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Mailed: 1 June 1962

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DEADLINE FOR NEXT ISSUE

JUNE 25, 1962

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THE BRITISH COAL UTILISATION RESEARCH ASSOCIATION

YOUR REF.

OUR REF. WRL/SA

REGISTERED OFFICE
RANDALLS ROAD
LEATHERHEAD, SURREY
TELEPHONE LEATHERHEAD 4411
GRAMS CURASSOC, LEATHERHEAD

10th April, 1962.

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

Dear Dr. Bothner-By,

Those of your readers who have been concerned at some time or other with attempting to elucidate the structure of complex insoluble materials containing OH groups might be interested in the following broad-line measurements on phenols.

A few years ago Dr. Richards¹ made the first NMR measurements on coals and found that the line-shape of the proton resonance at low temperatures varied with the carbon content of the coal. This variation in the line-shape reflects the changes that have taken place in the hydrogen distribution of coals during the progression from the brown coals relatively low in carbon to the high carbon anthracites. This NMR information, coupled with the knowledge of the line-shapes of pure compounds, is proving to be a valuable contribution to the knowledge of coal structure.

It is known that a small percentage of the hydrogen in coal occurs in phenolic structures and we have been studying the line-shapes of some pure phenols in order to obtain an estimate of the contribution to the line-shape from the phenols present in coal; the exact nature of this phenolic material is unknown.

These measurements have been carried out in a spectrometer which has a permanent magnet of 3.75 kilogauss and a $1\frac{1}{2}$ " gap. This gap is sufficient to surround the sample coil with a Dewar vessel. Liquid air was used as the refrigerant as this could be made readily available in the laboratory. The spectra were recorded where possible at several levels of radio frequency power to check for possible saturation effects.

We have made measurements on phenol, α -Naphthol, resorcinol, catechol and pyrogallol and the calculated second moments of the curves are shown below.

cont.../...

- 2 -

Dr. A.A. Bothner-By

10th April, 1962.

Phenol



$$S_2 = 9.3 \pm 0.3 \text{ g}^2$$

α -Naphthol



$$S_2 = 9.5 \pm 0.3 \text{ g}^2$$

Resorcinol



$$S_2 = 10.2 \pm 0.4 \text{ g}^2$$

Catechol



$$S_2 = 10.5 \pm 0.4 \text{ g}^2$$

Pyrogallol



$$S_2 = 11.2 \pm 0.4 \text{ g}^2$$

The second moment increases with the number of OH groups attached to the aromatic ring. In the case of phenol and α -Naphthol the values are slightly lower than the S_2 value of 9.7 g^2 for benzene. While on the other hand the second moments of resorcinol, catechol and pyrogallol are higher than that of benzene by $+0.5$, $+0.8$ and $+1.5 \text{ g}^2$ respectively. Only in the case of the trihydric phenol is there any pronounced difference from the second moment value for benzene itself.

The probability that there is any significant amount of trihydric phenols present in coals is extremely small. At most the hydrogen present as OH is only about 6% of the total and the probability that the OH groups are on adjoining sites must be very low. The results for these phenols lend support to the previous assumption^{1,2} that the contribution to the line-shape from the OH protons is similar to that from aromatic protons.

Yours sincerely,

W.R. Ledner

W.R. Ledner

A.E. Stacey

1. Richards, R.E. and Yorke, R.W. J. Chem. Soc., 1960, No. 503, 2489.
2. Ledner, W.R. and Stacey, A.E., Fuel, Lond., 1961, 40, 295.

1-47

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

April 30, 1962.

Dr. Aksel Bothner-By
Department of Chemistry
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel,

The report by Kreevoy, Charman and Vinard, J. Am. Chem. Soc., 83, 1978 (1961) regarding the very small coupling (<0.5 cps) between acetylenic and vinyl protons of vinylacetylene inspired us to look into the matter in some detail since this report violated our expectations based on similar systems (MELLONMR #34, p. 12).

We will soon publish data which prove that these couplings are in fact >>0.5 cps. The point of this letter is to show that even in some simple systems (this one is ABCX, with 9 pertinent parameters), an apparently highly successful application of the method of successive iterations without a definite plan (i.e., one based on robertsonian guess-work) can lead to shifts and coupling constants quite a bit off from the planned iterations made by J.D. Swalen's elegant NMRIT and NMREN programs. Unfortunately, we haven't been able to make LACCOON work satisfactorily so far and have not been able to compare its answers with those obtained from the Swalen programs.

Our example follows showing the agreement between calculated and observed line positions for beautifully resolved A-60 spectra (arbitrary zero) in the vinyl region for some twenty lines numbered as they come in the Wiberg program.

The fit given by the Swalen-derived parameters is phenomenally good, the average deviation being 0.030 cps, the Roberts iterations, after a correction of +0.09 cps for a constant error in the chemical shifts ν_1 , ν_2 , and ν_3 gives an average deviation of 0.050 cps which is certainly not far from experimental error!

I think that the difference in J_{14} (cis) and (trans) is definitely real and theoretically highly interesting.

With all good wishes,

Very truly yours,

Sach

John D. Roberts

JDR:nvl

	Observed	Roberts (2x10 ² iterations)	Swalen (50 iterations)
ν_1	-	34.00	34.07
ν_2	-	32.40	32.50
ν_3	-	13.20	13.29
ν_4	-	(-80.00)	(-200)
J_{12}	-	18.12	18.01
J_{13}	-	11.58	11.58
J_{14}	-	-2.40	-2.17
J_{23}	-	1.95	1.98
J_{24}	-	0.80	0.70
J_{34}	-	0.90	0.92
Line No.			
13	39.35	39.32	39.34
14	38.45	38.42	38.51
15	37.05	37.00	37.11
16	37.05	36.93	37.04
17	31.25	31.13	31.18
18	30.75	30.69	30.73
19	-	30.56	30.65
20	29.95	29.84	29.95
21	29.30	29.42	29.35
22	29.30	29.18	29.23
23	20.40	20.25	20.42
24	20.05	19.86	20.06
25	19.00	18.88	19.00
26	18.30	18.15	18.23
27	13.65	13.55	13.68
28	13.30	13.16	13.33
29	11.85	11.84	11.91
30	11.85	11.78	11.86
31	11.15	11.01	11.13
32	10.10	9.95	10.08
33	4.05	3.91	4.04
34	3.70	3.64	3.70

44-2

44-3

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

Spectrum analyzers all:

Since LAOCOON is working well on the local IBM 704, we thought we would give it a whirl on the problem described by Dr. Roberts in the foregoing letter. Unfortunately we did not have intensity data, so could not give it a meaningfully severe test - If we strayed too far from the correct values, we would have no way of checking on the identity of the lines.

We rounded off the parameters given by Dr. Roberts to the nearest half-cycle and hoped for no crossovers. The appended printouts show the convergence after one and two cycles of calculation. There seemed no point in carrying the calculations further. The average deviation is 0.023 cps. Recent calculations on allyl chloride with LAOCOON have given average deviations of 0.020 and 0.034 cps for neat and dilute solution samples. Forty lines were fitted.

Sincerely,

Aksel Bothner-By

SELF-CORRECTING
NUCLEAR MAGNETIC RESONANCE PROGRAM
FIRST REVISION
PART TWO

44-4

RUN NUMBER	RUN DATE	5- 3-62	VINYLACETYLENE ACCORDING TO ROBERTS				
NUCLEI	NOC	FRI	FR2	WIDTH	AMIN	COMB	
			50.000	-0-	0.0050	0.	

$\alpha(1) = -34.0000$
 $\alpha(2) = 32.5000$
 $\alpha(3) = -13.2900$
 $\alpha(4) = -100.0000$

$\alpha(1,2) = 18.0000$
 $\alpha(1,3) = 11.5000$
 $\alpha(1,4) = -2.5000$
 $\alpha(2,3) = -2.0000$
 $\alpha(2,4) = 1.0000$
 $\alpha(3,4) = -1.0000$

ADJUSTED VALUES FOR (W) MATRIX AND (A) MATRIX ARE AS FOLLOWS

$w(1) = -34.0502$
 $w(2) = 32.5129$
 $w(3) = -13.2920$
 $w(4) = -100.0000$

$\alpha(1,2) = 18.0299$
 $\alpha(1,3) = 11.5617$
 $\alpha(1,4) = -2.2739$
 $\alpha(2,3) = -2.0046$
 $\alpha(2,4) = 0.7324$
 $\alpha(3,4) = 0.3638$

MATRIX SQ ... 0.14903300E-05 EIGEN SQ ... 0.14903298E-05
MATRIX SQ ... 0.25198576E-05 EIGEN SQ ... 0.25198574E-05 REDUCED SET CONTAINS 23 LINES.
MATRIX SQ ... 0.10565883E-05 EIGEN SQ ... 0.10565881E-05

OBSERVED FREQ	FREQ	INTEN	ORIGIN
3.70	3.70	0.448	4
4.05	4.06	0.318	3
10.10	10.08	0.613	1
11.15	11.17	0.582	2
11.85	11.84	0.783	3
11.85	11.90	0.691	2
11.90	11.29	0.212	1
13.65	13.67	0.079	4
18.30	18.22	1.697	2
19.00	19.02	1.756	1
20.05	20.04	0.425	1
20.40	20.41	0.402	2
29.30	29.24	3.821	2
29.30	29.37	0.468	3
29.35	29.93	2.765	2
30.75	30.54	2.472	3
31.25	30.74	2.678	3
37.05	31.19	2.471	4
37.05	37.05	1.235	1
38.45	37.12	1.262	2
39.35	38.48	0.924	2
4.	39.33	1.009	3
4.	47.27	0.007	2

SELF-CORRECTING
NUCLEAR MAGNETIC RESONANCE PROGRAM
FIRST REVISION
PART TWO

RUN NUMBER	RUN DATE	5- 3-62	SECOND ITERATION				
NUCLEI	NOC	FRI	FR2	WIDTH	AMIN	COMB	
			50.000	-0-	0.0050	0.	

