

*Joseph V. Lambert*  
Mailed: January 4, 1963

Monthly  
Encumenical  
Letters from  
Laboratories  
Of  
N - M - R

No. 51

B.L.S. & A.A.B.	Concerning the Mailing of MELLONMR	1
Freeman	Effect of Substituents on Vicinal Couplings	2
Tincher & McMahon	Spectra of Racemic & <u>meso</u> 2,4-dichloropentane	3
Beach & Hanselman	Water Recirculator for the A-60; An Inexpensive Digital Voltmeter; Cats and Dogs	5
Fritz & Kreiter	Azulenenes and Metallo-Azulene Complexes	6
Swalen	Concerning the Analysis of ABC Systems	7
Brügel	NMR Spectra of Substituted Pyridines	8
Rogers	Long-Range F-F Couplings	9
Snyder	Temperature Dependence of Vicinal Coupling Constants	10
Hoffman & Gronowitz	Coupling Constants in Pyrrole; Concerning Long-Range Couplings	11
Jonás	Uridine and Azauridine Spectra	13
Knight & Erskine	Dehydroniovin and Niovin Structures	14
Meuche & Melera	The Proton Spectrum of Azulene	16
Sonnenbichler	Equipment to Combat Power Failures	18
Flautt	A-60 Modifications and Special Chart Paper	19

DEADLINE FOR NEXT ISSUE  
January 28, 1963

En månatlig samling informella brev från NMR-laboratorier. Innehållet i denna skrift är avsett enbart för läsarens personliga bruk. Det är förbjudet att citera eller referera utom efter direkt överenskommelse med brevets författare; i sådant fall måste referensen anges som "personligt meddelande".



## MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

MELLON INSTITUTE

-2-

2 January 1963

### CONCERNING THE MAILING OF MELLONMR

### AIR-MAIL POSTAGE COST FOR A TYPICAL ISSUE OF MELLONMR

Since the inception of MELLONMR, over 4 years ago, we have borne the entire cost of producing and mailing this Newsletter. It has been a pleasant and, we hope, a useful endeavor. Our mailing list has now grown to approximately 140 participants in some 16 countries. It must be readily apparent to all that to air-mail all the issues, particularly the foreign ones, would shorten the relaxation time of our budget by several orders of magnitude and would be completely prohibitive. However, several MELLONMR participants (particularly foreign ones) have indicated a strong interest in the possibility of getting MELLONMR faster than surface mail permits and we therefore propose the following options for the future receipt of MELLONMR, effective with issue No. 52:

(1) To continue exactly as at present. We will continue to bear all the costs, including that of surface mailing.

(2) To choose to receive the Newsletter by air-mail and to reimburse us for this expense. The table below indicates the cost of mailing a typical single issue of MELLONMR by air-mail to each of the countries indicated. Those who are interested in paying these enormous rates are invited to send us 9 times the appropriate amount listed below (by whatever payment schedule you please) and we will see that MELLONMR is dispatched by air each month. We leave it to each individual to find some form of payment which is payable in US funds here in Pittsburgh.

Please let us re-emphasize that this air-mail plan is merely an option which you may exercise if, and only if, you have so much money and are so very interested that surface mail is inadequate. For the indefinite future, we are still willing and able to continue the original system.

(Some participants have questioned us about why we do not make MELLONMR a more "regular", formal, journal-like affair, and charge a subscription price. It would be very difficult for us at Mellon Institute to do such a thing because of the legalities involved in the non-profit nature of our Institute even if we wished to do so, and we do not, for several reasons.)

As usual, your comments are invited.

B. L. Shapiro  
and  
A. A. Bothner-By

U.S.A. and Canada	\$ ,42
Argentina	1.50
Australia	2.50
Belgium	1.50
Czechoslovakia	1.50
England	1.50
France	1.50
Germany	1.50
Italy	1.50
Japan	2.50
The Netherlands	1.50
Scotland	1.50
South Africa	2.50
Sweden	1.50
Switzerland	1.50



November 30, 1962

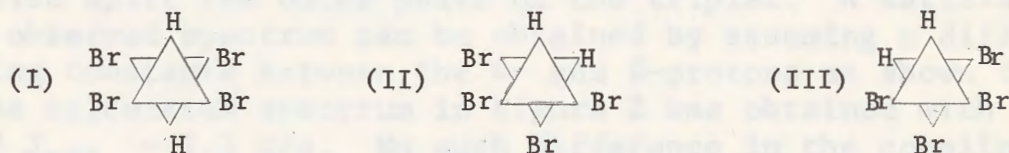
Dr. Barry Shapiro  
 Mellon Institute  
 4400 Fifth Avenue  
 Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

### Effect of Substituents on Vicinal Couplings

Karplus' calculation of the variation of vicinal proton couplings with dihedral angle between the CCH planes has enjoyed considerable success in accounting for experimental results, and has recently emerged unscathed from the controversy over the relative signs of geminal and vicinal couplings. It promises to be extremely important for studies of conformation of molecules, and some workers have already used it for this purpose, making the assumption that other factors which could influence the coupling constant are small enough to be ignored or allowed for in a scale factor in the  $\cos^2\phi$  formula. Although it is difficult to get evidence bearing on this assumption it does appear that anomalous couplings can result when the carbon atoms are very heavily substituted.

For example the vicinal coupling in 1,1,2,2-tetrabromoethane is only about 3 cps (measured from the  $C^{13}$  satellite signals<sup>1</sup>). This represents an average over the three rotational isomers:



Statistical weight:  $1-\alpha$

$\alpha/2$

$\alpha/2$

The Karplus equation would predict this to be essentially a gauche coupling ( $\alpha \rightarrow 1$ ) whereas since form I has less steric interactions between gauche bromine atoms than II or III, one would expect it to predominate ( $\alpha \rightarrow 0$ ). In general, studies of rotational isomerism of other bromine substituted ethanes usually form a consistent and logical picture--where steric and dipole effects would be expected to favor a trans configuration of protons the observed coupling is large, where they favor the gauche, the coupling is small. A very good illustration of this point is the recent work on meso and dl 2,3-dibromobutane<sup>2</sup>. Could it be that in tetrabromoethane the distortion of the CCH angle by the bromine atoms becomes an important factor in determining the coupling constant? It is perhaps significant that the  $C^{13} \cdot C \cdot H$  coupling (which we have measured by a double resonance method) is also anomalous, being only 1.1 cps.

Yours sincerely,

Ray Freeman

Ray Freeman

Instrument Division

<sup>1</sup> Sheppard and Turner, Proc. Roy. Soc. A252, 506 (1959).

<sup>2</sup> Bothner-By and Naar-Colin, J.A.C.S. 84, 743 (1962); Anet, J.A.C.S. 84, 747 (1962).



**CHEMSTRAND**  
RESEARCH CENTER, INC.

November 30, 1962

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

Dear Dr. Shapiro:

Recently, in our investigation of model compounds of polymers, we found an interesting difference in the coupling constants between the  $\alpha$ - (same carbon atom as the substituent) and  $\beta$ - (methylene) protons of some 2,4-disubstituted pentanes. Spectra of racemic and meso 2,4-dichloropentane are shown in Figure 1. In the meso compound the  $\beta$ -protons are magnetically nonequivalent giving rise to an AB quartet which is further split by coupling with the two adjacent  $\alpha$ -protons. In the racemic compound the  $\beta$ -protons are expected to be equivalent and the spectrum should be a triplet. A triplet is observed but the central peak is split by about 1.5 c/s. This split cannot be explained by assuming nonequivalence of the  $\beta$ -protons as this should also split the outer peaks of the triplet. A satisfactory fit with the observed spectrum can be obtained by assuming a difference in the coupling constants between the  $\alpha$ - and  $\beta$ -protons as shown in Figure 2. The calculated spectrum in Figure 2 was obtained with  $J_{\alpha\beta} = 5.8$  and  $J_{\alpha\beta'} = 7.1$  c/s. No such difference in the coupling constants is necessary to explain the spectrum of the meso compound.

This difference in the coupling constants could result from differences in the relative populations of the various conformers. It has been suggested by Shimanouchi and Tasumi (Spectrochimica Acta, 17, 755, 1961) that there is only one energetically favorable conformer of meso 2,4-dichloropentane but two favorable conformers of the racemic compound. It can be demonstrated from the models of the conformers proposed by Shimanouchi and Tasumi that, if the two conformations are equally populated, no difference should occur in the coupling constants between the  $\alpha$ - and  $\beta$ -protons. If, however, one of the conformations is more highly populated than the other, a difference in the coupling constants would be expected.

