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Mailed: August 3, 1961

Monthly Ecumenical Letters from Laboratories Of N-M-R

No. 34

Author Index

Prof. V. J. Kowalewski

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

BUENOS AIRES, 20 July 1961.-

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

Dear Dr. Bothner-By:

We have undertaken in this laboratory a systematic study of some pyridine derivatives and we think that a preliminary report of our results can be perhaps of interest to some of the MELLONMR readers.

We found that the 3 substituted pyridines (R=Cl, Br, acetyl, aldehyde) give spectra that can be nicely described by an ABKL approximation (perturbed ABXY). Details of both methods of approximation will be published elsewhere. In these second order spectra a useful iterative procedure was found. The lines due to the two most strongly coupled protons are treated as an AB system, that is, the coupling with the C & D are supposed nonexistent and the AB lines are averaged four by four to obtain a pure AB spectrum. This gives initial values for $(\nu_A)_o$, $(\nu_B)_o$ and $(J_{AB})_o$.

The C and D line positions are averaged out, what gives us the initial values for $(\nu_C)_o$ and $(\nu_D)_o$. The splittings (which unlike the ABC system, are not all equal though they repeat in each group of lines) are averaged to give the initial tentative values for the remaining J's.

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With these first tentative data, the spectrum is calculated and from this, the new $(J_{ij})_1$ and $(\nu_i)_1$ are obtained which are compared with the initial (experimental) ones. The differences are used now to improve the ν_i's and J_{ij}'s. The calculation is repeated several times until good agreement is found between the $(\nu_i)_o$'s and $(J_{ij})_n$'s $(\nu_i)_n$ being the correct values for the chemical shifts. The same holds for the J_{ij}'s. It was found that with the ABXY approximation the ν_i's are directly given by the $(\nu_i)_o$'s. Exact ABCD calculation for the parameters of the four substances has also been performed (with the IBM 650 and the Ferranti Mercury computers) and the results obtained give good agreement with the ABKL treatment.

Comparative results can be seen on the attached table. The ABKL calculated spectrum of the 3 Cl-pyridine is also included.