$\alpha(1) = -34.0500$
 $\alpha(2) = 32.5100$
 $\alpha(3) = -13.2900$
 $\alpha(4) = -100.0000$

$\alpha(1,2) = 18.0300$
 $\alpha(1,3) = 11.5600$
 $\alpha(1,4) = -2.2700$
 $\alpha(2,3) = -2.0000$
 $\alpha(2,4) = 0.7300$
 $\alpha(3,4) = -0.9600$

ADJUSTED VALUES FOR (W) MATRIX AND (A) MATRIX ARE AS FOLLOWS
 $\alpha(1) = -34.1243$
 $\alpha(2) = 32.4562$
 $\alpha(3) = -13.2750$
 $\alpha(4) = -100.0000$

$\alpha(1,2) = 17.9575$
 $\alpha(1,3) = 11.5542$
 $\alpha(1,4) = -2.2134$
 $\alpha(2,3) = -2.0500$
 $\alpha(2,4) = 0.7041$
 $\alpha(3,4) = -0.9238$

MATRIX SQ ... 0.14905158E-05 EIGEN SQ ... 0.14905157E-05
MATRIX SQ ... 0.25197138E-05 EIGEN SQ ... 0.25197136E-05 REDUCED SET CONTAINS 21 LINES.
MATRIX SQ ... 0.10564674E-05 EIGEN SQ ... 0.10564674E-05

OBSERVED FREQ	FREQ	INTEN	ORIGIN
3.70	3.71	0.449	4
4.05	4.05	0.325	3
10.10	10.10	0.614	1
11.15	11.15	0.586	2
11.85	11.85	0.782	3
11.85	11.94	0.694	2
13.65	13.65	0.075	4
18.30	18.24	1.699	2
19.00	19.00	1.756	1
20.05	20.05	0.423	1
20.40	20.40	0.400	2
29.30	29.23	2.508	2
29.30	29.31	0.461	3
29.35	29.74	2.766	2
36.75	36.63	2.477	3
31.25	30.73	2.660	3
37.05	31.19	2.473	4
37.05	37.05	1.234	1
38.45	37.12	1.259	2
39.35	38.48	1.331	2
4.	39.32	1.012	3
4.	47.23	0.008	2

DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY

LEEDS 2
England.

21 May, 196...

Dr. A. J. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh, 15, Pa.,
U.S.A.

Dear Dr. Bothner-By,

In a recent paper on the NMR spectra of the methyltin halides, Holmes and Kaez (J.A.C.S., 1961, 83, 3903) have shown that the spin-spin coupling constant $J(\text{Sn..Cl}_3)$ from the ^{117}Sn nucleus to the H nuclei of the methyl groups in $(\text{CH}_3)_3\text{SnCl}$ changes from 56.0 c/s in 38% CD_3Cl to 65.2 c/s in 90% H_2O solutions, both at 31°C . The authors attribute these changes to rehybridization of the Sn atom which occurs when the $(\text{CH}_3)_3\text{SnCl}$ molecule ionizes in water, by analogy with the dependence of the $^{13}\text{C} - \text{H}$ coupling constant on the s-character of the C orbitals. It is interesting to note that this behaviour does not occur with the trimethylplatinum group; table 1 lists a number of spin-spin coupling constants $J(^{195}\text{Pt..H})$ for five compounds containing this group, recorded on a high-resolution spectrometer working at 40.55 Mc/s and a temperature of 35.5°C .

Table 1. Spin-spin coupling constants for the $(\text{CH}_3)_3\text{Pt}$ group.

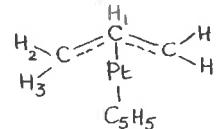
Compound	$J(^{195}\text{Pt..H})$ (c/s)	Solvent
Trimethylplatinum iodide	77.9 (± 1)	C_6H_6
Trimethylplatinum iodide	77.7	CHCl_3
Trimethylplatinum nitrate	77.3	H_2O
Trimethylplatinum acetylacetone	78.9	C_6H_6

Trimethylplatinum dipropionylmethane	71.6	C_6H_6
Trimethylplatinum dibutyrylmethane	74.9	C_6H_6

The changes accompanying the ionization of trimethylplatinum nitrate in water do not significantly affect the value of the spin-spin coupling constant relative to trimethylplatinum iodide; it seems to be more sensitive to rather remote changes in groups attached to β -diketone ligands.

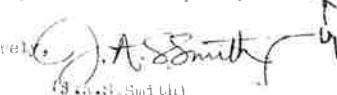
In Table 2, we compare J values from ^{195}Pt to H in other types of ligand.

Table 2. Spin-spin coupling constants in Pt alkyl compounds.

Compound	$J(^{195}\text{Pt..H})$ (c/s)	References
$(\text{CH}_3)_3\text{PtI}_3$	77.8	-
$(\text{C}_6\text{H}_5)_3\text{PtCl}_2$ (in D_2O)	34	Powell and Sheppard, J.C.S., 1960, 2519.
$(\text{CH}_3)_3\text{PtCl}_2\text{Py}_2$	83	Adams, Chatt, and Guy, Proc. Chem. Soc., 1960, 179.
	54 (H_3) 29 (H_2) 10.5 (C_5H_5)	Shaw and Sheppard, Chem. and Ind., 1961, 517.

In trimethylplatinum iodide and $(\text{CH}_3)_3\text{PtCl}_2\text{Py}_2$, where similar bonding between C and Pt appears to occur, the J values are of comparable magnitude; they drop sharply when C_6H_5 or C_5H_5 groups are attached and have intermediate values in the allyl group. It would be interesting to know the theoretical reason for these changes; the values of J in the alkyl derivatives of Pt may provide a useful guide to their structure.

With much appreciation of the usefulness of Mellon NMR reports,

Yours sincerely,

(G.J.A. Smith)



Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich
Prof. H. Primas

ZÜRICH, May 7, 1962
Universitätsstrasse 22
Tel. (061) 327330

Dr. A.A. Bothmer-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania
U.S.A.

Dear Dr. Bothmer-By,

Many of your MELLONMR enthusiasts were asking for a detailed circuit diagram for the linear audio oscillator we used for our frequency stabilizer with internal standard (cf. MELLONMR No. 33) but I disappointed them with my laziness. Because this type of oscillator proved to be very useful for double-resonance experiments, too, it may be worthwhile to give a short description of this oscillator.

Principle of the linear RC-oscillator: cf. fig. 1. Neglecting the correction networks C_4/R_{13} , C_5/R_{14} , R_{15}/P_3 and P_2 and assuming that the operational amplifiers V_1, V_2, V_3, V_4 have a very high gain, then the transfer function $T(\omega)$ of the null network of the bridge-type oscillator is given by

$$e_2 = T(\omega) e_1 \quad \text{with} \quad T(\omega) = H_2 / i\omega C_1 R_1 R_2 + i\omega C_2 R_2 R_4 / H_1$$

If H_1 and H_2 are precision Helipots with the total resistance H and the shaft angle ($0 \leq \alpha \leq 1$) and if we introduce the abbreviations

$$\omega_1 = H/C_1 R_1 R_2 \quad \text{and} \quad \omega_2 = C_2 R_2 R_4 / H$$

then the transferfunction T is given by

$$T(\omega) = \alpha \omega_1 / i\omega + i\omega / \alpha \omega_2.$$

If the main amplifier V_5 shows no phase shift errors, then the oscillating frequency is given by the zero of $T(\omega)$, i.e. by

$$\omega_0 = \sqrt{\omega_1 \omega_2}$$

Therefore the oscillating frequency is exactly proportional to the rotation angle α of the Helipots H_1 and H_2 . The networks C_4/R_{13} , C_5/R_{14} and R_{15}/P_3 are for the phase corrections of the Helipots (P_3 = adjusting

of the linearity at high frequencies). The exact calibration of the oscillator is made by P_2 . The amplitude is stabilized with the aid of the thermistor T and is adjusted with P_1 to one half of the maximal possible amplitude. The Zenerdiodes Z_1 and Z_2 are for improving the transient behaviour of the oscillator but are inoperative in the normal operation of the oscillator.