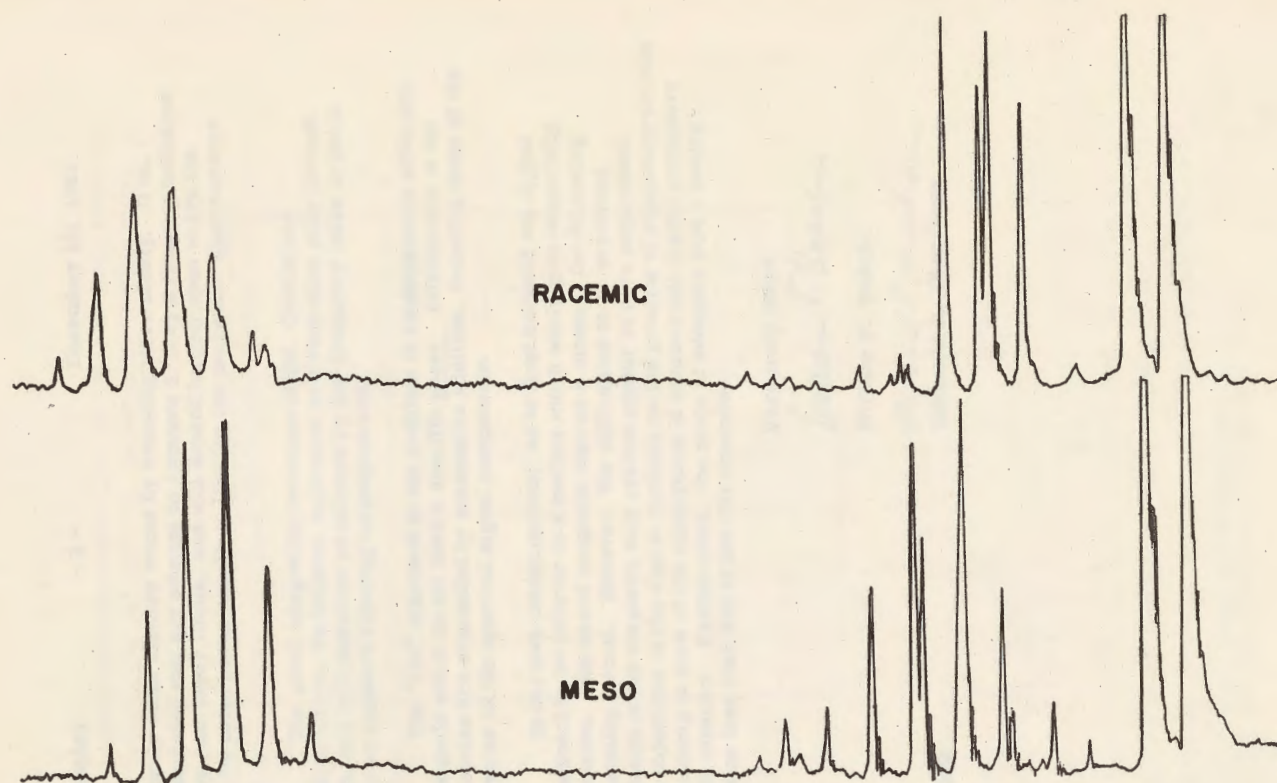
We are presently investigating this split in the central peak of the triplet in the racemic compound as a function of temperature in an attempt to determine the energy difference between the two conformers.

Sincerely,

*W. C. Tincher*  
W. C. Tincher

*P. E. McMahon*  
P. E. McMahon





NMR SPECTRA OF 2,4-DICHLOROPENTANES

FIGURE 1

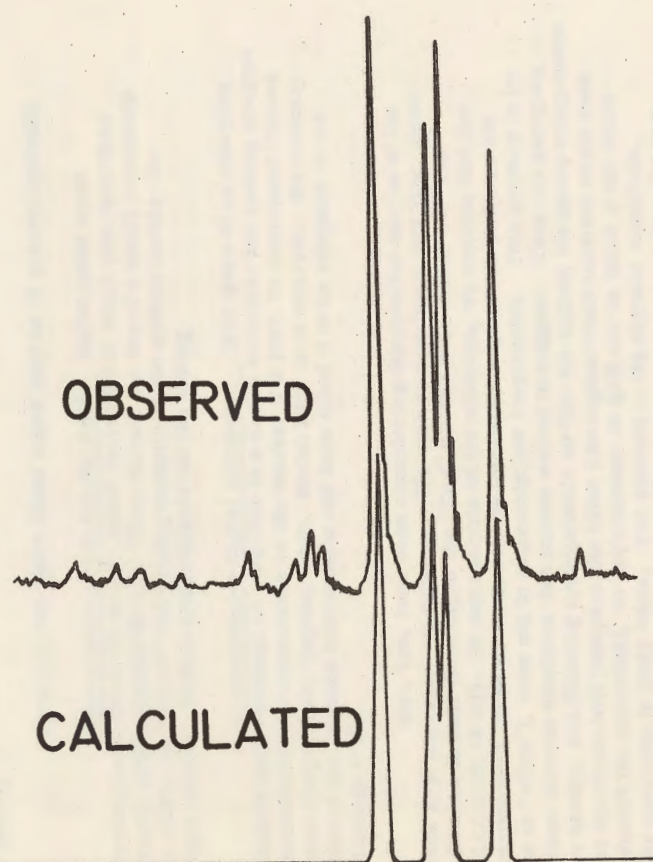


FIGURE 2 SPECTRA OF  $\beta$ -PROTONS  
OF RACEMIC 2,4-DICHLOROPENTANE





RIVER ROAD, BOUND BROOK, N. J.

December 11, 1962

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

Dear Barry,

Here are two short items which may be of general interest:

Water recirculator for the A-60: We've made some improvements in the A-60 magnet water recirculator which was described previously (MELLONMR 42-17). They include the use of a small laboratory water chiller to "top off" the cooling capacity of the system during the summer months. Details are available for the asking.

An inexpensive digital voltmeter: For those of us who have questioned the investment of ~\$1000 in a digital voltmeter for making integral measurements, the appearance on the market of a \$287.50 instrument (United Systems Corporation, Dayton, Ohio; Model 200) is of interest. We recently purchased one of these instruments and have found it to be adequate in our preliminary trials.

We, too, have been considering the relative merits of the various S/N improvement schemes. We wish to take issue with Drs. Ernst and Primas in their favoring of the "Dog" method over that of the "Cat" (MELLONMR 48-21). In our analysis of the situation, we assume that the spectrometer's noise power spectrum amplitude stays constant (i.e., its noise is "white"), even out to extremely low frequencies. This appears to be the least adverse condition that anyone wishes to suggest. Thus, by sweeping more slowly, and filtering appropriately so that the highest frequency components of the spectrum will just pass the filter (the highest time constant which does not distort the spectrum), no improvement in S/N can be made if the noise power spectrum is truly white. For relative to the signals' amplitude, the amplitude of the noise at frequencies the same as or less than the new, reduced signal frequencies will remain in constant ratio. An improvement in S/N by sweeping more slowly could only be achieved if the amplitude of the noise power spectrum were to decrease with decreasing frequency. If the noise power spectrum of the spectrometer increases with decreasing frequency,

Dr. B. L. Shapiro

- 2 -

December 11, 1962

one would merely make matters worse by sweeping more slowly. It is, therefore, concluded that any attempt to improve S/N by a filtering technique will have very real lower limits, and will depend largely upon where the minimum of the noise power spectrum lies for the particular spectrometer in use.

The novel integrating technique of Dr. Crutchfield (MELLONMR 47-27) is, we believe, equivalent to a very slow scan through the spectrum, and will therefore be affected by low frequency noise in much the same way as standard filtering techniques are.

The "Cat" approach to the problem is fundamentally different, because all signals which do not bear a specific phase relationship to the triggering impulse are attenuated by successive addition, including those of the same frequencies as the spectral signal components.

In our own investigations, we at first believed the digital computer approach to be inferior to a method which would give essentially infinite resolution: the use of magnetic tape as a memory for an analog computer summing circuit. However, the difficulties to be overcome in the automation of the magnetic tape system appear to have suppressed our original objections to the digital methods on the grounds of resolution-to-cost ratio, particularly in view of the appearance of commercial digital computers of convenient capacity. Furthermore, the price of adequate tape - analog apparatus is no less than that of the Cat computer.

Very truly yours,

William F. Beach

Raymond B. Hanselman

WFB:RBH:mjk



Herrn Dr. B.L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.  
U.S.A.

Sehr geehrter Herr Shapiro!

In den vergangenen Monaten haben wir uns vor allem mit NMR-Spektren von  $\pi$ -Komplexen beschäftigt und da offensichtlich die Azulen-Chemie großes Interesse findet, möchten wir über Messungen an Verbindungen des Azulenium-Ions berichten.

Von E.O.Fischer<sup>1)</sup> wurden vor kurzem Komplexe des Typs  $\pi$ -Azulenium- $\text{Cr}(\text{C}_5\text{H}_5)$  dargestellt. Ein Vergleich ihrer Protonenresonanz-Spektren mit denen des Azulenium-Kations [Azulen in  $\text{CF}_3\text{COOH}$ , nach loc.cit 2)] oder homologer Ionen ergab für die Komplexe und die freien Ionen im Prinzip ähnliche Spektren. In der Tabelle sind die chemical shifts der stärksten Linien in ppm gegen TMS als äußerem Standard zusammengestellt. Dabei handelt es sich um Ringprotonen oder Protonen von Methylsubstituenten an den betreffenden Stellungen des Azulengerüsts.

Während die Signale des Fünfringes stets recht ähnliche chemical shifts und bei hoher Auflösung auch ähnliche Aufspaltungen zeigen, treten bei den Siebenring-Protonen größere Unterschiede auf. Bemerkenswert ist die starke Aufspaltung der Siebenring-Protonen der Komplexe. Die entsprechende Erscheinung, daß sich nämlich die (4,5,6,7,8) Stellungen am Siebenring in den Komplexen in ihrer elektronischen Umgebung stärker voneinander unterscheiden, folgt aus den chemical shifts der Methylgruppen-Protonen. Für das 4,6,8-Trimethyl-azulenium-Kation finden sich drei Signale bei 2,66, 2,62 und 2,56 ppm, im komplex gebundenen Zustand jedoch bei 3,00, 2,88 und 2,75 ppm gegen TMS bei tieferen Feldern.

Zur Zeit sind wir damit beschäftigt, mittels FREQINT IV, das wir von Herrn Prof. Bothner-By (z.Zt. hier in München) bekamen, zu einer befriedigenden Interpretation der Spektren zu gelangen.