Sincerely yours,

Dora G. de Kowalewski   Valdemar J. Kowalewski

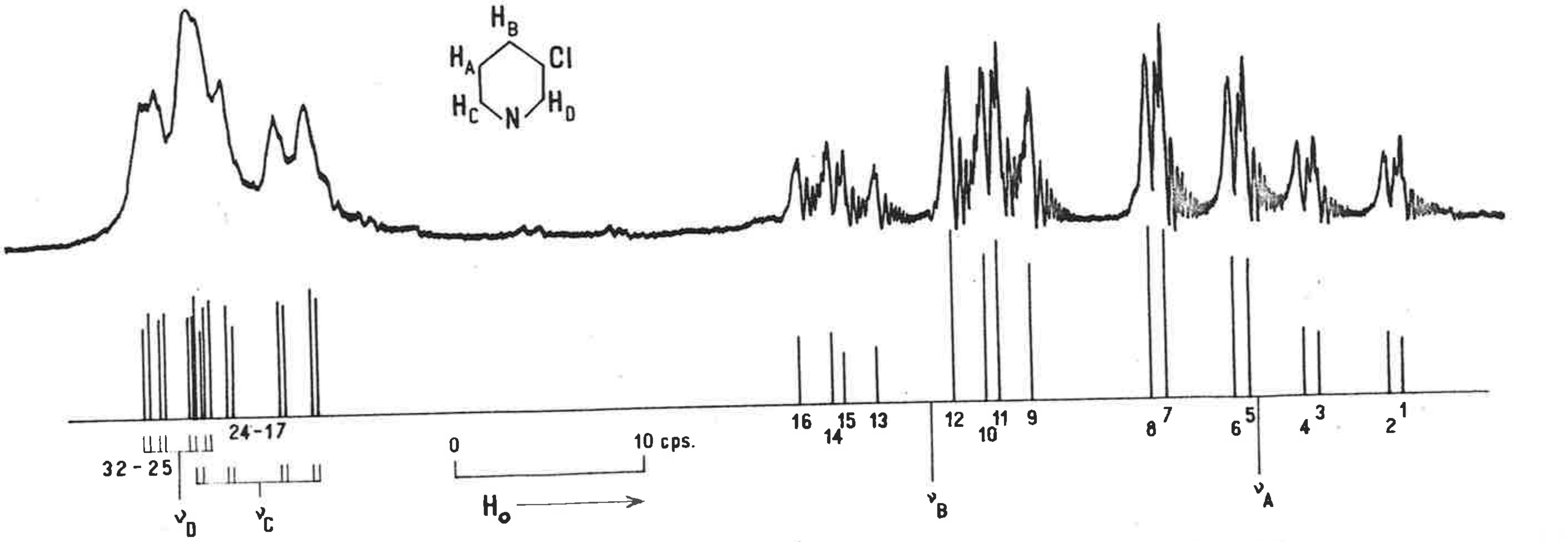
TABLE VIII

NMR Molecular parameters for the 3-pyridines

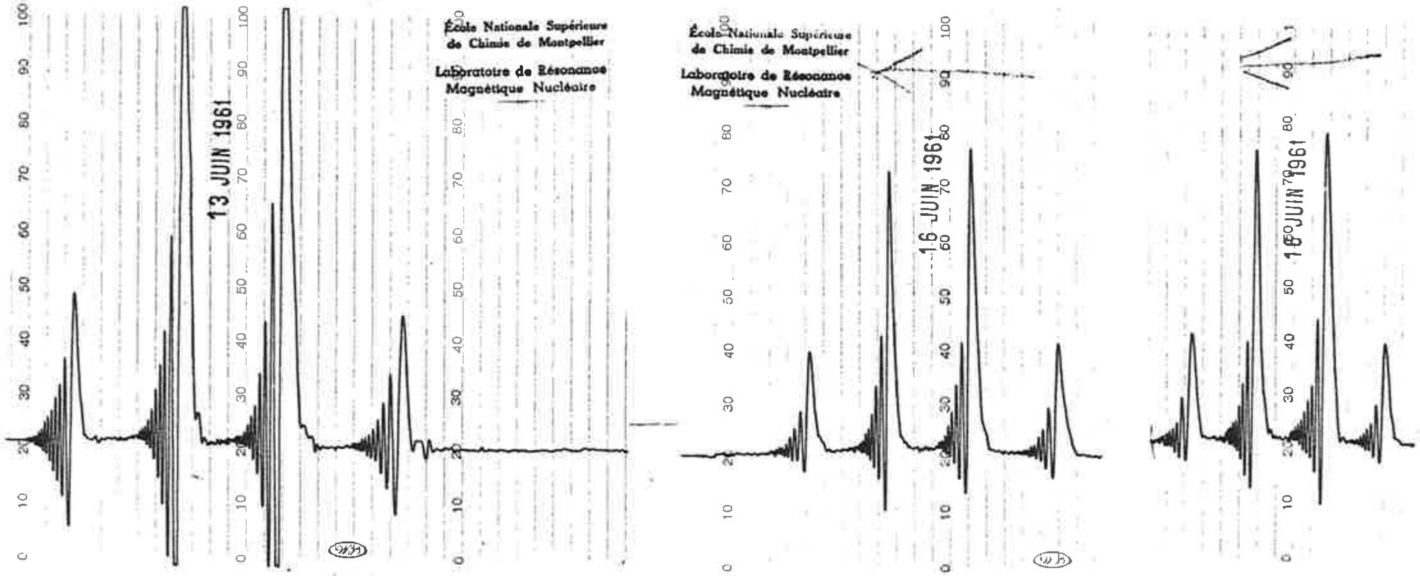
R	method	J_{AB}	J_{AC}	J_{BC}	J_{AD}	J_{BD}	J_{CD}		ν_A	ν_B	ν_C	ν_D	δ_{AB}	δ_{CD} in cps.
$COCH_3$	1st.order$(J_{ij})_o$:	8.00	4.78	1.87	0.85	2.10	0.00	$(\nu_i)_o$:	74.46	44.26	20.00	5.50	30.20	14.50
	ABXY	8.00	4.82	1.82	0.82	2.12	0.00		74.46	44.26	20.00	5.50	30.20	14.50
	ABKL	8.00	4.87	1.79	0.83	2.12	0.00		74.35	44.19	20.15	5.53	30.16	14.62
	ABCD	7.99	4.87	1.79	0.83	2.12	0.00		74.35	44.19	20.14	5.53	30.16	14.61
COH	1st.order$(J_{ij})_o$:	7.85	4.90	1.90	0.90	2.00	0.00	$(\nu_i)_o$:	66.20	39.10	12.40	1.50	27.10	10.90
	ABXY	7.85	4.96	1.84	0.88	2.02	0.00		66.21	39.09	12.40	1.50	27.12	10.90
	ABKL	7.85	5.00	1.80	0.88	2.02	0.00		66.07	39.03	12.55	1.53	27.04	11.02
	ABCD	7.85	5.00	1.81	0.88	2.02	0.00		66.08	39.04	12.55	1.53	27.04	11.02
Br	1st.order$(J_{ij})_o$:	7.80	4.65	1.55	0.85	2.35	0.30	$(\nu_i)_o$:	63.85	39.60	8.80	1.50	24.25	7.30
	ABXY	7.80	4.73	1.47	0.81	2.37	0.30		63.85	39.60	8.80	1.50	24.25	7.30
	ABKL	7.80	4.76	1.44	0.82	2.38	0.30		63.74	39.54	8.92	1.54	24.20	7.38
	ABCD	7.81	4.76	1.44	0.81	2.39	0.30		63.74	39.55	8.92	1.54	24.19	7.38
Cl	1st. order	8.20	4.50	1.70	0.80	2.40	0.30	$(\nu_i)_o$:	59.25	41.75	5.80	1.67	17.50	4.13
	ABXY	8.20	4.66	1.54	0.73	2.47	0.30		59.25	41.76	5.81	1.67	17.50	4.13
	ABKL	8.20	4.67	1.53	0.71	2.48	0.30		59.14	41.71	5.92	1.70	17.43	4.22
	ABCD	8.22	4.69	1.52	0.71	2.49	0.30		59.14	41.71	5.91	1.68	17.43	4.23

Final data of relative chemical shifts of the ring protons of the 3-pyridines in dimensionless units (ppm.)