Construction details: All resistors and potentiometers are wire wound or metalfilm resistors. The critical condensators C_1 and C_2 are polystyrene condensators, all others either polyester or mica. There is no compensation for temperature influences but the Helipots and the condensators C_1, C_2 are well separated from hot electronic parts. The lo-tourns Helipots (Type A) have a linearity of $0,02\%$, mounted on the same axis with a precision calibration drum (calibrated from 0 to 10 ppm in 0,001 ppm units). Via a magnetic clutch the lo-tourns Helipots can be driven by synchromotors, by choice 60, 10 or 1 revolutions per hour.

Performance:

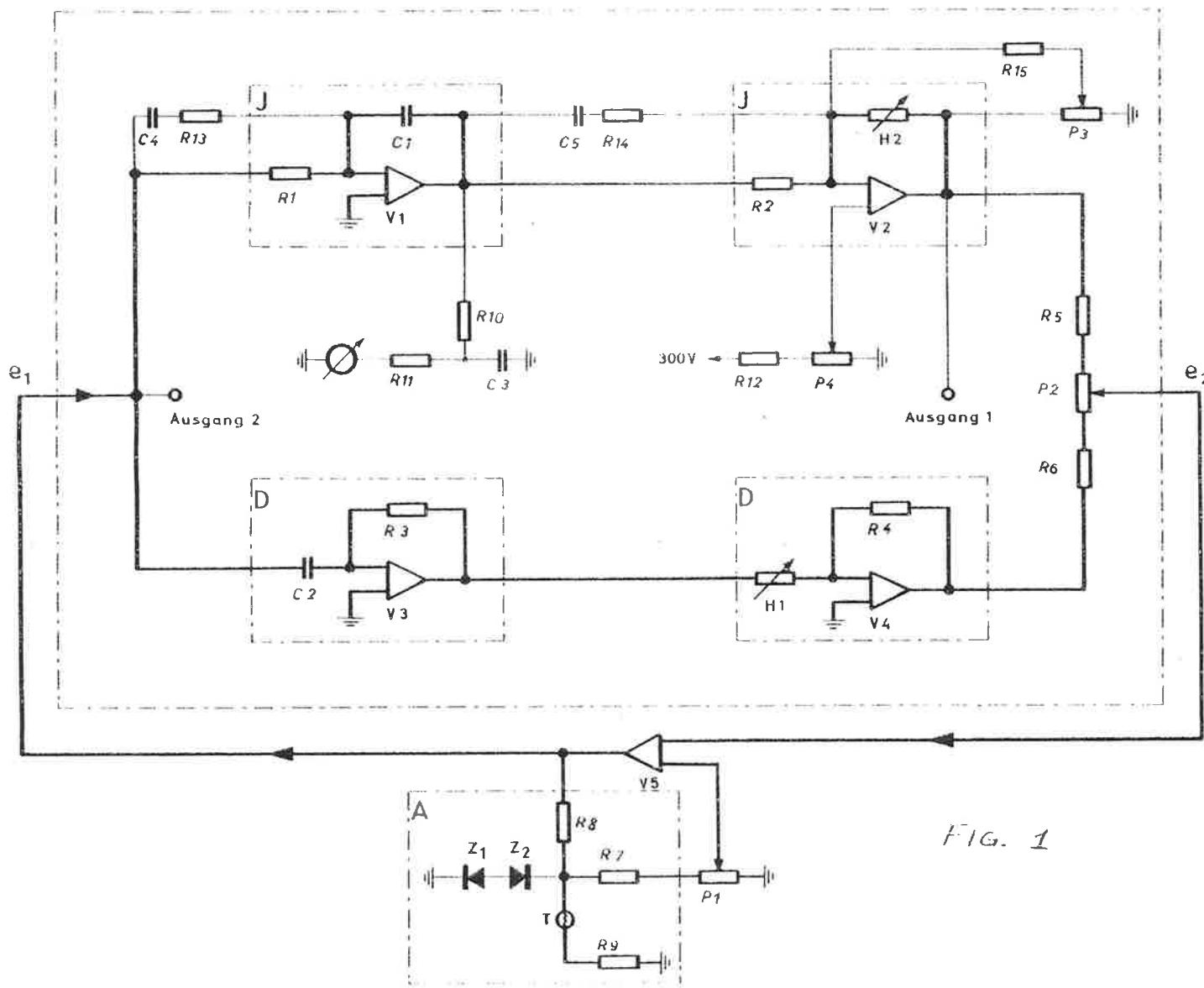
range	5 ... 250 cps
linearity	better than $0,1$ cps in the whole range (no adjustments necessary for months)
stability	better than $0,1$ cps over months without any adjustments (in a thermostated nmr laboratory)

Warning: We do not recommend to extend the range of this oscillator to higher frequencies. This oscillator was designed as part of a 25 Mcps proton spectrometer but is now also used as modulating oscillator for a 5 Mcps oscillator from which variable frequencies up to 100 Mcps can be derived.

Yours sincerely

Hans Dieder

4-474



$R_1 = 100 \text{ k}\Omega$
 $R_2 = 100 \text{ k}\Omega$
 $R_3 = 6,3 \text{ k}\Omega$
 $R_4 = 3,9 \text{ k}\Omega$
 $R_5 = 4,7 \text{ k}\Omega$
 $R_6 = 4,7 \text{ k}\Omega$
 $R_7 = 10 \text{ k}\Omega$
 $R_8 = 1 \text{ k}\Omega$
 $R_9 = 460 \text{ }\Omega$
 $R_{10} = 100 \text{ k}\Omega$
 $R_{11} = 100 \text{ k}\Omega$
 $R_{12} = 1 \text{ M}\Omega$
 $R_{13} = 4,7 \text{ k}\Omega$
 $R_{14} = 4,7 \text{ k}\Omega$
 $R_{15} = 15 \text{ M}\Omega$

$C_1 = 0,2 \mu\text{F}$
 $C_2 = 0,1 \mu\text{F}$
 $C_3 = 1 \mu\text{F}$
 $C_4 = 550 \mu\text{F}$
 $C_5 = 350 \mu\text{F}$

$P_1 = 100 \Omega$
 $P_2 = 100 \Omega$
 $P_3 = 50 \text{ k}\Omega$

$H_1 = 100 \text{ k}\Omega$
 $H_2 = 100 \text{ k}\Omega$

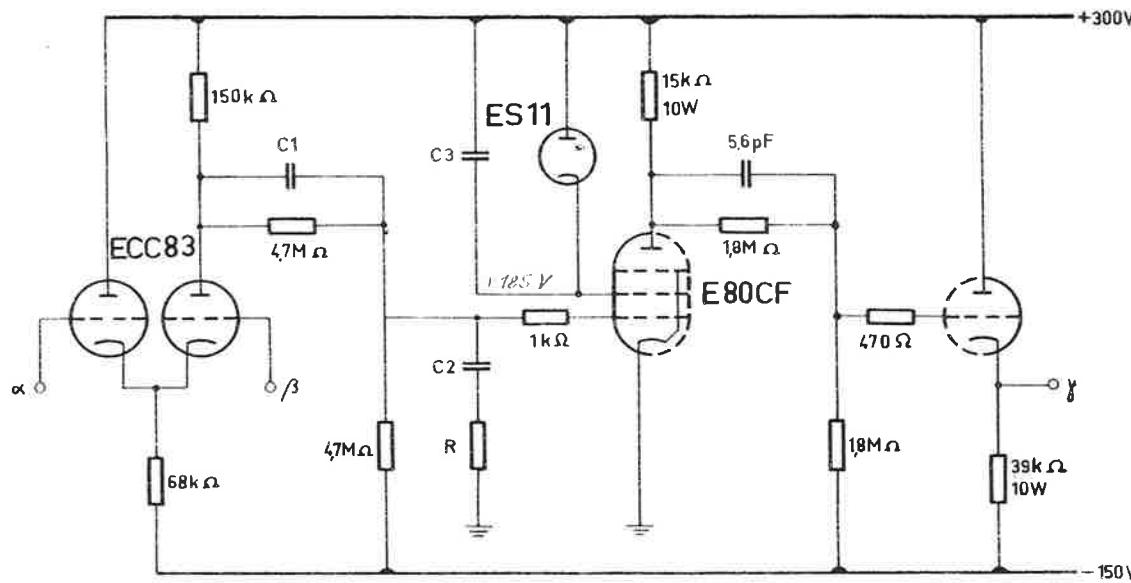
$T = \text{Varistor-Thermistor}$
 $4,7 \text{ k}\Omega/250 \Omega$
 $0,1 \text{ mW}/6 \Omega$

$Z_1, Z_2 = \text{Zenerdioden}$
 $\text{Telefunken 0A 126/4}$
 $E_Z = 5 \text{ Volt}$

FIG. 1

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OPERATIONAL AMPLIFIER FÜR INTEGRATOREN J₁, J₂ UND
DIFFERENZIATOREN D₁, D₂



	C ₁	C ₂	C ₃	R
J ₁	39 nF	39 nF	—	0 Ω
J ₂	39 nF	12 nF	—	0 Ω
D ₁	10 nF	10 nF	47 nF	180 Ω
D ₂	10 nF	33 nF	47 nF	120 Ω