Für die regelmäßige Sendung der MELLONMR Letters, die uns viele Anregungen bieten, darf ich Ihnen recht herzlich danken.

Mit freundlichen Grüßen !

Heinz P. Fritz

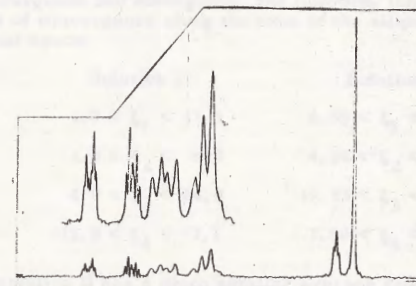
( Heinz P. Fritz )

C. F. Kreiter

( C. Kreiter )

$\delta$ -Werte von Azulenium-Verbindungen [ppm gg. TMS, äußerer Standard, bei tieferen Feldstärken bz. auf TMS, gemessen mit Varian A-60]

Substanz	Lsg.mittel	Stellungen am Azulen-Gerüst							
		1,1'	2	3	4	6	8	5	7
Azulen	CF <sub>3</sub> COOH	3,96	7.11	7.30	8.41 8.47 8.51 8.53 8.65				
4,6,8-Trimethyl-azulen	CF <sub>3</sub> COOH	3,74	7.25	7.33	2,66 2.62 2,56		8,21 8,08		
2,4,6,8-Tetra-methyl-azulen	CF <sub>3</sub> COOH	3,63	2,13	6,90	2.55 2.52		8,11 7,94		
Azulenium-Cr(C <sub>5</sub> H <sub>5</sub> )	CS <sub>2</sub>	3,93	6.55	7,11	6,24 6,05 5,64 5,60 5,48				
4,6,8-Trimethyl-azulenium-Cr(C <sub>5</sub> H <sub>5</sub> )	CS <sub>2</sub>	3,61	6.60	7.32	3,00 2,88 2.75		5,66 5,61		



Protonenresonanz-Spektrum des Azulenium- $\text{Cr}(\text{C}_5\text{H}_5)$

Die Azulene wurden freundlicherweise von Herrn Prof. K.Hafner zur Verfügung gestellt.

- 1) E.O.Fischer et al., noch unveröffentlicht  
2) S.S.Danyluck und W.G.Schneider, JACS 82, 997 [1960]



Dr. Bernard L. Shapiro

-3-

November 21, 1962

the case because the trace conditions were not satisfied. After one iteration which will force the trace relations to be satisfied, the real starting values are  $\zeta_1 = 13.6$ ,  $\zeta_2 = 4.3$ ,  $\zeta_3 = 6.1$ , and  $\zeta_4 = 0.4$ . Further, it should be noted the  $\zeta_1$  and  $\zeta_2$  have in general smaller radii. Hence, the shielding values must be known much better than the coupling constants - a surprising result.

In conclusion it may be stated that for highly mixed ABC systems many iterations, maybe in the order of a thousand, are needed for convergence. Some of the solutions will probably converge more readily than others. The inversion of pairs of energy levels has been found by Charlie Reilly to lead to a convergence to the other solutions. He, at present, is investigating this technique. H. Kummer (MELLONMR 49) has recently pointed out some other sum rules which if incorporated in the iteration scheme may aid in this problem.

Best regards to you and the readers of MELLONMR.

Sincerely yours,

*Jerry*  
J. D. Swalen

JDS:jk

M  
E  
L  
L  
O  
N-M-R

A monthly collection of informal private letters from laboratories of nmr.  
Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

BASF



Badische Anilin & Soda Fabrik AG

LUDWIGSHAFEN A. RHEIN  
Hauptlaboratorium

Dr. Barry L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pa., USA

IHRE ZEICHEN

IHRE NACHRICHT VOM

UNSERE NACHRICHT VOM

UNSERE ZEICHEN

TAG

Dr. Brü/Hr

6.12.1962

BETREFF Dear Dr. Shapiro,

This is my first contribution to MELLO-N-M-R. I apologize for the delay, but you know the troubles with my eyes.

SCHNEIDER, BERNSTEIN and POPLÉ - in their fine investigation about the NMR-spectrum of pyridine (Can.J.Chem. 35, 1487, 1957) - reported the influence of the solvent on the spectrum, especially on the chemical shift difference  $\nu_3 - \nu_4$  and  $\nu_5 - \nu_6$ .

Investigating the NMR-spectra of substituted pyridines (Z. Elektrochem. 66, 159, 1962) I was interested in this effect. As a test substance I took 4-Methylpyridine ( $\gamma$ -picoline) the simple spectrum of which allows to gain the chemical shift difference  $\nu_3 - \nu_4$  immediately without further calculation. I used the VARIAN-V-4300-HR-instrument (60 MHz) at a temperature of about 26°C. The concentration of the solutions was approximately 20 % by vol. (of course, the molar concentration would be a better figure for this purpose, but it is more time consuming to work with; I checked several points of the results with solutions of a mole ratio 1 : 10 and found at the whole the same behavior).

Trying to arrange the measured chemical shift differences by a physical parameter characteristic of the solvent I failed until I chose the electrical dipole moment (usual table values). The graph shows the results. There are three clearly distinct groups:

1. Strongly associated solvents as water, alcohols and acids with a dipole moment of about 1.8 D show various chemical shift difference without knowable regularity;
2. Aromatic and quasi-aromatic solvents show an approximately linear decay of the chemical shift difference with rising dipole moment;
3. Non-aromatic solvents give an approximately linear dependence too.

May be the electric dipole moment is not the best way to coordinate the relationship between the chemical shift difference and the solvent, but I did not find another one. Perhaps, these results encourage the theorists to some ideas upon the measured effect.

Yours sincerely

(W. Brügel)

010 500 100 000 010

Drehwort: BASF Ludwigshafen - Fernsprecher 4621 - Fernschreiber 04 64811 - Konten: Landeszentralbank Ludwigshafen a. Rh., Girokonto 41/82, Postcheck Ludwigshafen a. Rh. 6816

518





# ESSO RESEARCH AND ENGINEERING COMPANY

CENTRAL BASIC RESEARCH LABORATORY

P. O. BOX 45, LINDEN, N. J.

D. L. BAEDER  
DIRECTOR  
P. V. SMITH, JR.  
ASST. DIRECTOR

December 10, 1962

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

Dear Dr. Shapiro:

The question of the temperature dependence of vicinal coupling constants, arising from changes in torsional motion, has been raised in various forms in the past. We have recently evaluated the temperature dependence of the couplings between nuclei gauche or trans oriented using a potential of the form  $V = V_0/2(1 + \cos 3\phi)$ , and assuming an angular dependence of the coupling constants  $J = J_0 \cos 2\phi$ . Assuming a Boltzmann distribution, then

$$\frac{\langle J \rangle}{J_0} = \frac{\int_0^{120^\circ} \cos^2(120m + \phi) (e^{-\frac{V_0 \cos 3\phi}{2RT}}) d\phi}{\int_0^{120^\circ} (e^{-\frac{V_0 \cos 3\phi}{2RT}}) d\phi}$$

where  $m=1$  for trans nuclei,  $m=2$  for gauche nuclei. Numerical integration on a digital computer gave the following dynamic values of  $\langle J \rangle/J_0$ . For the static problem ( $\phi=180^\circ, 60^\circ$ ) this ratio for trans and gauche is 1.00 and 0.25, resp.

$V_0/T$ (cal deg <sup>-1</sup> K)	$\langle J \rangle/J_0$		$V_0/T$ (cal deg <sup>-1</sup> K)	$\langle J \rangle/J_0$	
	trans	gauche		trans	gauche
50.0	0.9909	0.2541	15.0	0.9659	0.2671
40.0	0.9885	0.2558	10.0	0.9429	0.2785
30.0	0.9844	0.2578	8.0	0.9243	0.2878
25.0	0.9810	0.2595	6.0	0.8950	0.3025
20.0	0.9757	0.2622	4.0	0.8500	0.3252

Dr. B. L. Shapiro

Page 2

Interestingly, variations of 5% in the individual couplings may be expected to occur in an accessible range of temperature, even though the observed coupling in systems with 3-fold symmetry,  $J(\text{observed}) = J(\text{trans}) + 2J(\text{gauche}) = 1.5J_0$ , is temperature invariant. The latter has previously been demonstrated by Gutowsky, who used a similar theoretical model and who also furnished experimental confirmation (J. Chem. Phys. 33, 843, (1960)).

Sincerely,

*Eugene I. Snyder*  
EUGENE I. SNYDER

EIS/jp



# ESSO RESEARCH AND ENGINEERING COMPANY

CENTRAL BASIC RESEARCH LABORATORY

P. O. BOX 45, LINDEN, N. J.

D. L. BAEDER  
DIRECTOR  
P. V. SMITH, JR.  
ASST. DIRECTOR

December 21, 1962

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

Dear Dr. Shapiro:

In my recent contribution to MELLONMR, dated December 10, 1962, I have made an obvious error of fact to which you should call attention. On page 2 I state, "... in systems with 3-fold symmetry,  $J(\text{observed}) = J(\text{trans}) + 2J(\text{gauche}) = 1.5J_0$ ...", whereas the correct statement should read, "... in systems with 3-fold symmetry,  $J(\text{observed}) = 1/3(J(\text{trans}) + 2J(\text{gauche})) = 0.5J_0$ ..."

I'll try to be more careful in the future!