R	AB	BC	CD	AD
$COCH_3$	0.754	0.601	0.365	1.721
COH	0.676	0.662	0.276	1.616
Br	0.605	0.766	0.185	1.555
Cl	0.436	0.895	0.106	1.437



V. J. Kowalewski



34-3

UNIVERSITE DE MONTPELLIER

ÉCOLE NATIONALE SUPÉRIEURE
DE CHIMIE

8, RUE DE L'ÉCOLE-NORMALE
TÉLÉPHONE 72.49.19

Prof. Max Mousseron,
Director.

Montpellier, le 23rd June, 1961

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

Dear Dr. Bothner-By,

Thank you very much for your letter of the 31st May, with enclosures. I think MEELON-M-R is of enormous value to everybody and particularly to people in Europe, and I was most enthusiastic to read the copies you have sent me. I should be grateful if you could place me on your mailing list, if you should consider that our contributions can be sufficient. We quite agree concerning the points mentioned in your letter, viz. the sine qua non condition for participation and the private nature of the information contained in the letters.

As I mentioned in my last letter, we have a Varian V-4311 56.4(or 60) Mc/sec. installed here since October, 1960- thatis, the instrument was delivered then- and perhaps you would be interested in certain detai ls of the set-up. The apparatus is in a room on the ground floor of the building, which room has been air conditioned with a temperature control better than ± 0.5°C., summer and winter. The magnet cooling water is of the closed loop type, with heat exhhanger ~~fmx~~ cooled by tap water, a cooling group of 2600 Frigories/h controled by a contact thermometer. The temperature control is ± 0.1°C., operating temperature 17.3°C. We have added a supplementary sand water filter, the filter on the magnet being insufficient (frequent clogging); the sand water filter can be regenerated rapidly by washing.

Perhaps you would be interested in some work we have done on some i-sterols. I do not know if the N.MR spectra of such compounds have been published. Prof. Crastes de Paulet, of the Institut de Biologie here, was interested to know if we could distinguish the 3,5 cyclo structure from the double bond structure in a steroid. His research student, M. Bascoul, accordingly prepared the known compound, 17-β-hydroxy-3,5-cycloandrostane, and we compared its spectrum with that of 17-β-hydroxyandrostane. The spectrum of the latter compound showed up the well known sterol pattern, the highest field peaks being the angular methyl groups. The spectrum of the i-sterol showed at a field higher than the angular methyls several peaks at a field value closely corrésponding to the cyclopropane chemical shift. These high field peaks look rather like an AB_2 structure, but do not fit quantitatively with theoretical AB_2 spectra. This is rather to be expected, as there is a cyclic $-CH_2$ next to the carbon atom on the cyclopropane ring.

I enclose a tracing of the spectrum of the 3,5-cyclo compound. The values quoted are in c/sec from benzene used as internal reference.

Concerning this, I know I ought to be using T.M.S as an internal reference as well as an external reference, but for the time being we are having some difficulty in obtaining TMS, the best sourde being FLUKA in Switzerland, who cannot for the moment supply us with the pure compound. For the external reference, I am awaiting the supply of a coaxial cell.

Concerning resolution, we check this each time by recording the acetaldehyde quartet and I enclose a few specimen as exemples.