FIG. 2

8-44

HAUPTVERSTÄRKER HV

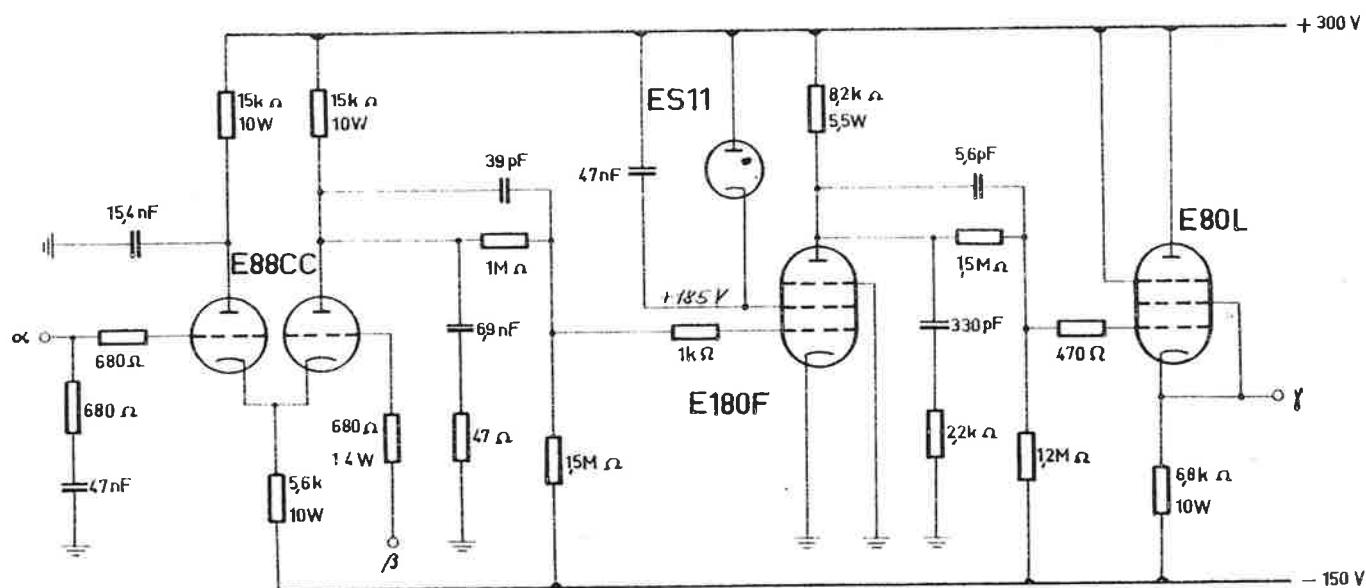


FIG. 3

b7ff

UNIVERSITÉ DE STRASBOURG
Faculté des Sciences

INSTITUT DE CHIMIE

Téléphone 35.43.00
Boîte postale 296

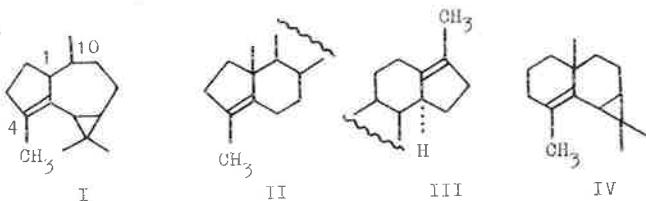
Strasbourg, le May 11 1962
2, rue Goethe

D^r A. Bothner-By
Mellon Institute
PITTSBURGH

Dear D^r Bothner-By :

1) We have a mystery, complete to us, to report.

The sesquiterpene, α -gurjunene, has now been firmly shown to be (I). The configuration of C-1 and C-10 are still undecided. Figure 1, overleaf, shows a 60Mc spectrum of α -gurjunene. The insert details the signal of the C-4 allylic methyl group.



β -Methyl A-nor-steroids (II), β -androstenes (III; spectra shown by D^r Wylde), and maaliene (IV; spectrum sent by Professor G. Büchi), show at most slightly dirty methyl signals, but no visible splitting. We can of course think many long-range splittings in I, but they would have to be so critically structure-sensitive that we can no longer think of suitable, and accessible, models to try.

Despite your kind suggestion about foreign languages in MellonMR - 42, 25, this was written in English because we would really like to have suggestions from your readers or yourself.

2) En 1952, Gutowsky, McCall, Garvey et Meyer ont montré que le signal de ^{19}F dans des fluorobenzènes para- et méta-substitués, 1, varie linéairement en fonction des constantes de Hammett σ des substituants. En 1961, Diehl a également relié à σ l'effet des substituants sur le déplacement des protons dans les benzènes substitués 2.



Nous avons examiné une série d'une vingtaine d'anisoles para- et méta-substitués 3; le signal du méthyl du groupe méthoxy est déplacé, par rapport à celui de l'anisole (X=H), d'une quantité $\Delta\delta$ variant entre +6 et -8cps pour les substituants étudiés. La figure 2 représente les variations de $\Delta\delta$ en fonction de σ . Une relation linéaire est observée, à peine plus mauvaise que bien d'autres.

Nous étendons ces mesures à divers autres dérivés aromatiques méthoxylés, et discuterons l'application à ce système de relations plus élaborées, comme celles que Taft a utilisées.

Du point de vue expérimental, les mesures de $\Delta\delta$ ont été faites en utilisant l'anisole comme référence interne, en concentration équimoléculaire avec le produit étudié, en diluant progressivement la solution (dans CCl_4), et en extrapolant à concentration nulle. Entre ces valeurs limites et les $\Delta\delta$ observés avec des concentrations normales, de 10% environ, les écarts sont notables ($\pm 0-4$ cps).