Sincerely,

*Eugene I. Snyder*  
Eugene I. Snyder



$$J_{\text{CH}_3-\text{CH}_3} = + 1.0 \text{ cps} \quad \text{in II} \quad (15)$$

$$J_{\text{H}-\text{CH}_2} = - 2.4 \text{ cps} \quad \text{in III} \quad (17)$$

$$J_{14} = J_{\text{CH}_3-\text{CH}_2} = + 2.6 \text{ cps} \quad \text{in IV} \quad (18)$$

all have the magnitudes and signs (relative to the vicinal CH-CH coupling) predicted by theory<sup>14</sup>.

b) The couplings are expected to have a  $\cos^2 \theta$  dependence on the angle  $\theta$  between the  $\pi$  orbital on  $C_1$  and the  $C_1-C_2-H$  plane<sup>14</sup>. In this way the large five-bond couplings in V to VIII are to be rationalized.

$$J_{\text{CH}_3-\text{CH}_2} = 2.5 \text{ cps} \quad \text{in V} \quad (\text{ref 19})$$

$$J_{\text{CH}_3-\text{CH}_2} = 2 \text{ cps} \quad \text{in VI} \quad (2)$$

$$J_{\text{CH}_3-\text{CH}_2} = 2.15 \text{ cps} \quad \text{in VII} \quad (20)$$

$$J_{25} = J_{\text{CH}_3-\text{CH}_2} = 3 \text{ cps} \quad \text{in VIII} \quad (21)$$

It also appears to us, that the long range coupling reported by Randall<sup>4</sup> belongs to the methyl group category and thus does not require any of the diene-like structures of Shacca and Freeman<sup>3</sup>. (The diene-like structure in their example 7 unfortunately connects the hydrogens with the smaller long range coupling. It is interesting to note, that a similar structure was drawn by Gutowsky and Porte to explain the fact the  $J_{75}$  is larger than  $J_{56}$  in trieno[3.2-b]pyrrole).

We apologize for filling up such a lot of space with reference to published material, but since there has been some discussion on matters where this information has - apparently - been missing we

thought it might be helpful to put it under the eyes of those interested.

Yours sincerely,

*Ragnar A. Hoffman*  
Ragnar A. Hoffman

*Salo Gronowitz*  
Salo Gronowitz

#### References:

1. Dischler, *MELLOMER* 43.20
2. Gagnaire and Csakvary, *ibid* 45.9
3. Shacca and Freeman, *ibid* 47.11
4. Randall, *ibid* 49.22
5. Gronowitz, Hörnfeldt, Gestblom and Hoffman, *Arkiv Kemi* **18**, 133 (1962)
6. - , *ibid* **18**, 151 (1962)
7. Abraham and Bernstein, *Can.J.Chem.* **39**, 905 (1961)
8. Pople, Bernstein, Schneider, *ibid* **35**, 1960 (1957)
9. Sanwell and Sheppard, contribution # 14 at the discussion of the Faraday Society, Oxford 1962
10. Gronowitz and Hoffman, *Acta Chem. Scand.* **13**, 1687 (1959)
11. - , *Arkiv Kemi* **16**, 563 (1960),  
(Cf. also *MELLOMER* 28.2)
12. - , *ibid* **16**, 471 (1960)
13. Hoffman, *ibid* **17**, 1 (1960)
14. Karplus, *J. Chem. Phys.* **33**, 1842 (1960)
15. Pople and Schneider, *Vol. Phys.* **3**, 547 (1960)
16. Freeman, *Vol. Phys.* **4**, 305 (1961)
17. Barasimham and Rogers, *J. Chem. Phys.* **32**, 727 (1960)
18. Private communication from B. Brailon
19. Gronowitz and Hoffman, *Arkiv Kemi* **15**, 499 (1960)
20. Weidler, Bergson and Lathiasson, to appear in *Acta Chem. Scand.*
21. Shoolery, contribution # 13 at the Discussion of the Faraday Society, Oxford 1962



CZECHOSLOVAK ACADEMY OF SCIENCE  
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

Na cvičení 2,  
PRAHA 6

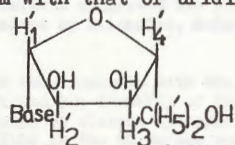
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.  
U.S.A.

December 12, 1962

Dear Dr. Shapiro:

I appreciate very much you have added my name on your mailing list for the MELLONMR Newsletter and I find your information journal a very enjoyable reading.

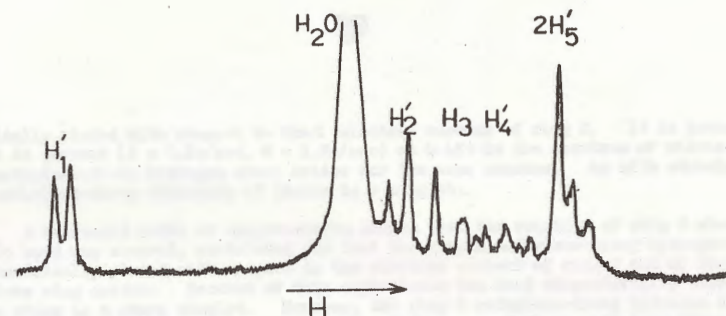
In connection with our previous studies of various physico-chemical properties of the biologically active compound - 6-azauracil riboside<sup>1</sup> (6-azauridine) I have also measured its NMR spectrum in order to determine its conformation and to compare its spectrum with that of uridine.



Considerable attention has recently been devoted to conformational studies of various nucleosides<sup>2,3</sup> in aqueous solution by NMR using the Karplus<sup>4</sup> relation.

I found the following coupling constants  $J_{H_1H_2}$  for some of our compounds: 6-azauridine  $3.1 \pm 0.2$  cps, uridine  $3.8 \pm 0.4$  cps; 4-thio-6-azauridine  $3.2 \pm 0.4$  cps. From these values it might be assumed that the conformational differences between the above compounds are small. A feature characteristic of the ribose part in the NMR spectra of uridine and cytidine, as previously observed by Jardetzky<sup>2</sup>, is the presence of two prominent groups of peaks - one due to  $H_2'$ ,  $H_3'$ ,  $H_4'$  and the second to  $2H_5'$ . The spectrum of 6-azauridine is, however, quite different in this region (see Fig. 1): The peaks due to  $H_2'$ ,  $H_3'$ ,  $H_4'$  are well separated and spread over a larger frequency range.

- 2 -



The introduction of nitrogen into the base (uridine - 6-azauridine) is seen to produce a marked change in the spectrum of ribose in spite of the near values of their  $J_{H_1H_2}$  coupling constants. The ribose part of the NMR spectrum<sup>1,2</sup> of 6-azauridine resembles more the corresponding spectra of purine ribosides<sup>2</sup>.

We hope to carry out a detailed analysis of the NMR spectrum of 6-azauridine and related compounds in order to throw light on this experimental finding.

The sample of 6-azauridine was a high purity product obtained by fermentation process<sup>1</sup>. The measurements were performed on a Czechoslovak high resolution NMR spectrometer operating at 40 Mc/s. Sample volume 1 ml; 20 wt. % solutions in  $D_2O$ .

References: (1) J. Škoda, V. F. Hess, and F. Šorm: *Experientia* 13, 150 (1957); (2) C. D. Jardetzky: *J. Am. Chem. Soc.* 82, 229 (1960); (3) R. U. Lemieux: *Can. J. Chem.* 39, 116 (1961); (4) M. Karplus: *J. Chem. Phys.* 30, 11 (1959).

Yours sincerely,

*J. Janáček*  
J. Janáček





# BP RESEARCH CENTRE

PETROLEUM DIVISION

SUNBURY-ON-THAMES

ENGLAND

## DEHYDRONIOVIN AND NIOVIN STRUCTURES

Recently we were asked to confirm the structure of niovin, a substance obtained by Dr. F.E. King and J.J. Hobbs from a hardwood extract, and its dehydrogenation product dehydroniovin. The spectra of these two compounds, Figures 1 and 2 were obtained at 80 Mc/sec, the frequency at which we are now operating our modified Varian spectrometer (Mellonmr No. 41).

The physical constants of dehydroniovin suggested its possible identity with tetrahydro-otobain which was recently examined by Gilchrist, Hodges and Porte (J, 1962, 1980).

A comparison of the  $H^1$  spectra of dehydroniovin with the spectrum of tetrahydro-otobain published by Gilchrist et al, confirmed the identity of these two compounds, whilst a quantitative spectrum confirmed the presence of sixteen hydrogen atoms. Our 80 Mc/sec spectrum, however, showed features not visible in the 60 Mc/sec spectrum, which further defined the structure of dehydroniovin as I. In the aromatic region there were two AB quartets and two singlets. The two high field members of the quartet centred at 3.36  $\tau$  showed fine splitting (2c/sec) characteristic of meta coupling. Thus the structure of one aromatic ring in the molecule must be II. Given the chemical evidence that the remaining two aromatic rings were fixed as in naphthalene and the two methyl groups were in the 2, 3 positions, the presence of the second AB quartet in the spectrum eliminated the possibility that one methylene-dioxy group was attached to the 6, 7 positions. The two methylene-dioxy groups were characterised by bands at 4.00  $\tau$  and 4.28  $\tau$ .

The formula for niovin was thought from chemical evidence ie C and H analyses and absence of reducible double bonds, to be  $C_{20}H_{20}O_4$ , a phenyltetrahydro naphthalene derivative, but the integral of its NMR spectrum was equivalent to only eighteen hydrogen atoms. This result showed that another double bond was present. The presence of cyclopropane hydrogen atoms was eliminated by the absence of absorption in the 9.4  $\tau$  region. One methyl group was attached to a saturated CH group while the other was attached to an unsaturated carbon atom. There were only five aromatic hydrogen atoms in the molecule thus the only position for the double bond is between positions 3 and 4 (III). Complex multiplets of the correct intensity between 6.9 and 7.9  $\tau$  confirm the presence of the benzylic type hydrogen atoms on positions 1 and 2.