Yours sincerely,

J. Wylde

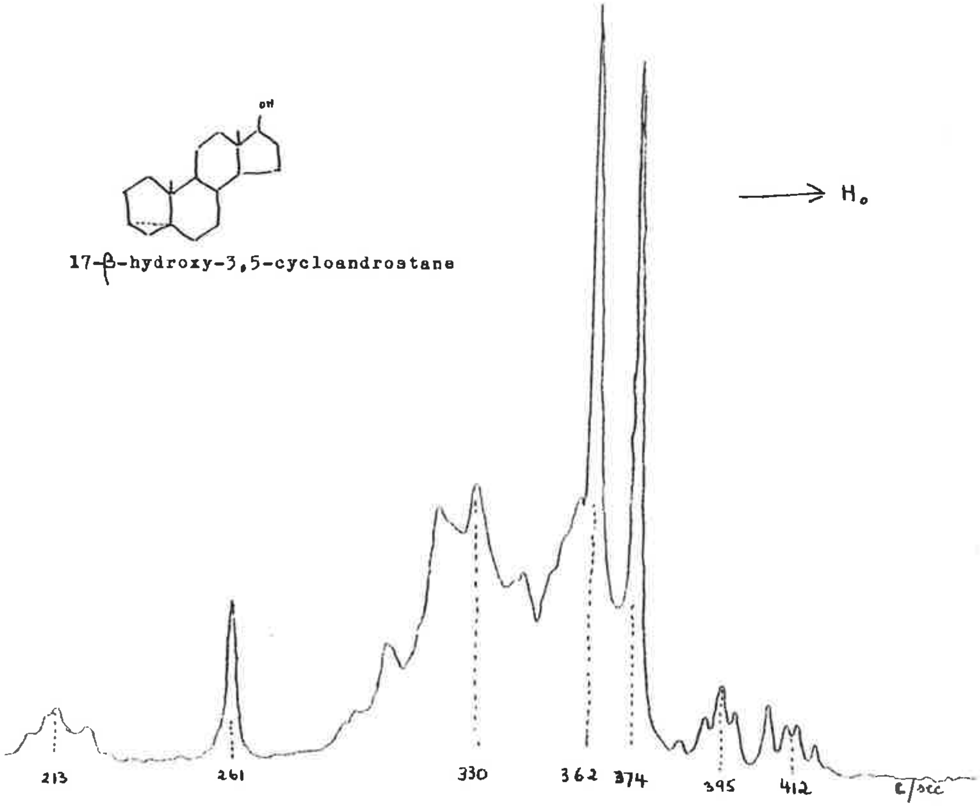
J. WYLDE
Chargé de Recherches, C.N.R.S.

Laboratoire de Résonance
Magnétique Nucléaire

34-4

Universite de Montpellier

R.F. Frequency:- 56.4 Mc/sec.
Solvent:- CCl_4
Concentration: 10% app.
Reference: Internal Benzene, 5%
Sweep rate and direction:- 1.28 c/sec/sec, from high to low fields
Paper rate:- 1mm/sec
Modulation frequency: 500c/sec
Estimated resolution:- 1 - 1.5 c/sec



17-β-hydroxy-3,5-cycloandrostane

Fluorine N.M.R. Spectroscopy. V. A Carbon-13 Study of Coupling Constants Between <u>Cis</u> and <u>Trans</u> CF_3 Groups in Highly Fluorinated Olefins.

George Van Dyke Tiers

Contribution No. 204 from the Central Research Department of the Minnesota Mining and Manufacturing Co., St. Paul 19, Minnesota.

The empirical correlation of nuclear magnetic resonance (N.M.R.) spectral data with stereoisomeric structure is well established for organic compounds. In the field of fluorine chemistry, however, very few stereoisomers have been isolated and identified with reasonable certainty, and relatively few chemical and physical techniques are available for such identification, or even for the intercomparison of these with other materials. When <u>cis-trans</u> isomerism about a double bond is being studied, intercomparisons may be done by N.M.R. means, but for the original proof of structure it is necessary to appeal to an "absolute" method, such as the well-known absence of the C=C stretching infrared absorption for a symmetrical <u>trans</u>-olefin. In this manner the <u>cis</u>- and <u>trans</u>- 2,3-dichlorohexafluorobutene-2 isomers have been identified[1]; the N.M.R. study of these isomers, reported here, yields characteristic shielding values and spin-spin coupling constants for CF_3 groups so located. Owing to the magnetic equivalence of the CF_3 groups, the coupling constants could only be ascertained from the "C^{13} satellite" peaks, which result from the presence, in natural abundance, of molecules bearing $C^{13}F_3$ groups at one end. This elegant method, due to Sheppard[2-4], has heretofore only

(1) F. Dickinson, R. Hill and J. Muray, J. Chem. Soc., 1441 (19[illegible])

(2) A. D. Cohen, N. Sheppard and J. J. Turner, Proc. Chem. Soc. (London) 118 (1958)

(3) N. Sheppard and J. J. Turner, Proc. Roy. Soc. (London) A252, 506 (1959)

(4) N. Sheppard and J. J. Turner, Mol. Phys. 3, 158 (1960)

been applied to proton compounds.

Experimental

Commercial 2,3-dichlorohexafluorobutene-2 (Hooker Chemical Co.) was found to have a cis/trans ratio of about 15/85, other impurities also being present. Vapor phase chromatography (VPC) over "Kel-F" oil KF-3 (Minn. Mining & Mfg. Co.) resulted in a highly pure sample of trans - 2,3-dichlorohexafluorobutene-2, n_D^{25} 1.3440, f.p. ca. -55° to -60°, having a very weak C=C infrared band, and containing only 0.2% of the cis-isomer. Commercial 2,2,3,3-tetrachlorohexafluorobutane (Hooker Chemical Co.) was dechlorinated[1] to give the olefin in a cis/trans ratio of 60/40, from which pure cis-2,3-dichlorohexafluorobutene-2, containing only 0.6% trans isomer, was isolated by the VPC technique already described. High purity was required as the isomer peaks (at 40 Mc/s) tend to obscure the C^{13} satellites.