G. Ourisson

J. Streith

J.P. Marthe

1-44

44/1

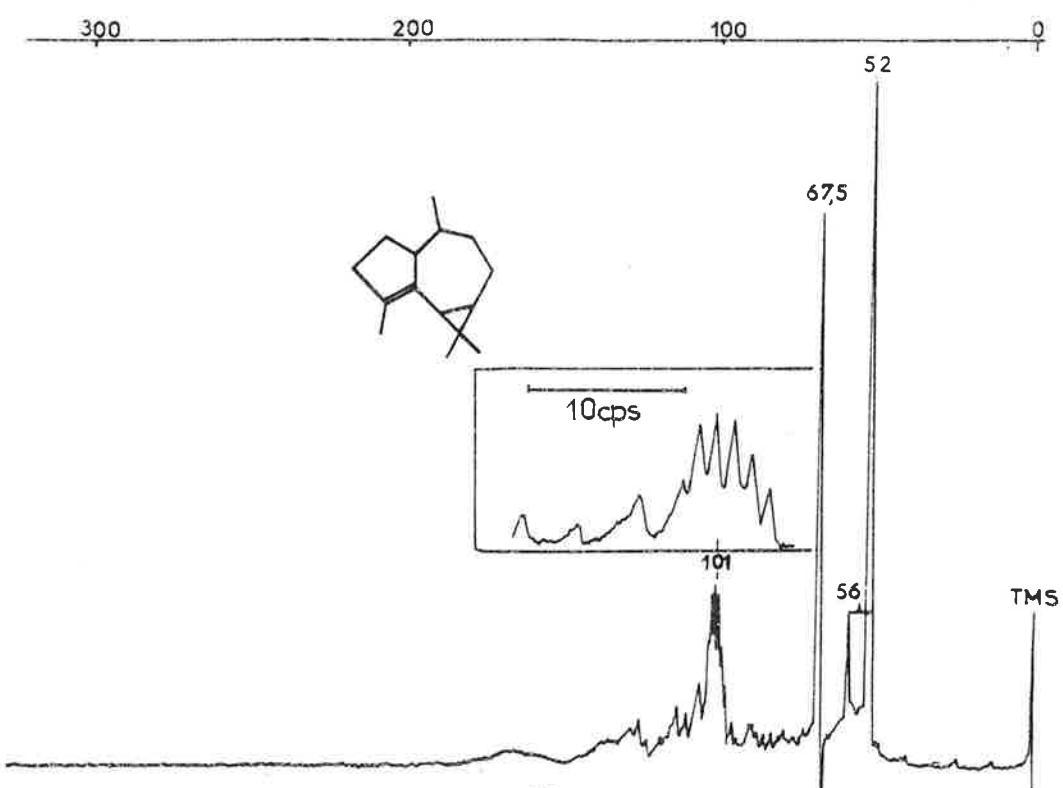


Fig.1

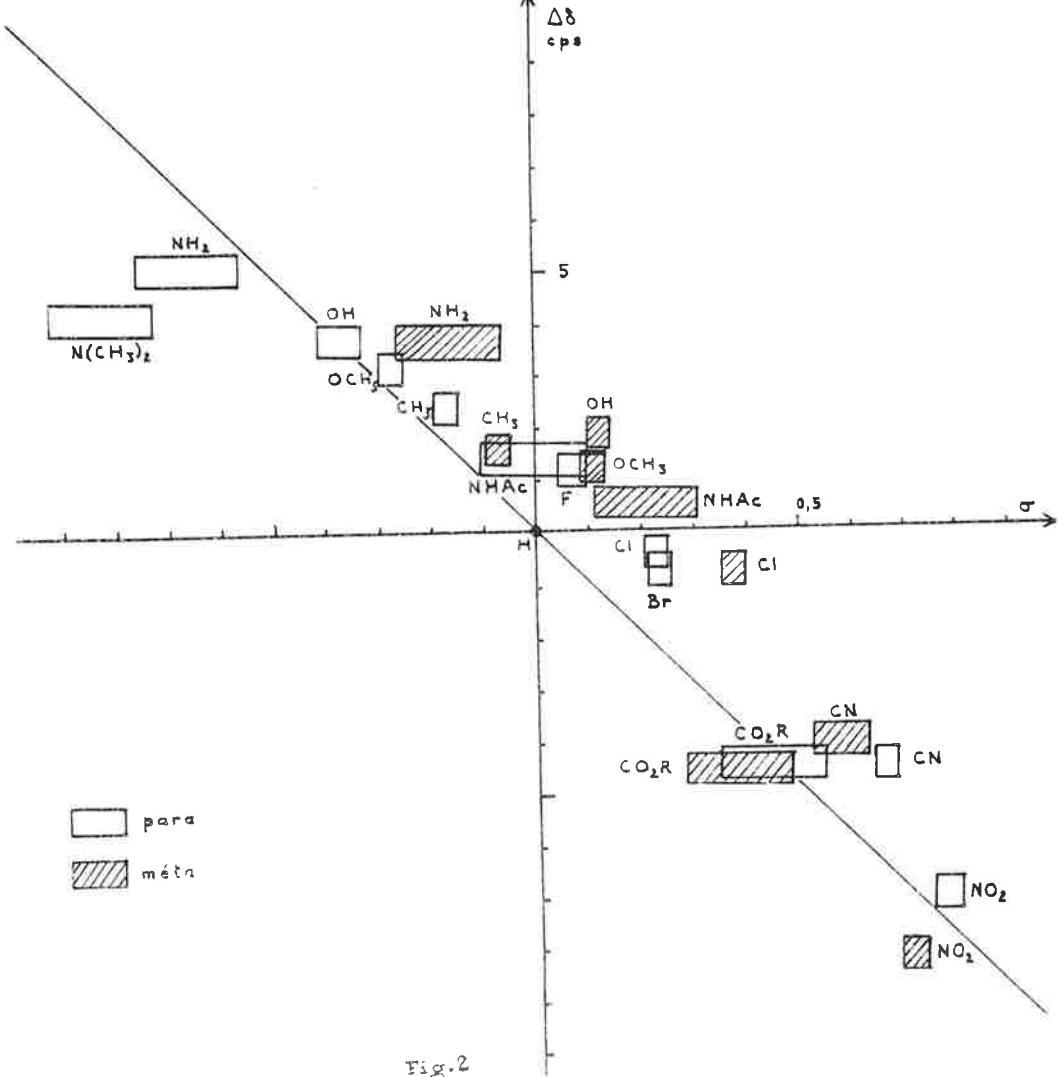


Fig.2

Physikalisch-Chemischer und Elektronomischer
Forschung der Technischen Hochschule Ilmenau

Direktor: Prof. Dr. G. SCHIEBEL

Dr. Werner Zimmermann

Ergebnisse der Physik
Band 16, Heft 1, 1966
Abbildung 10

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

Sehr geehrter Dr. Bothner-By

Protonenresonanzuntersuchungen an den Assoziaten des
4(5)-Methyl-imidazols

4(5)-Methyl-imidazol bildet in Benzol als Lösungsmittel bei genügend hohen Konzentrationen Assoziate¹⁾. Die Assoziation erfolgt über intermolekulare N-H...N-Wasserstoffbrückenbindungen. Sie wurde an Hand von Protonenresonanzspektren untersucht. In Abb. 1 ist das Spektrum einer 1,7 m Lösung wiedergegeben. In dieser Lösung sind die Moleküle vorwiegend assoziiert. Das Spektrum zeigt drei CH- Signale bei -0,3, +0,5 und +5,0 ppm, bezogen auf Benzol als internen Standard. Bei kleiner Feldstärke beobachtet man das NH- Signal. Es ist bemerkenswert, dass die Halbwertsbreite des NH- Signals praktisch nicht verschieden ist von den Halbwertsbreiten der CH- Signale. Die Lage des NH- Signals ist im Gegensatz zu den CH- Signalen außerordentlich stark konzentrationsabhängig. Das Signal wird mit steigender Konzentration, und damit bei Zunahme der Assoziation, in Richtung kleiner Feldstärke verschoben. In dem von uns untersuchten Konzentrationsbereich beträgt die Verschiebung ca. 10 ppm. Die chemische Verschiebung der CH- und

NH- Signale in Abhängigkeit von der molaren Konzentration ist in Abb. 2 dargestellt. Die chemische Verschiebung ist wieder bezogen auf Benzol als internen Standard.

Das Signal der Assoziate liegt bei ungewöhnlich kleiner Feldstärke. Dadurch wird angezeigt, dass die Abschirmung des Protons in der Wasserstoffbrückenbindung außergewöhnlich klein ist. Nach unseren Vorstellungen bewegt sich das Proton in der Brückenbindung in einem Potential mit Doppelminimum. Es werden Protonenzustände ausgebildet, die sich darstellen lassen als Linearkombination der tautomeren Grenzstrukturen der Brückenbindung:

$$\Psi = a \cdot \Psi^-(N-H \dots N) + b \cdot \Psi^+(N \dots H-N)$$

In der polaren Grenzstruktur befindet sich das Proton in der Nachbarschaft eines positivierten Stickstoffatoms und demnach in einer Umgebung, die ein Elektronendefizit aufweist. Die Beteiligung dieser Grenzstruktur an den Protonenzuständen der Brückenbindung bewirkt die ungewöhnlich grosse Verschiebung des NH- Protonensignals in Richtung kleiner Feldstärke.

Mit freundlichen Grüßen

H. Zimmermann

A. Joop
N. Joop

1) H. Zimmermann, Z. Elektrochem., Ber. Bunsenges. phys. Chem., 65, 821 (1961)