However, in contrast to dehydroniovin it was the high field methylene-dioxy resonance and not the low field one which was a closely spaced quartet of bands.

Porte (loc. cit.) observed that the high field (ring A) methylene-dioxy resonance of otobain, IV, was an AB quartet. He explained that this arose because the two hydrogen atoms of the methylene-dioxy group which was attached to positions 5 and 6 were not

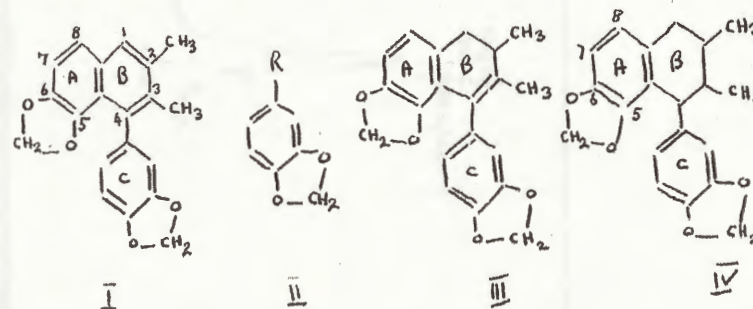


symmetrically placed with respect to the  $\pi$  electron current of ring C. It is probable that the AB quartet ( $J = 1.5c/sec$ ,  $\delta = 5.2c/sec$ ) at 4.45  $\tau$  in the spectrum of niovin due to the methylene-dioxy hydrogen atoms arises for the same reasons. As with otobain the ring C methylene-dioxy resonance of niovin is a singlet.

A Courtauld model of dehydroniovin showed that the rotation of ring C about the  $C_4$  and  $C_9$  bond was severely restricted and that the ring A methylene-dioxy hydrogen atoms were symmetrically placed with respect to the electron current of ring C and of the naphthalene ring system. Because of this equivalence the band characterising these two hydrogen atoms is a sharp singlet. However, the ring C methylene-dioxy hydrogen atoms are not symmetrically disposed to the shielding influences of the naphthalene rings, thus a small ( $\delta = 1.9c/sec$ ) chemical shift between their resonances is observed.

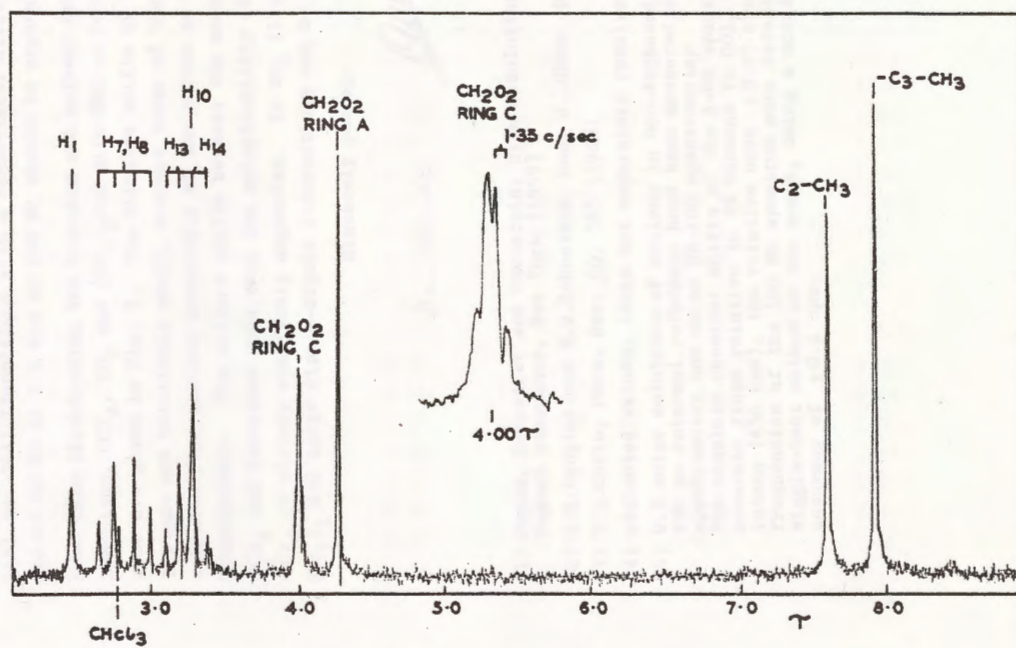
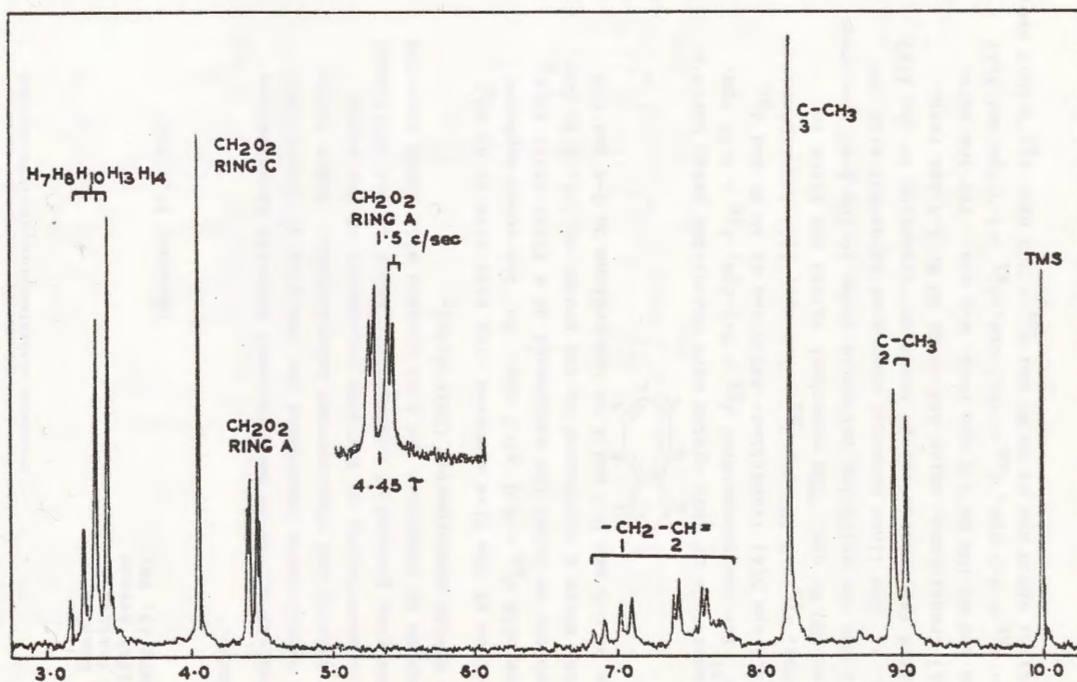
From the molecular model of niovin it can be seen that the slightly greater degree of rotational freedom of ring C might average out the much weaker shielding influence of the dihydronaphthalene ring system at the ring C methylene-dioxy hydrogen atoms and consequently they are characterised by a single sharp resonance.

We should like to thank Dr. F.E. King for permission to use this material which will be incorporated in a future paper on the structure of niovin and dehydroniovin.

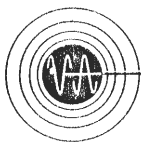


S.A. Knight

R.L. Brakins

FIG. 1 DEHYDRONIOVIN 80 Mc/sec, CD Cl<sub>3</sub>FIG. 2 NIOVIN 80 Mc/sec, CD Cl<sub>3</sub>





**VARIAN AG • SWITZERLAND**

HEAD OFFICE GUBELSTRASSE 7 • ZUG • TELEPHONE 042/44555 • TELEX 53452

THE RESEARCH LABORATORY • ZÜRICH 8  
Please reply to KLAUSSTRASSE 43 • TELEPHONE 051/472420

Dr. B. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburg 13, Pa.  
USA

December 15, 1962

Dear Barry,

The chemical shifts of non-alternant aromatic hydrocarbons are of considerable importance for checking of theoretical charge density and ring-current calculations. Since there is still uncertainty in the line assignment of the seven membered ring protons of azulene<sup>1)2)</sup> we hoped to get additional information by comparing the A-60 spectra with those measured on the HR-100 spectrometer (Palo Alto).

The protons of the five membered ring give rise to an AB<sub>2</sub> spectrum with J<sub>AB</sub> = 4.0 ± 0.2 cps. For the seven membered ring protons we tried the assignment of a first order AB<sub>2</sub>X<sub>2</sub> spectrum, where A correspond to the proton on C-6, B to the protons on C-5 and C-7 and X to the protons on C-4 and C-8.