The N.M.R. equipment and techniques were as previously described,[5,6,7]

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

(6) G. Filipovich and G.V.D. Tiers, ibid., 63, 761 (1959)

(7) G.V.D. Tiers, J. Phys. Soc. Japan, 15, 354 (1960)

except that Varian field homogeneity control coils had been added.

Table I

Shielding Values and Coupling Constants for the Cis and Trans Isotopic Isomers of 2,3-Dichlorohexafluorobutene-2.

Isomer	Cis	Trans
ϕ^*, p.p.m.[a]	+60.446 ± 0.007	+63.730 ± 0.008
ϕ^*(trans)-ϕ^*(cis) p.p.m.[b,c]	+ 3.374 ± 0.003	+ 3.351 ± 0.001
$\Delta\phi$, p.p.m.[b,d] ($C^{13}F_3$-$C^{12}F_3$)	+ 0.196 ± 0.002	+ 0.132 ± 0.001
J ($C^{13}F_3$) c/s[b]	275.83[e] ± 0.13	275.66 ± 0.06
J (FF') c/s[b,f]	13.39[e] ± 0.07	1.44 ± 0.02

[a]See ref. 6; concentration 10.0% by volume in CCl_3F, measurement temp. 25° ± 1°. [b]Neat (undiluted) samples were used. [c]When at 10% conc. by volume in CCl_3F, this difference is +3.284 ±0.001; note that the three values cited need not be identical, since the "solvents" used are different. [d]See refs. 7 and 9. [e]From approx. A_3B_3 analysis; see text. [f]Here F' represents fluorine attached to C^{13}.

34-6

Carbon - 13 Isotope Effects and Coupling Constants in the F^{19} Spectra of Oxalyl Fluoride and Oxalylchoridefluoride

A relatively large isotopic shift in the F^{19} resonance between $C^{12}F$ and $C^{13}F$ and a rather small isotopic shift between C^{12}-C^{12}-F and C^{13}-C^{12}-F have been reported for a few compounds in earlier numbers of MELLONMR (Lauterbur 5, 9; Tiers 13, 8). We have recently obtained the spectra of oxalyl fluoride $(COF)_2$ and oxalyl-chloridefluoride COCl.COF. The C^{13} satellites in the F^{19} spectrum of $(COF)_2$ consist of two overlapping quartets at +218.8, +167.5, +81.3, +29.6, -27.6, -79.1, -152.5, -204.2 c/s from the $C^{12}F$ line at 56.4 Mc/s. By considering each quartet as an AB spectrum the coupling constants and isotopic shifts given in the following table were deduced. Four C^{13} satellites were observed in the spectrum of COClCOF at +195.7, +49.3, -47.7 and -180.8 c/s from the $C^{12}F$ line, at 56.4 Mc/s from which the coupling constants and isotopio shifts given in the table were obtained directly.

TABLE

	J_{FF} c/s	$J_{C^{13}F}$ c/s	Isotope shift c/s (at 56.4 Mc/s)	p.p.m.	$J_{C^{13}C^{12}F}$ c/s	Isotope shift c/s (at 56.4 Mc/s)	p.p.m.
$(COF)_2$	51.5	366.0	+7.5	0.133	103.2	+0.9	0.016
COF.COCl		376.5	+7.5	0.133	97.0	+0.8	0.014

The two substances were examined as a mixture prepared by fluorinating oxalyl chloride with NaF (C. W. Tullock and D. D. Coffman

J. Org. Chem 25, 2016 (1960)). The two spectra were easily indentified by means of the C^{13} satellite patterns. The $C^{13}C^{12}F$ coupling constants appear to be rather larger than have been observed previously but the isotopic shifts are very similar to previous measurements (Lauterbur, Tiers)

J. Bacon and R. J. Gillespie
Department of Chemistry
McMaster University
Hamilton, Ontario, Canada.

RJA/DMT

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

National Physical Laboratory

TEDDINGTON · MIDDLESEX

Telegrams : Physics, Teddington   Telephone : Molesey 1380, Ext. 199

Please reply to the DIRECTOR and quote our reference

OUR REF: BP.A.A.1   BASIC PHYSICS DIVISION

YOUR REF:

26th July, 1961.

Dear Dr. Bothner-By,

I noticed a typing mistake in my last MELLON subscription (MELLON No. 33, p.23). Instead of

(b) For the iodoform methyl iodide complex

one should, of course, read

(b) For the methyl iodidetoluene complex

$\Delta H = 1.3 \pm 0.5$ kcals/mole
$\Delta S = 4.9 \pm 0.4$ e.u.

My apologies.