44-13

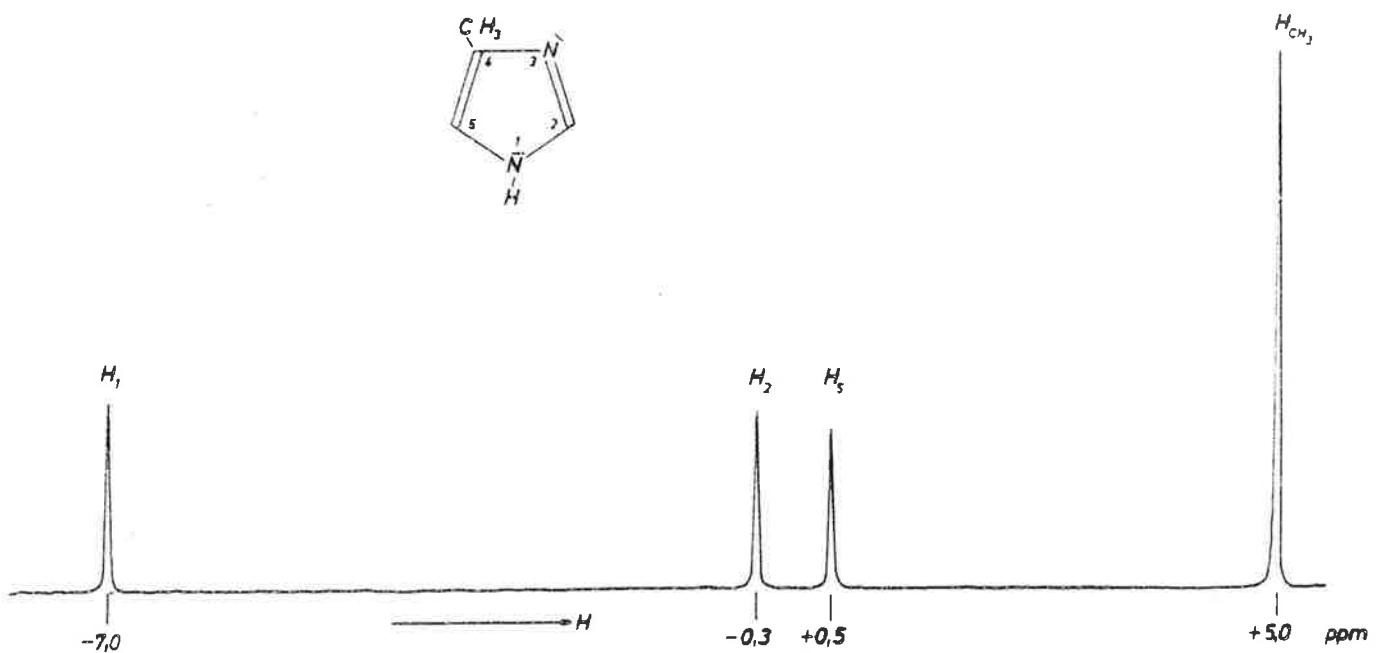


Abb. 1

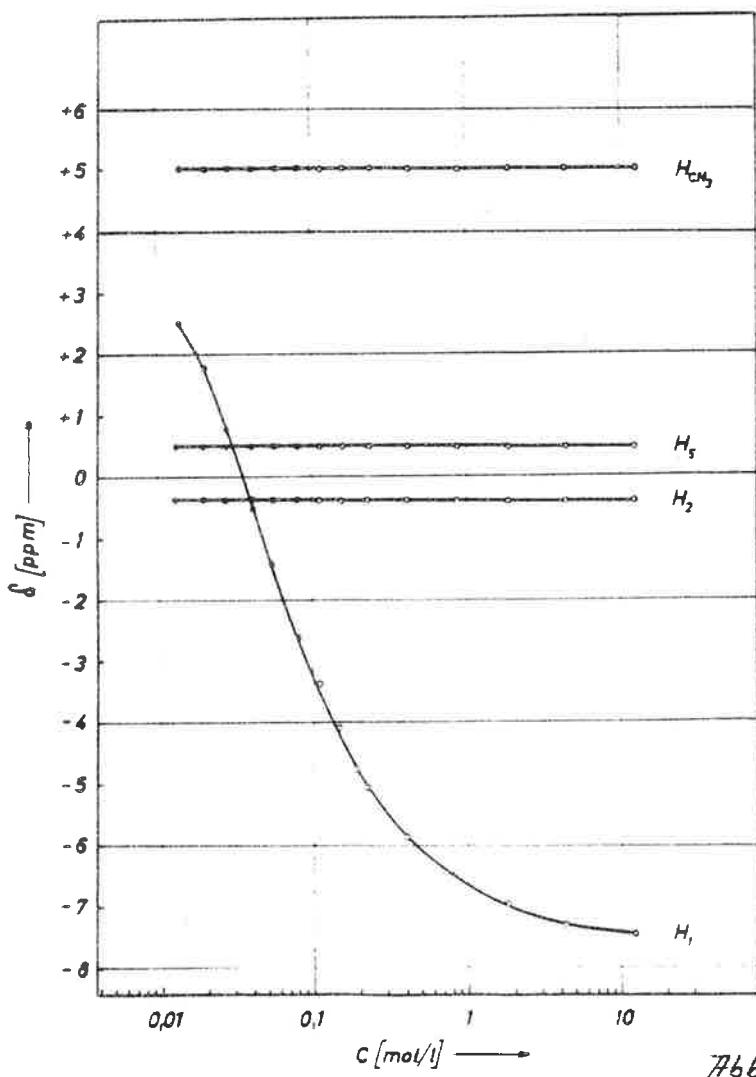


Abb. 2

INSTITUT FÜR ELEKTROWERKSTOFFE

DEPARTMENT OF ELECTROCHEMICAL MATERIALS FOR ELECTRIC CELLS

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

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

- 2 -

Ihr Zeichen Ihre Nachricht vom Unter Zeichen

FERNRUF NR 5514
FREIBURG I. BR.
ECKERSTRASSE 4
May 18th, 1962

Dear Dr. Bothner-By:

Judging from the contribution of G.M. Androes in Mellonmr No. 43/19, we believe that you may be interested in hearing about our investigations on the interconversion of enantiomers of seven membered rings such as 1,2-Dithiepane (cf. table, compound I-II), 1,2- and 1,3-Dithiabenzocycloheptene (III-V) and 1,2,3-Trithia-5,6-benzocycloheptene (VI). This is a continuation of our previous work on 1,2-Dithiane¹⁾ and the methylated 1,3-Dithiane and 1,3-Dioxane²⁾.

We have measured the free energy of activation ΔF^\ddagger (by use of the Eyring-equation) and in one case the activation energy ΔH^\ddagger . We found some interesting relations between the molecular structure and ΔF^\ddagger . I would like to point out here the increase of ΔF^\ddagger in compound III, as compared with compound I and II, upon the introduction of double bonds into the ring.

In compound IV and V, where the two sulfurs are separated by a carbon, ΔF^\ddagger is lower than in III. As a result of substituting two CH_3 groups (V) in place of two hydrogens (IV), ΔF^\ddagger is increased.

We have found, that 1,2,3-Trithia-5,6-benzocycloheptene (VI) is the only compound, showing sufficient slow conversion of the conformers to give at room-temperature for the two methylene protons at C(4) and C(7), a AB-quartet coalescing to a single line at +110°C.

We intend to investigate the corresponding O-compounds, and we shall try and find out a bit more about the conformation. A more detailed discussion of these results will be published elsewhere.

In relation to the investigation of ortho substituted 1,2-Dithiepane planned by Dr. Androes may we say that we do not intend to either synthesize or measure the characteristics of this compound.

Our investigations have been done in collaboration with Mr. S. Kabuss from the Chem. Institut der Universität Freiburg/Br.

Sincerely yours,
Horst Friebolin
Horst Friebolin

- 1) A.Lüttringhaus, S.Kabuss, W.Maier, H.Friebolin
Z.f.Naturf. 16b, 761 (1961)
2) W.Maier, H.Friebolin, S.Kabuss, A.Lüttringhaus
Tetrahedron Letters, in press.

Compound	obs. sign	T_A °C	$\Delta \tau_{co}$	ΔY_{co} B2	ΔF^\ddagger kcal/Mol]	ΔH^\ddagger kcal/Mol]	Solvent
I		<-90			< 9		Aceton
II	CH_3	-64	9,0	7,4	11,0		Aceton
III	II(3)	-3	5,95	25,9	13,6	14,8	CS_2
IV	II(2)	-55	6,05	40	10,7		CHCl_3
V	CH_3 II(4,7)	-33 -20	3,23 6,06	25,7 39,8	12,1 12,2		CH_2Cl_2
VI	II(4,7)	+110 +5	3,7	44,7	19,3		CS_2

T_A = coalescing temperature

$\Delta \tau_{co}$ = max separation of signals

#/144

TEL: WESTERN 8855
EXT.



CHEMISTRY DEPARTMENT
THE UNIVERSITY
GLASGOW, W.2

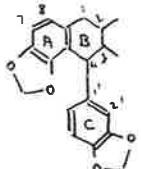
18th May, 1962.

Dr. A. A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURG 19,
Pa.,
U.S.A.

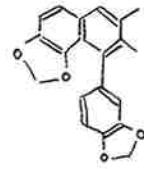
Dear Dr. Bothner-By,

We have been examining the proton magnetic resonance spectra of a series of compounds obtained from the oil expressed from the fruit of *Myristica* Otoba and used in some parts of South America for the treatment of skin diseases of domestic animals.

As a result of degradation studies, n.v. and n.m.r. evidence, one of these compounds, otobain, has been shown to have the structure I.



I



II

The n.m.r. evidence not only indicates that the structure is I but it also completely specifies the conformation of ring B and the configurations of the carbon atoms in that ring. In tetradehydro-otobain (II) the CH_2 on ring A appears as a singlet at $\gamma = 4.23$ and the CH_2 on ring C appears, as a singlet, at $\gamma = 3.95$. Restriction in rotation about $\text{C}(1) - \text{C}(1')$ causes the absorption peak of the CH_2 on ring A to be at the higher field. In II these latter protons are symmetrically placed relative to the normal through the centre of ring C and so are chemically equivalent.

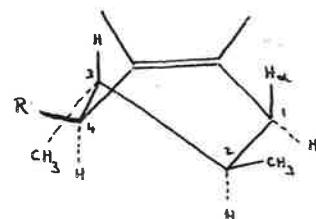
On/

Dr. A. A. Bothner-By

- 2 -

18/5/62.

On the other hand, in otobain (I) the CH_2 on ring C appears at $\gamma = 4.12$ but the spectrum obtained from the CH_2 on ring A is of the AB-type in which the chemical shifts of the A and B nuclei are $\gamma = 4.33$ and $\gamma = 4.42$ respectively, and $J_{AB} = 1.2$ c.p.s., i.e. the protons of the CH_2 group on ring A are not symmetrically arranged relative to the aromatic ring C. Furthermore, the coupling constant $J_{3,4} = 9.6$ c.p.s. and the average value of the coupling constants $J_{2,1a}$ and $J_{2,1b}$ is 6 c.p.s. All of these observations are consistent only with the pseudo-chair conformation and configurations shown in formula III.



III

With best wishes,

Andrew Porte

Andrew L. Porte.

5/5/62

UNIVERSITÉ D'OTTAWA
ÉCOLE DES SCIENCES PURES ET APPLIQUÉES



UNIVERSITY OF OTTAWA
FACULTY OF PURE AND APPLIED SCIENCES

OTTAWA 2, CANADA

DÉPARTEMENT DE CHIMIE
365, RUE NICHOLAS

DEPARTMENT OF CHEMISTRY
365 NICHOLAS ST.

May 23rd, 1962.

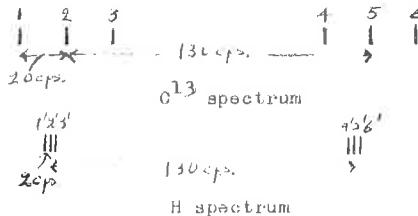
Dr. A.A. Bothmer-By,
Director of Research,
Mellon Institute,
44 W. Fifth Avenue,
Pittsburgh 13, Pa.,
U.S.A.