The transitions of this system were calculated using Corio's tables<sup>3)</sup> for the parameters: J<sub>BX</sub> = 9.5 cps, J<sub>AB</sub> = 9.35 cps, J<sub>AX</sub> = 1.5 cps 3(A) transition: 449.0 cps at 60 Mc and J<sub>BX</sub> = 9.5 cps, J<sub>AB</sub> = 9.30 cps, J<sub>AX</sub> = 1.5 cps, 3(A) transition: 748.8 at 100 Mc cps. The numerical values are given in table 1 and the splitting pattern is shown in the A-60 spectrum in fig. 1. The lines observed show good agreement with the calculated frequencies except those corresponding to the 4(A) and 2(A) transitions, which differ at 60 Mc 1.4 cps resp. 1.7 cps and at 100 Mc 1.2 cps resp. 0.5 cps. For the parameters: J<sub>BX</sub> = 9.5 cps, J<sub>AB</sub> = 10.3 cps, J<sub>AX</sub> = 1.5 cps and 3(A) transition: 448.0 cps at 60 Mc and J<sub>BX</sub> = 9.5 cps, J<sub>AB</sub> = 10.3 cps,

- 2 -

J<sub>AX</sub> = 1.5 cps, 3(A) transition : 749.8 cps at 100 Mc better agreement for the 4(A) and 2(A) transition is obtained. Though there is a further splitting by J<sub>AX</sub> into small triplets the 2(A) and 3(A) transitions with a theoretical difference of 3.9 cps at 60 Mc or 2.5 cps at 100 Mc should be separately resolved.

Some data illustrating the dilution and solvent dependence in isooctane, CCl<sub>4</sub>, SO<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>S=O with TMS as internal reference are given in fig. 3. The dilution shifts of the five ring protons are relatively small, whereas those of the seven membered ring protons especially of the proton on C-6 are considerable. The solvent shifts between the measurements in CCl<sub>4</sub> and isooctane show that the polarisability of azulene in CCl<sub>4</sub> is already remarkably augmented. In SO<sub>2</sub> (liquid) and (CH<sub>3</sub>)<sub>2</sub>S=O large dipole-dipole interactions can be observed.

Sincerely yours,

*Don. Schneider* *Qua*

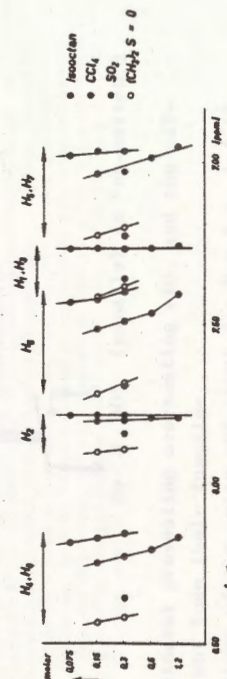
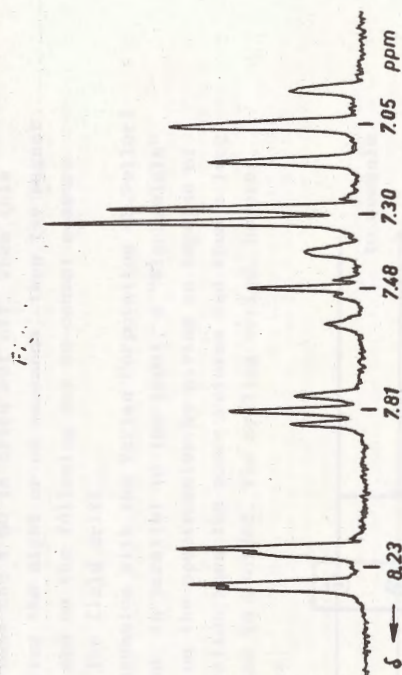
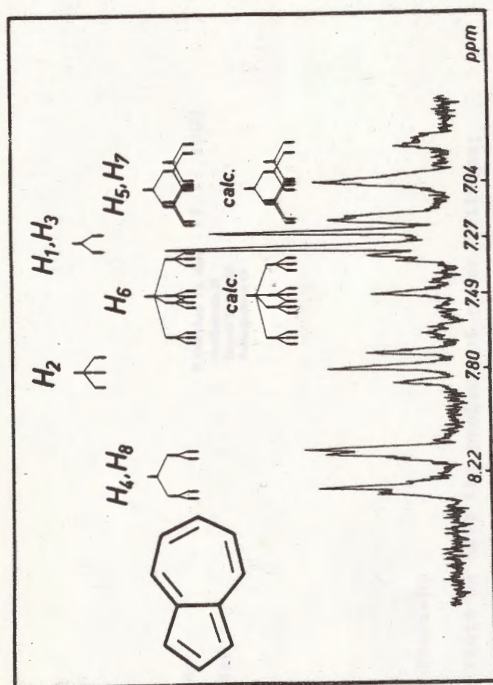
- 1) Pople, Schneider and Bernstein, High Resolution Nuclear Magnet Resonance, New York (1959)
- 2) S.S.Danyluk and W.G.Schneider, Can. J. Chem. 40, 1777 (1962)
- 3) P.L.Corio, Chem. Rev. 60, 363 (1960)
- 4) estimated values, lines not separately resolved.
- 5) 0.5 molar solutions of azulene in non-degassed CCl<sub>4</sub> with TMS as internal reference have been measured on a A-60 spectrometer and on an HR-100 spectrometer. The absolute chemical shifts of the A-60 spectrum should be accurate ±1cps relative to 2% benzene in CCl<sub>4</sub> with TMS intern (436 cps), the relative ones ±0.25 cps. The line frequencies of the 100 Mc spectrum were determined by the wobble-beat method on the scope, using a counter with an accuracy of ±0.1 cps.

TABLE 1

A  $B_2X_2$  spectrum of seven membered ring protons in azulene<sup>5)</sup>

transition <sup>1)</sup>	60 Mc			100 Mc		
	experimental frequencies	calculated <sup>3)</sup> frequencies	intensities	experimental frequencies	calculated <sup>3)</sup> frequencies	intensities
		$J/\Delta=0.35$ ; $J_{AB}=9.35$ cps			$J/\Delta=0.22$ ; $J_{AB}=9.3$ cps	
1 (A)	10.5	10.7	0.49	10.1	10.2	0.63
2 (A)	1.5 <sup>4)</sup>	3.2	0.71	1.5 <sup>4)</sup>	2.0	0.87
3 (A)	0 $\rightarrow$ (449.4 cps)	0	1.00	0 $\rightarrow$ (748.8 cps)	0	1.00
4 (A)	- 9.0	- 7.6	1.80	- 9.6	8.4	1.50
5 (B)	-22.25 <sup>4)</sup>	-22.6	2.80	-37.6 <sup>4)</sup>	-37.8	2.50
6 (B)	-23.25 <sup>4)</sup>	-23.4	2.51	-38.6 <sup>4)</sup>	-38.6	2.36
7 (B)	-31.25	-31.0	1.49	-46.9	-46.7	1.63
8 (B)	-33.25	-33.3	1.20	-48.4	-48.0	1.50

$J/\Delta=0.40$ ; $J_{AB}=10.3$ cps			$J/\Delta=0.25$ ; $J_{AB}=10.3$ cps			
1 (A)	11.5	11.9	0.44	11.1	11.4	0.60
2 (A)	2.5 <sup>4)</sup>	3.9	0.65	2.5 <sup>4)</sup>	2.5	0.84
3 (A)	0 $\rightarrow$ (448.0 cps)	0	1.00	0 $\rightarrow$ (749.8 cps)	-	1.00
4 (A)	- 8.0	- 8.0	1.91	- 8.6	- 8.9	1.57
5 (B)	-21.3 <sup>4)</sup>	-21.3	2.90	-36.6 <sup>4)</sup>	-36.4	2.57
6 (B)	-22.2 <sup>4)</sup>	-22.2	2.56	-37.6 <sup>4)</sup>	-37.2	2.40
7 (B)	-30.2	-30.2	1.44	-45.9	-46.1	1.60
8 (B)	-33.2	-33.2	1.09	-47.4	-47.8	1.43





Max-Planck-Institut für Biochemie

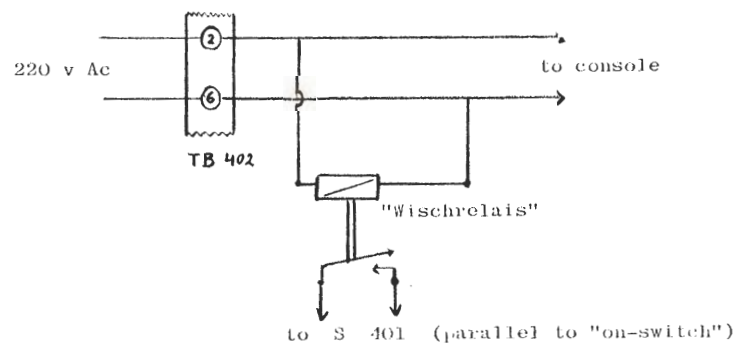
Dr. J. Sonnenbichler

8 München 15, den 17.12.1962  
Goethestraße 31  
Fernruf 59 42 61/63  
Postschloß 64

Dear Dr. Bothner-By :

In our institute we have the problem of power failures; this means that the A 60 is often cut off. When this happens during the night or on weekends, then the magnet cools down and on the following day we cannot measure because of the field drift.

After a discussion with the Varian Corporation (F.Peller) we connected, in parallel to the input, a "Wischrelais" that turns on the spectrometer by giving an impulse of 0.5 sec duration when the power returns and thus a long cooling phase is avoided. The cycling period, however, again occurs.



Safety equipment preventing overheating etc. and the off-button do not lose their function.

The dimensions of the relay are about 7 x 6 x 2 cm and it can be easily fixed on the back cover of the power control unit.

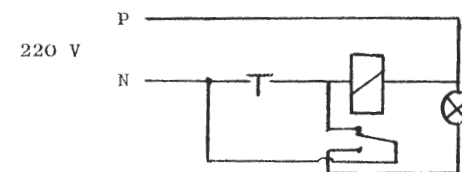
Max-Planck-Institut für Biochemie

2. Blatt zum Schreiben vom 17.12.62 an Dr. Bothner-By

Firm: E. Tesch, Wuppertal-Vohwinkel  
Industrieschaltgerät nach VDE 0660-52  
Typ ECWe 0.5, 220 V, 50 Hz

Kosten: 38.50 DM

A control relay, connected to the institute power supply with a signal lamp, shows if power had been interrupted.