Yours sincerely,

R J Abraham

R.J. Abraham
Basic Physics Division

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

The Protonation of Anilines

In a recent number of MELLONMR (28, 8) Shoolery and Johnson reported that they found the NH_2 resonance in the proton spectra of liquid aniline and of a dilute solution of aniline in carbon tetrachloride to be very narrow lines and they attributed this to a large electric field gradient at the nitrogen nucleus rather than to proton exchange. In trifluoracetic acid as solvent they found that the amino group was protonated and that the NH_3^+ resonance was quite broad. They considered that proton exchange was unlikely in this system and they attributed the broadening of the resonance to the reduction of the N^{14} quadrupole relaxation due to an increase in the electrical symmetry around the nitrogen nucleus on protonation.

We find, however, that if aniline is allowed to stand over potassium hydroxide and is then distilled the NH_2 resonance is broad with a width of 8 c/s, although aniline "straight from the bottle" has a very narrow NH_2 resonance as reported by Shoolery and Johnson. In a dilute solution of the redistilled aniline in carbon tetrachloride the line width is reduced to 4c/s but in dimethylsulphoxide it is increased to 11c/s. We conclude therefore that the very narrow resonance is due to proton exchange that is catalysed by some impurity, such as water or acid, in the aniline. The reduction of the line width of the redistilled aniline in carbon tetrachloride solution is probably to be attributed to some impurity in the carbon tetrachloride. We have also found that the broad NH_3^+ peak that is observed in trifluoracetic acid solutions becomes somewhat narrower in $CF_3CO_2H - H_2SO_4$ mixtures reaching a constant width of about 15 c/s in solutions containing more than 60mol % H_2SO_4. We conclude therefore that proton exchange is still occuring on trifluoracetic acid but is probably negligibly slow in 100% sulphuric acid. The breadth of the NH_3^+ peak under these conditions must be attributed to N^{14} quadrupole relaxation.

In similar studies on o- and p-nitroanilines we find that although the NH_2 resonance is narrow for both compounds in nitromethane as solvent it was 8 c/s wide in dimethylsulphoxide and for p-nitroaniline 20 c/s wide in acetone. We conclude that some impurity in the nitromethane is catalysing the exchange. In the case of N-methyl-4-chloro-2-nitroaniline protonation on the nitrogen can be conveniently followed by observing the spin-spin coupling between the NH protons and the methyl protons. Thus in a saturated solution in nitromethane the methyl group signal consists of a doublet with J = 4.8 c/s, but on dilution, or raising the temperature to ~80° the doublet collapes to a single line. In trifluoracetic acid the methyl resonance is a single peak but with the addition of sulphuric acid this gradually splits into a rather broad, incompletely resolved, triplet with J = 4.5 c/s. These results indicate that there is no proton exchange in nitromethane, that there is protonation and rapid exchange in trifluoracetic acid, but on increasing the acididty of the medium by the addition of sulphuric acid the proton exchange becomes negligibly slow. That aniline and o- and p-nitroanilines apparently undergo proton exchange in nitromethane but N-methyl-4-chloro-2-nitroaniline does not, can probably be attributed to the weaker basicity of the latter.

T. Birchall and R. J. Gillespie
Department of Chemistry
McMaster University, Hamilton, Ontario.

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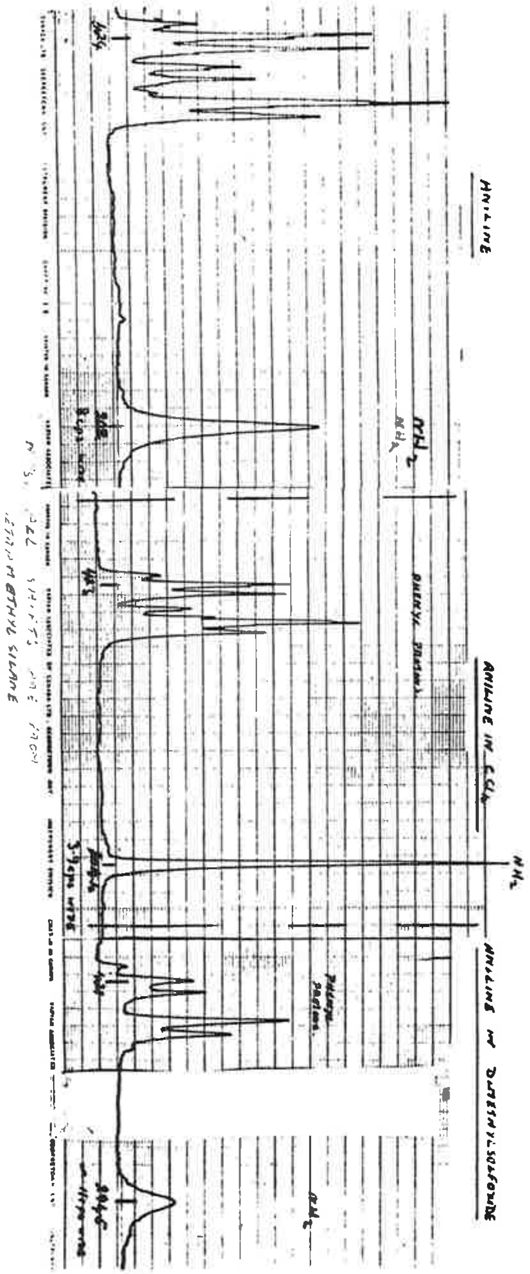
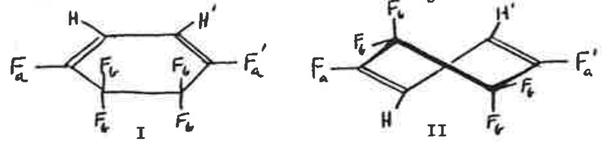