Dear Dr. Bothmer-By,

The letter of Dr. Karplus in the last MELLON-M-R greatly interested me because we have some work going along similar lines. In particular, we are interested in relating the signs of the $\text{^{13}C}$ -H to the $\text{^{13}C}$ -H coupling constants in saturated compounds for the reasons that Dr. Karplus has already discussed.

For convenience, we wanted to observe proton spectra rather than $\text{^{13}C}$ or D spectra. The usual decoupling procedure cannot be used here because of the relative magnitude of the coupling constants ($\text{^{13}C}$ -H, ca 130 cps; $\text{^{13}C}$ -D ca 20 cps; H-D, ca 2 cps).

An examination of the theory of double irradiation (Bloom and Shoolery) shows that if in a compound HRC^{13}HD ($\text{^{13}C}$ can be in natural abundance), the $\text{^{13}C}$ is irradiated with a weak r.f. field (say $\frac{\omega_0}{2\pi} = 5$ cps.) at a frequency corresponding to (say) line 1 of $\text{^{13}C}$ spectrum shown, then an examination of the proton spectrum will give the relative signs of $J_{\text{C}^{13}-\text{H}}$ and $J_{\text{H}-\text{D}}$.



- 2 -

The results are simple for a frequency sweep method. In that case, either lines 1' and 4' or lines 3' and 6' will be perturbed appreciably, depending on the relative signs of the J's mentioned above. The perturbation takes the form of a splitting into a symmetrical doublet of separation ca 5 cps. (for the decoupling field given above). Similar experiments can be performed on lines 3, 4 and 6.

For a field sweep method, the spectrum is a little more complicated because the decoupling field does not remain on one line of the $\text{^{13}C}$ resonance. If the decoupling frequency is set on line 1 when the proton frequency is on one of the $\text{^{13}C}$ satellites, then the results are much the same as the frequency sweep method as far as that satellite is concerned. The perturbed line will now be a doublet with somewhat different splitting (5.7 c.p.s.) than before.

Experiments on the lines mentioned above are being undertaken.

Yours sincerely,

F. A. L. Anet

F. A. L. Anet.

44-16

UNITED STATES DEPARTMENT OF AGRICULTURE
 AGRICULTURAL RESEARCH SERVICE
 WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
 800 BUCHANAN STREET, ALBANY 10, CALIFORNIA

May 23, 1962

AIRMAIL

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

Dear Dr. Bothner-By:

Sorry I have been so slow to get my subscription renewal in. Some of your readers may be interested in these operating techniques which we have found useful on our DP-60 instrument.

For some time we had noticed that over a period of many weeks our magnetic field would gradually develop a domed configuration that eventually could not be removed with the homogeneity control unit. We even changed our cycling procedure so that we started in with a maximum correctable dished field. Eventually we found that the source of this difficulty came from shutting off of our superstabilizer when it was in a slightly unbalanced condition. Balancing the stabilizer current as carefully as possible with the fine-current power supply control before switching to the balance position has markedly increased the useful "life" of our field. Also a help in this regard is setting the sweep gain potentiometer at zero while the stabilizer is switched from balance to operate. Then if the unit goes out of control during switching, the large output is not fed back to the power supply and the field is unaffected. I wonder if others are having as much trouble with the printed circuit switch as we have had?

I have more or less settled on a nitrogen-saturated ten percent aqueous solution of dimethylformamide for use in setting up or checking my resolution. The strong water peak is useful for coarse adjustment and the more shielded of the two doublet-split N-methyl resonances with its 0.8 cps splitting and extreme sharpness is very convenient for the final field adjustments.

We immediately tried out the spin-decoupling method described by Roy Johnson in the May issue and found it to be both very simple to set up and use. We are using the sweep amplifier in the broad-line section of our instrument to boost the output from our audio oscillator up to the power level needed for decoupling. This setup also completely isolates the oscillator and counter from the 200K and 100KC voltages in the modulation coil circuit, eliminating the need for any kind of filter between oscillator and counter.

Sincerely yours,

R. E. Lundin, Chemist
 Fiber Physics Investigations
 Wool and Mohair Laboratory

P.S. Let me echo the sentiments of your other readers by saying how very valuable I feel your newsletter is to NMR spectroscopists.

ROHM & HAAS COMPANY

REDSTONE ARSENAL



RESEARCH DIVISION

HUNTSVILLE, ALABAMA

May 23, 1962

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

Dear Dr. Bothner-By:

I have observed an interesting chemical shift associated with the conversion of aliphatic azo compounds to azoxy compounds, which may be of interest to readers of Mellon-NMR. It was originally anticipated that the protons in both groups attached to the nitrogen atoms of the azo compound would suffer a downfield shift upon oxidation with those in the group attached to the oxidized nitrogen experiencing the greater shift. However, in three examples studied, one of the groups (presumably that attached to the unoxidized nitrogen) undergoes an upfield shift:

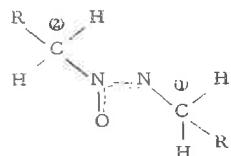
Compound	Chemical Shift (τ)
$\text{C}_6\text{H}_5\text{CH}_2\text{N}=\text{NCH}_2\text{C}_6\text{H}_5$	5.15
O ↑	
$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+=\text{NCH}_2\text{C}_6\text{H}_5$	5.65, 4.98
$\text{CH}_3\text{N}=\text{NCH}_3$	6.32
O ↑	
$\text{CH}_3\text{N}^+=\text{NCH}_3$	6.93, 5.95

L/H

	6.37
	6.85
$(\text{CH}_3)_3\text{CN}=\text{NC}(\text{CH}_3)_3$	8.87
$(\text{CH}_3)_3\text{CN}=\text{NC}(\text{CH}_3)_3$ ↑ O	8.72, 8.52

In the case of azoisobutane, however, where the protons are on a β -carbon, the anticipated downfield shift of both groups was observed.

I would like to associate the upfield shift with the stereochemistry of the compounds. It is presumed in the literature that the azo compounds have the trans configuration and that no isomerization occurs upon oxidation. Therefore, the azoxy compounds may be portrayed as follows:



Is it reasonable to assume that the upfield shift of the methylene group $\textcircled{2}$ is due to diamagnetic shielding from the nitrogen-oxygen bond? The cis isomer of ω -azoxytoluene is known but so far because of its extremely low solubility in organic solvents, I have not been able to obtain its spectrum. Based on the stereochemical argument I would predict that both methylene groups in the cis isomer would undergo a downfield shift with respect to the azo compound. It is presumed that in azoxyisobutane the removal of the proton to the β -carbon takes it out of the effective field of the nitrogen-oxygen bond and that is subject simply to the inductive effect of the azoxy group.

In partial confirmation of these suggestions we have observed that the methyl groups of trans-nitrosomethane dimer (I) resonate at higher field than those of the cis-dimer (II) (6.03τ vs. 5.80τ)



I would appreciate any comments on these data and suggestions for solvents to get spectra of the cis-azoxy compounds. I hope that this contribution to the partial or complete mystery class will suffice to continue our subscription which is sent to Dr. C. B. Colburn of the Division.

Sincerely yours,
Jeremiah P. Freeman

JPF:lb

8/1/44

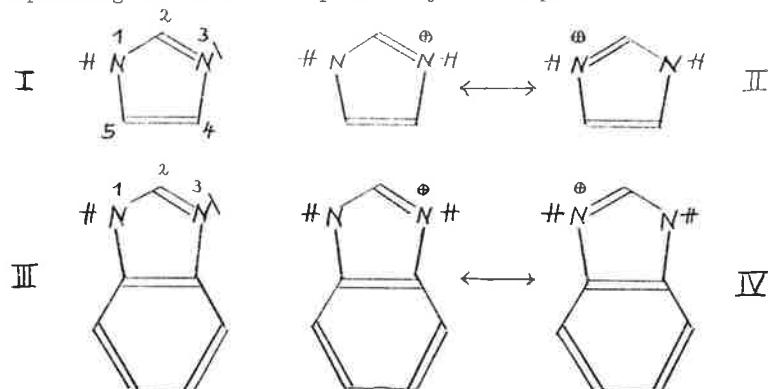
69 HEIDELBERG, May 24, 1962
Tiergartenstraße
Tel. 27121 (über Chorag Klunk)

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

Dear Dr. Bothner-By:

Concerning the note of R. Jacquier and J. Wyldé in MELLON-M-R No. 42, p.12, we would like to report some results we obtained on proton resonance and proton exchange in the diazole series.

The NMR spectra of imidazole(I) in neutral organic solvents show H_4 and H_5 to be magnetically equivalent because of rapid exchange of the N_1 proton¹⁾. Accordingly, the spectra consist of a triplet (H_2) and a doublet of twice the triplet intensity ($H_4 + H_5$), and there is no further spin-spin splitting by interaction with the N_1 proton. Analogous results have now been obtained with benzimidazole whereas in the spectra of the less acidic heterocycles pyrrole and indole in neutral solutions splitting due to N-H has previously been reported²⁾.



