrs. O. D. Geisel has been working on developing a self-correcting program. We have one that works (part of the time anyway), and will be working on refining it over the next few months. We also hope to work on programs which will permit calculations of spectra with two kinds of nuclei (e.g. H & F) and which will incorporate group theory factoring to allow economical calculation of spectra of systems with more than 7 spins.

Finally, we are working in long range collaboration with Dr. P. Enslin (S. Africa) and Professor D. H. R. Barton on the structures of the natural products known as the Cucurbitacins.

Best wishes for the New Year to all!

Ye Ed.

P. S. Next deadline, Friday 26th January.