THE NMR SPECTRUM OF 2,3-DIHYDROHEXAFLUOROCYCLOHEXA-1,3-DIENE

The NMR spectrum of this compound, which was made by Mr. W.J. Feast of this Department, has some unusual features.

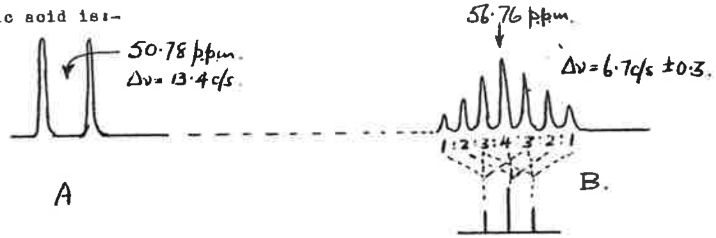
The compound may be represented in the planar form I, but the sterically favoured configuration is as in II, where nuclei F_b should be distinguishable



as pseudo-axial and pseudo-equatorial. The absence of any such distinction in the ^{19}F spectrum indicates that the molecule has a relatively rapid inversion frequency at room temperature giving the time-averaged configuration I.

The proton spectrum (32Mc/s) is a simple triplet of separation 6.8 c/s at τ = 4.24.

The fluorine spectrum (30.107 Mc/s) measured relative to external trifluoroacetic acid is:-



On overall intensity, doublet A is assigned to the F_b pairs, each of which is coupled to the adjacent F_a with $J_{F_aF_b} \simeq$ 13.4 c/s. The F_a signal (B) should therefore be split into triplets of separation 13.4 c/s , which is just twice the observed separation of the components of the septet, and simplification in this way yields a triplet identical with the proton spectrum.

The protons and F_a constitute an A_2X_2 system which must therefore be approaching the limiting case where $J_{HH'}$ and $J_{F_aF_a'}$ are inaccessible and where, using the usual nomenclature, N = 13.4 c/s and L → 0.

i.e. $J_{HF} \simeq J_{H'F} \simeq$ 6.7 c/s., though,on line-width considerations, the coupling constants could differ by up to 1 c/s. This rather unexpected feature and the 2:1 ratio of the constants together with conformational inversion combine to produce the relatively simple spectrum observed.

J. Homer
L.F. Thomas

Department of Chemistry,
The University,
Edgbaston,
Birmingham 15.

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES
GIF-SUR-YVETTE (S.-&-O.)

TEL. : 928 50-05

Gif, July 11th 1961

Dr. A. A. BOTHNER-BY
Mellon Institute
4400 Fifth Avenue
PITTSBURGH 13 - Penna.

Dear Dr. Bothner-By,

In the course of the structure determination of some diterpenes, we investigated ABC-type spectra shown by the vinyl grouping of the molecule. We were able to compute coupling constants and chemical shifts by the method of S. Castellano and J. S. Waugh +.

Two of the compounds studied were manool (I) and sclareol (II). We have taken their spectra (60 Mc) in 5% acetone solution containing 1% of TMS as internal reference.

Coupling constants are given in cps, whereas chemical shifts are in τ units.

We were surprised to notice that J cis and J trans are nearly equal in those cases. Nonetheless, it was pleasant to find that the vinyl lines of the spectrum are sensitive to differences in the molecular structure several bonds away.

We shall carry on this kind of studies, and try to find some correlations between the variations of the coupling constants and structural as well as stereochemical features of the molecules.

We wish to add how glad we are to receive the MELLONMR letters : they are very useful.