For imidazolium chloride we expected the exchange rate to be decreased since the most efficient proton acceptor in imidazole

solutions in organic solvents doubtless should be the basic N_3 atom of imidazole itself (cf. the very strong N...H-N hydrogen bonds in imidazole solutions³). Nevertheless NMR spectra of the protonated imidazole(II) — imidazole in dil. H_2SO_4 /ethanol and imidazolium chloride in dimethylsulfoxide — likewise showed only the doublet and triplet. In conc. H_2SO_4 , however, proton exchange is decreased enough to allow spin-spin splitting by N-H to appear (fig.1). The spectrum looks rather simple and is well accounted for by the assumption that H_4, H_5 resonance is due to A_2X_2 splitting with $J_{15} = J_{14}$. Calculated coupling constants are shown in table 1. J_{12} and J_{15} are of the same order of magnitude as are the corresponding N-H coupling constants known from pyrrole spectra²⁾. Another and perhaps the more reasonable interpretation of the spectrum, following from the discussion of the furan system by R.J. Abraham and H.J. Bernstein⁴⁾, results in $J_{14} + J_{15} = 4.4$ cps.

	Solvent	τ_2	τ_4	τ_5	$J_{12}=J_{23}$	J_{24}	J_{25}
Imidazole	CDCl ₃	2.27	2.86	2.86	-	1.0	1.0
Hydrochloride	DMSO	0.56	2.14	2.14	-	1.4	1.4
Imidazole	c. H_2SO_4	1.4	2.4	2.4	2.3	1.4	1.4
Benzimidazole	THF	1.88	-	-	-	-	-
Hydrochloride	DMSO	0.20	-	-	-	-	-
Benzimidazole	c. H_2SO_4	1.0	-	-	2.5	-	-

Table 1

Similar results have been obtained with benzimidazole(III, fig.2). In NMR spectra of benzimidazole in organic solvents there is a single H_2 peak whereas in conc. H_2SO_4 this peak is split into a 1:2:1 triplet ($J_{12} = J_{23} = 2.5$ cps) by interaction with the two equivalent N_1 and N_3 protons of protonated benzimidazole(IV).

Sincerely yours,

Albrecht Mannschreck
Albrecht Mannschreck

Heinz A. Staab
Heinz A. Staab

61-147

44-20

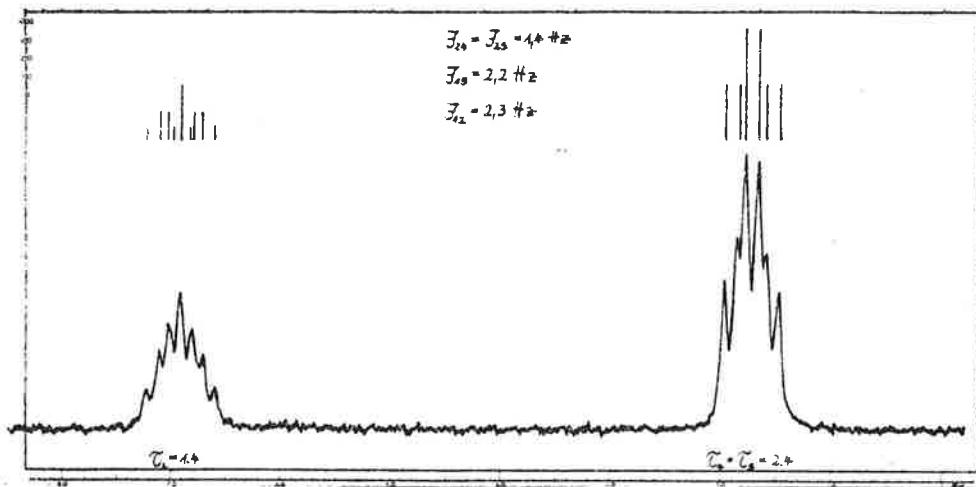


Fig. 1

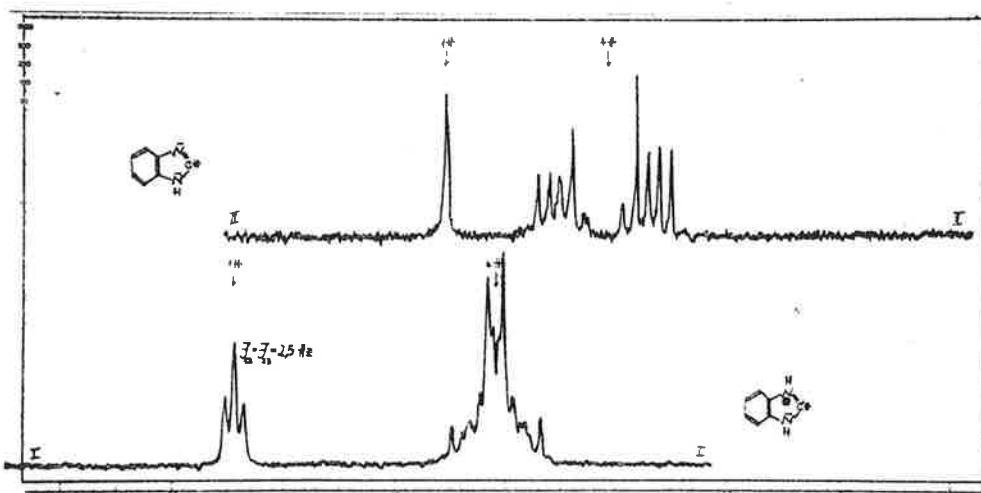


Fig. 2

References:

- 1) See also G.S.Reddy, R.T.Hobgood jr. and J.H.Goldstein, J.Amer.Chem.Soc. 84, 336 (1962).
- 2) R.J.Abraham et al., Canad.J.Chem. 37, 1056 (1959); 37, 1859 (1959). J.D.Roberts, Nuclear Magnetic Resonance, New York 1959, p.85. B.Dischler and G.Englert, Z. Naturforsch. 16a, 1180 (1961). L.A.Cohen, J.W.Daly, H.Kny and B.Witkop, J.Amer.Chem.Soc. 82, 2184 (1960).
- 3) H.Zimmermann, Z. Elektrochem. 65, 821 (1961).
- 4) R.J.Abraham and H.J.Bernstein, Canad.J.Chem. 39, 221 (1961).

HARVARD MEDICAL SCHOOL
THE DEPARTMENT OF PHARMACOLOGY
25 SHATTUCK ST., BOSTON 15, MASS.

May 25, 1962

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

Dear Aksel,

In the course of our efforts to distinguish intra- from intermolecular hydrogen bonds in some aliphatic compounds, we have made an observation which might be of some interest to you, since you had shown some time ago, that the H-C-C-H coupling constants are of the order of 6-7 cps in compounds in which free rotation about the C-C bond can be assumed. It appears that the coupling constant in certain diols is more dependent on the solvent than in the case of homologous monohydroxy alcohols. In the propanol series, for example the $\text{HC}_{(1)} - \text{C}_{(2)}\text{H}$ and $\text{HC}_{(2)} - \text{C}_{(3)}\text{H}$ coupling constants for N-propanol are 6.3 and 6.7 cps respectively and are the same within experimental error in the pure liquid, in aqueous, in CDCl_3 or in acetone solution. On the other hand in the 1,3 propanediol the $\text{O}-\text{H}_2 - \text{C}-\text{CH}_2$ coupling constant is 6.5 cps on 1M solution in water and 5.4 cps in a 1M solution in acetone. For 1,2 propanediol we get values of 6.5 and 6.1 cps for the $\text{CH}_3 - \text{CH}$ coupling constant and 5.9 and 4.6 for the $\text{CH}_2 - \text{CH}$ coupling constant in water and acetone respectively (1M), although the latter values might be too small.

It is conceivable that one is dealing here with an effect of the solvent on the electronic ΔE . It is however also possible that this reflects a restriction of internal rotation in solvents less favorable for intermolecular hydrogen bonding. There is some additional evidence leading us to favor the latter point of view at the moment. In concentrations of $\sim 1\text{M}$ the $-\text{OH}$ peak of water, methanol and propanol in acetone is found at $\sim +270$ cps with respect to benzene and shows a very strong concentration dependence, gradually moving to a position of $\sim +120 - 160$ cps. The $-\text{OH}$ peak in the diols or in the amino-alcohols, on the other hand, can be found at $+180 - 200$ cps at comparable concentrations and begins to show a concentration dependence at somewhat higher concentrations. This seems in general agreement with

Dr. Aksel A. Bothner-By

-2-

May 25, 1962

the findings in CDCl_3 (e.g. Varian HR spectra catalog), indicating that hydroxyl hydrogens which can be involved in an intramolecular H-bond are found at lower fields ($+100 - 200$ cps with respect to benzene, or less), than $-\text{OH}$ hydrogens which can form only intermolecular bonds $+200 - 300$ cps and suggests that in acetone H bonding to the $\text{C} = \text{O}$ group of the solvent (a) is not very strong and (b) is not preferred over the formation of an intramolecular bond.

If changes of coupling constants can indeed be correlated with the formation and breakage of intramolecular hydrogen bonds (as one might expect they could be), the study of the stability of intramolecular bonds under different conditions will be greatly simplified. The data available at present are too few to justify a generalization however and we would, therefore, appreciate hearing from anyone who has made relevant observations.

Sincerely yours,

Oleg Ardetzky
Oleg Ardetzky

OJ:mt

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