By means of an electric clock we record the total time of power loss.

With best regards I remain

Sincerely yours,

*J. Sonnenbichler*



THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175  
CINCINNATI 39, OHIO

December 20, 1962

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

Dear Barry:

Here are some A-60 modifications which may be of interest to readers of MELLONMR. The first is the addition of an attenuator in the R. F. field control. The attenuator is placed in series with the cable which comes from the trombone attenuator on the instrument. The circuit is housed in a small minibox attached to the front panel with the switch available to the operator. The 500  $\Omega$  potentiometer is adjusted so that the radio frequency signal is attenuated by 10 when the switch is flipped.

The second modification achieves a very slow sweep for the A-60 -- increasing the maximum scan time from 500 seconds to 5000 seconds. We purchased a 2 RPM Bodine synchronous motor electrically and mechanically equivalent to the 25 RPM motor used in the magnetic field sweep (Model KYC-22RC). Because we wanted to achieve an exact 10 fold decrease in speed, a gear was machined with 50 teeth (the gear in the spectrometer has 40). This motor and gear were mounted in a metal bracket so that it can easily be attached and detached by removing four screws. Electrical connections are made by using a 3 pronged Cinch Jones connector. Motors can be changed in about two minutes. This modification is useful only for those who have the new type of recorder bed and gear box combination.

The third modification is the addition of a slave recorder. Our system differs from those proposed in the past in that 1) the slave recorder follows the recorder zero -- this is particularly important when expanding the scale or for repeat integrations; 2) the pen lift of the recorder is slaved to the A-60 pen; 3) we have had a chart printed for the slave recorder.

You will notice that the connections for the y axis are taken from the center tap of the spectrometer y axis recording potentiometer. Therefore the slave recorder moves with the recorder zero. For this sort of connection it is important that the recorder used be transistorized (we use a Moseley model 135) because the filament hum in a vacuum tube model (such as a Moseley 1 or 2) will introduce noise into the spectrometer recorder. We have chosen to employ a mechanically linked potentiometer with its own mercury battery power supply for the x axis signal so that grounding problems will be at a minimum. I am not certain that this refinement is necessary.

THE PROCTER & GAMBLE COMPANY

Dr. B. L. Shapiro

Page 2

December 20, 1962

The chart design takes its inspiration from Mary Crutchfield's MELLONMR 43 contribution for the dimensions and general layout. It was printed on an offset press by the Mailway Advertising Co. in Cincinnati. Cost is about 2¢ a sheet after the initial artwork expenses. We have incorporated some features which we think are an improvement on the Varian chart. First the grid calibration is in ppm. so that the chemical shift may be measured by inspection. Cps. may be obtained by using a centimeter rule-- at a normal sweep width of 500 cps. on the A-60, one cm. = 20 cps. on the slave chart. Secondly, the grid is printed on the back side of the sheet so that it may be eliminated more easily by photography and so that it will not interfere with the transfer of recorder ink to the paper (we have found, in preparation of spectra for publication, that many times the ink did not take at the grid lines).

Hope these suggestions will help.

Yours very truly,

THE PROCTER & GAMBLE COMPANY  
Research & Development Department

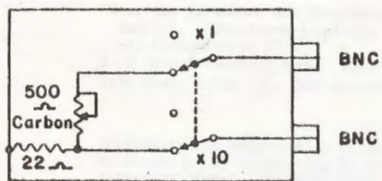
*Tom*

T. J. Flautt  
Research Division

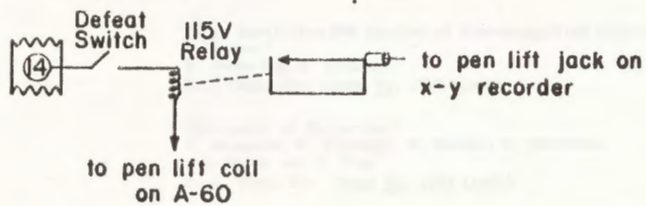
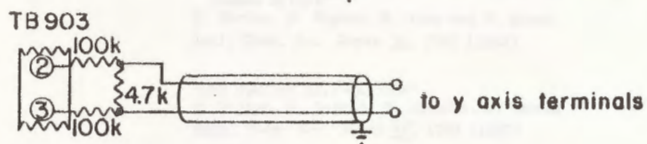
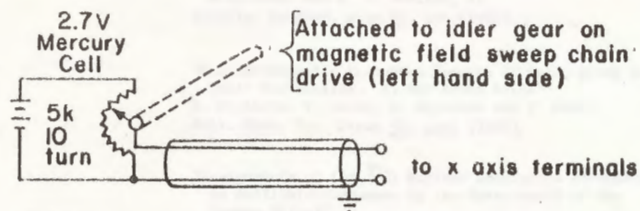
CW



## 10x ATTENUATOR for R.F. FIELD CONTROL



## SLAVE RECORDER CONNECTIONS



PROCTER & GAMBLE NMR SPECTRUM		SAMPLE		REMARKS	
NO.				Filter Bandwidth _____ cps.	
OPERATOR -----				R.F. Field _____ mg	
DATE -----		SOLVENT -----		Sweep Time _____ sec.	
				1 cm. = _____ cps.	
				Spectrum Amp. _____	
				Integral Amp. _____	
10	9				
9	8				
8	7				
7	6				
6	5				
5	4				
4	3				
3	2				
2	1				
1	0				
0	-1				
-1	-2				
-2	-3				
-3	-4				
-4	-5				
-5	-6				
-6	-7				
-7	-8				
-8	-9				
-9	-10				



"The Electronic Spectra of Thioamides and Thiohydrazides.  
Part I. LCAO-MO Treatment and Band Classification  
for Thiobenzamides"  
J. Sandström  
Acta Chem. Scand. 16, 1616 (1962)

"Über das Vorkommen von Cucurbitacin E und I in Iberis  
amara L. (Cruciferae) und die Identität von "Tbamarin"  
mit Cucurbitacin I"  
J. B. Son Bredenberg and R. Gmelin  
Acta Chem. Scand. 16, 1802 (1962)

"Grindelic and Oxygrindelic Acids"  
T. Bruun, L. M. Jackman and E. Stenhagen  
Acta Chem. Scand. 16, 1675 (1962)

"Konformationsbestimmung der Pantothensäure und des  
Pantoylamids durch Protonenresonanzspektroskopie"  
H. Fritz and W. Löwe  
Angew. Chem. 74, 751 (1962)

" $\beta$ -Carboxy- $\beta$ -hydroxyisocaproic acid formation by micro-  
organisms"  
W. R. Martin, W. H. Coleman, N. E. Wideburg, R. Cantrell,  
M. Jackson, and F. W. Denison, Jr.  
Biochim. Biophys. Acta 62, 165 (1962)

"Nuclear Magnetic Resonance Spectra of Amino Acids and  
Their Derivatives. I. DNP Amino Acids"  
S. Fujiwara, Y. Arata, N. Hayakawa and H. Momoi  
Bull. Chem. Soc. Japan 35, 1658 (1962)

"Assignments of the  $^{35}\text{Cl}$  Nuclear Quadrupole Resonance Spectra  
in Multichlorobenzenes by the Measurement of the  
Zeeman Effect"  
Y. Morino, M. Toyama, K. Itoh and S. Kyono  
Bull. Chem. Soc. Japan 35, 1667 (1962)

"NMR Spectra of  $\alpha$ -Glycols"  
S. Fujise, G. Hazato, T. Ikenoue, S. Sasaki  
Bull. Chem. Soc. Japan 35, 1742 (1962)

"High Resolution NMR Spectra of Stereoregulated Polyvinyl  
Alcohol"  
A. Danmo and N. Hayakawa  
Bull. Chem. Soc. Japan 35, 1748 (1962)

"Structure of Isojervine"  
T. Masamune, M. Takasugi, H. Suzuki, S. Kawahara,  
M. Gohda and T. Irie  
Bull. Chem. Soc. Japan 35, 1749 (1962)

"Alkaloid Studies. The Constitution of Lochneridine"  
Y. Nakagawa, J. M. Wilson, H. Budzikiewicz and C. Djerassi  
Chem. & Ind. 1986 (1962)

"Détermination théorique de la constante d'écran  
magnétique associée aux protons de la molécule  
d'acétylène"  
F. Cabaret, J.-R. Didry et J. Guy  
Compt. Rend. 255, 1090 (1962)

"Kernresonanz im gasförmigen Xenon"  
D. Brinkmann, E. Brun und H. H. Staub  
Helv. Phys. Acta 35, 431 (1962)

"On the Signs of CH and HH Coupling Constants"  
P. C. Lauterbur and R. J. Kurland  
J. Am. Chem. Soc. 84, 3405 (1962)

"Fluorine N.M.R. Spectroscopy. XII Proof of Opposite Signs  
for the 'Direct' Carbon-13 Coupling Constants to Hydrogen  
and to Fluorine"  
G. V. D. Tiers  
J. Am. Chem. Soc. 84, 3972 (1962)

"Proton Magnetic Resonance Spectra of Tetravinylsilicon,  
Methyl- and Ethylvinylketone"  
S. Castellano and J. S. Waugh  
J. Chem. Phys. 37, 1951 (1962)

"Use of Weak Perturbing Radio-Frequency Fields in Nuclear  
Magnetic Double Resonance"  
R. Freeman and W. A. Anderson  
J. Chem. Phys. 37, 2053 (1962)

"NMR Splittings Due to Molecular Asymmetry"  
H. S. Gutowsky  
J. Chem. Phys. 37, 2196 (1962)

"Valence-Bond Studies of the Dependence upon Substituents  
of C $^{13}$ -H and Si $^{29}$ -H Coupling"  
C. Juan and H. S. Gutowsky  
J. Chem. Phys. 37, 2198 (1962)

"Proton Magnetic Resonance Studies of Polycrystalline  
Uranium Oxide Hydrates. III.  $\text{UO}_2\cdot 2\text{H}_2\text{O}$ "  
A. L. Porte, H. S. Gutowsky and J. E. Boggs  
J. Chem. Phys. 37, 2318 (1962)

"Nuclear Magnetic Double Resonance Spectra of Three Spin  
Systems"  
B. D. Nageswara Rao and J. D. Baldeschwieler  
J. Chem. Phys. 37, 2473 (1962)

"Relative Signs of Geminal and Vicinal Coupling Constants in  
1,1,4,4-Tetramethylcyclohexyl-cis-2,6-Diacetate"  
B. D. Nageswara Rao and J. D. Baldeschwieler and J. I. Musher  
J. Chem. Phys. 37, 2480 (1962)

"Heterocyclic Polyfluoro-compounds. Part II. Some Reactions  
of Undecafluoropiperidine: The Preparation of Perfluoro-  
2,5,8,5-tetrahydro-pyridine and Perfluoro-(1-methyl-  
pyrrolidine)"  
R. E. Banks, W. M. Cheng and R. N. Haszeldine  
J. Chem. Soc. 3407 (1962)

"Acetals and Oligoacetals. Part I. Preparation and  
Properties of Reactive Oligoformals"  
R. F. Webb, A. J. Duke and L. S. A. Smith  
J. Chem. Soc. 4307 (1962)

"The Structure of Linderone and Methyl-linderone"  
A. K. Kiang, H. H. Lee, and K. Y. Sim  
J. Chem. Soc. 4338 (1962)

"The Reaction of Dimethyl Acetylenedicarboxylate with  
Quinaldin:"  
A. Crabtree, L. M. Jackman, and A. W. Johnson  
J. Chem. Soc. 4417 (1962)

" $\eta$ -Cyclohexadienyl Compounds of Manganese, Rhenium, Iron  
and Ruthenium"  
D. Jones, L. Pratt, and G. Wilkinson  
J. Chem. Soc. 4458 (1962)

"Reactions of Organic Peroxides. Part I. The Reaction of  
Ascaridole with Ferrous Sulphate"  
D. Brown, B. T. Davis, T. G. Halsall, and A. R. Hands  
(With an Appendix by J. V. Hatton and R. E. Richards)  
J. Chem. Soc. 4492 (1962)

"The Structure of the Self-condensation Products of  
Glutaconic Esters"  
J. Harley-Mason and J. C. W. Tims  
J. Chem. Soc. 4719 (1962)

"Phosphine Imide Dimers"  
S. Trippett  
J. Chem. Soc. 4731 (1962)

"Nuclear Magnetic Resonance Spectra of Some Trimethyl-  
platinum Compounds"  
J. A. S. Smith  
J. Chem. Soc. 4736 (1962)

"The Autoxidation of Isobutyrophenone"  
J. E. Baldwin, D. H. R. Berton, D. J. Faulkner  
and J. F. Templeton  
J. Chem. Soc. 4743 (1962)

"Etude Expérimentale de L'anisotropie Magnétique de la  
Liaison Localisée. I. Exposé général de la méthode.  
Application à l'étude magnétique de l'iode"  
J. de Villepin  
J. Chim. Phys. 59, 901 (1962)

"The Relative Signs of the NMR Coupling Constants in  
Styrene Oxide by Double Resonance"  
D. D. Elleman and S. L. Manatt  
J. Mol. Spec. 2, 477 (1962)

"Nuclear Magnetic Resonance in Hydrates of Sodium Tetra-  
borates"  
S. S. Dharmatti, S. A. Iyer and R. Vijayaraghavan  
J. Phys. Soc. Japan 17, 1736 (1962)

"The Magnetic Anisotropy Constant in the Case of  
Strong Anisotropy"  
J. Kanamori and H. Minatono  
J. Phys. Soc. Japan 17, 1759 (1962)



"Proton Magnetic Resonance Spectra of Paraxylylene-Methylmethacrylate Copolymer in Chloroform Solution"  
A. Nishioka, Y. Kato and H. Mitsuoka  
J. Poly. Sci. 62, S9 (1962)

"Proton Magnetic Resonance Spectra of Styrene-Methylmethacrylate Copolymer in CCl<sub>4</sub> Solution"  
A. Nishioka, Y. Kato, and N. Ashikari  
J. Poly. Sci. 62, S10 (1962)

"Polymer NMR Spectroscopy. VI. Methyl Methacrylate-Styrene and Methyl Methacrylate- $\alpha$ -Methylstyrene Copolymers"  
F. A. Bovey  
J. Poly. Sci. 62, 197 (1962)

"A Method for Unravelling Complex Spectra"  
L. C. Allen  
Nature 196, 663 (1962)

"Eini Methode Zur Messung Der Kernmagnetischen Relaxationszeiten in Zwei-Phasen-Systemen"  
H. Pfeifer  
Phys. Letters 2, 351 (1962)

"Nuclear Magnetic Resonance in UAl<sub>2</sub>"  
A. C. Gossard, V. Jaccarino, and J. H. Wernick  
Phys. Rev. 128, 1038 (1962)

"A Fokker-Planck Equation for Spin Relaxation"  
A. Yoshimori and J. Korringa  
Phys. Rev. 128, 1054 (1962)

"Theory of Relaxation of a Two-Spin System"  
J. Korringa and A. Yoshimori  
Phys. Rev. 128, 1060 (1962)

"Nuclear Quadrupole Moment of Yb"  
J. S. Ross, and K. Murakawa  
Phys. Rev. 128, 1159 (1962)

"Zur Kernresonanzabsorption schwefeldotierter AgBr-Polykristalle"  
J. Kluge  
Phys. Status Solidi 2, K133 (1962)

"The Direct Measurement of the <sup>17</sup>O-Proton Spin-Spin Coupling in Water"  
J. Reuben, A. Tzalmona, and D. Samuel  
Proc. Chem. Soc. 353 (1962)

1,5-Transannular Shift of Hydrogen in Cycloheptatriene and Related Compounds"  
A. P. ter Borg, H. Kloosterziel and N. Van Meurs  
Proc. Chem. Soc. 359 (1962)

"Evidence for Carbon-1 Protonation of 1-Nitro-4,6,8-trimethylazulene"  
J. Schulze and F. A. Long  
Proc. Chem. Soc. 364 (1962)

"Applications of Modulation Techniques to High Resolution Nuclear Magnetic Resonance Spectrometers"  
W. A. Anderson  
Rev. Sci. Instrum. 33, 1160 (1962)

"The Relationship Between Acidity and the Chemical Shift of Proton Magnetic Resonance of Aqueous Solutions of Strong Acids"  
N. G. Zarakhani and M. I. Vinnik  
Russian J. Phys. Chem. 36, 483 (1962)

"Cyclopropane Ring Formation in the Deamination of 18-Aminosteroids"  
J. Hora, V. Cerny and F. Sorm  
Tetrahedron Letters 501 (1962)

13 17  
"C and O N.M.R. Spectra of Metal Carbonyl Compounds"  
R. Bramley, B. N. Figgis and R. S. Nyholm  
Trans. Faraday Soc. 58, 1893 (1962)

"Some Aminophosphines"  
G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane  
J. Chem. Soc. 3984 (1962)

"Terpenoids. Part LI. The Isolation of Some New Cyclopropane-containing Triterpenes from Spanish Moss (Tillandsia usneoides, L.)"  
C. Djerassi, and R. McCrindle  
J. Chem. Soc. 4034 (1962)

"Studies in Mycological Chemistry. Part XI. The Structure of Isosterigmatocystin and an Amended Structure for Sterigmatocystin"  
E. Bullock, J. C. Roberts, and J. G. Underwood  
J. Chem. Soc. 4179 (1962)

"Role de l'Hybridation du Second ordre et de l'electro-negativite des carbones dans la transmission des couplages spin-spin en resonance magnetique du Proton"  
G. Mavel  
J. Chim. Phys. 59, 683 (1962)

"Phenomenes de desassociation, complexation, ionisation, d'alcools et de phenols, etudies par resonance magnetique nucleaire"  
M. Martin  
J. Chim. Phys. 59, 736 (1962)

"Etude par resonance magnetique nucleaire de composés organophosphores: III. Groupements CH<sub>3</sub>OP et CH<sub>3</sub>SP"  
G. Mavel and G. Martin  
J. Chim. Phys. 59, 762 (1962)

"Proton Resonance Spectra and Tacticity of Polystyrene and Deuteriopolystyrenes"  
S. Brownstein, S. Bywater, and D. J. Worsfold  
J. Phys. Chem. 66, 2067 (1962)

"New Evidence on the Boron Co-Ordination of Alkali Borate Glasses"  
J. Krogh-Moe  
Phys. Chem. Glasses 3, 1 (1962)

"Boron Nuclear Magnetic Resonance in Rare Earth Intermetallic Compounds"  
A. C. Gossard and V. Jaccarino  
Proc. Phys. Soc. 80, 877 (1962)

"Oxygen-17 nuclear magnetic resonance of inorganic compounds"  
B. N. Figgis, R. G. Kidd and R. S. Nyholm  
Proc. Royal Soc. 269, 469 (1962)