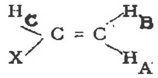
Sincerely yours,

+S. Castellano, J. S. Waugh, J. Chem. Phys., 34, 295 (1961)

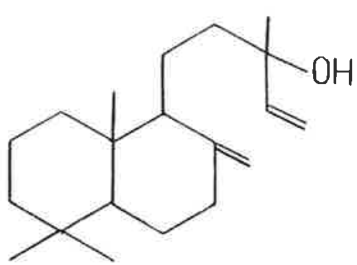
E. Lederer — E. Lederer

P. Laszlo — Pierre Laszlo

A. Gaudemer — Alain Gaudemer

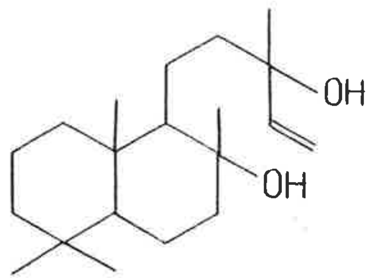


J_{BC}	J_{AB}	J_{AC}	H_C	H_B	H_A	
15,1	0,8	14,4	4,113	4,822	5,056	I
15,4	0,8	13,6	4,117	4,837	5,107	II



Manool

I



Sclaréol

II

THE UNIVERSITY OF TEXAS
DEPARTMENT OF CHEMISTRY
AUSTIN 12

July 19, 1961

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

Dear Dr. Bothner-By,

I must apologize for having required so much prompting in order to make another contribution to MELLONMR. The fact is, that after a long time of having to play the interested by-stander, we have just recently installed a spectrometer here and are now in business again. As a result I hope that a very brief resume of some of our current work will serve as a temporary bolster to my subscription and I will promise to follow up shortly with more details on some of our projects.

Since our spectrometer was put into operation I have again had the opportunity to do some work with hydrogen-bonding systems along the lines that I reported last year. The primary problem has been in trying to untangle all the hydrogen-bonded species that are generally present in a solution at the same time. The inability to make definite chemical shift assignments for dimer species in alcohols, for example, has made it impossible to decide conclusively on monomer-dimer equilibrium constants and heats of dimerization. In order to get around this difficulty we have synthesized several highly hindered alcohols such as di-i-propyl-n-propyl carbinol which are either too highly hindered to hydrogen-bond at all or can at best form only dimers. We are currently investigating solutions of these alcohols at different concentrations and temperatures by both infra-red and nmr techniques with the hope of obtaining unambiguous equilibrium constants and related quantities. It also appears that it may be possible to establish relationships between the nmr and IR data which will permit estimating dimer chemical shifts in solutions where higher polymers may prevent a simple and direct measurement of these shifts.

Along these same lines, Mrs. Lila Gatlin and I are conducting studies of the proton spectra of amino acids, purines, pyrimidines, ribosides, and nucleotides in solvents such as dimethyl sulfoxide and trichloroacetic acid. The former solvent appears to be ideally suited for these systems and a number of NH and OH protons which were formerly unseen have been located in this solvent. In addition, there have appeared some interesting splittings and broadenings which vary with concentration and temperature indicating some interesting exchange and conformational changes. I hope we can report more details on this work in the very near future.

Another project now under way involves a study of the B^{11} spectra of tetrahedrally substituted boron ions such as BF_4^-, BCl_4^-, $B(CH_3)_4^-$, etc.. In these ions changes in substituents on the boron should not change the hybridization of the boron so long as all four substituents are the same. Thus one would expect a rather regular dependence of the B^{11} shielding on the electronegativities of the substituents and our studies have confirmed this. In addition it seems plausible to assign significant electronegativities to other groups such as CH_3, OCH_3, etc., on the basis of the B^{11} shifts. More on this soon, also. Some work has also begun on association and exchange phenomena in B^{11} and Al^{27} compounds using both the metal and proton spectra.

Finally, we have begun some studies of the structures and internal motions of dibenzene chromium and related compounds, particularly wide-line work. These compounds are rather interesting from the standpoint that x-ray analysis indicates that the benene ring in these compounds may consist of C-C bonds close to the normal single and double bond lengths rather than having all the C-C bonds of the same length. If this is true there may be some rather interesting possibilities in terms of bonding, restricted intramolecular motion, and isomers.

Let me also take this opportunity to congratulate your group on MELLONMR. It is an invaluable source of information and is eagerly awaited every month. I hope this note will serve to keep me on the mailing list until more substantial results can be reported. Thanks.

Sincerely yours,

Jeff Davis

Jeff C. Davis, Jr.

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

July 14, 1961

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

Dear Dr. Bothner-By:

During my two years here as a postdoctoral fellow working for Dr. Roberts I have derived immense benefit from MELLON-M-R. Now that I'm about to leave I find that the loss of the availability of this publication would cause a void virtually impossible to fill, and I would very much appreciate being put on your mailing list. As an initial contribution I would like to report some results of an investigation into long-range proton-proton coupling constants.

I have taken spectra of allenes and polyacetylenes and have determined coupling between protons separated by 5 to 9 bonds (J_{14} to J_{18}). The magnitude of the coupling constants are tabulated below; the sign of J_{14} (relative to J_{12}) in 1-chlorobutadiene-1, 2 was determined both by analysis of the ABX_3 spectrum and by recording the spectrum at 40 and 60 mc. Coupling in symmetrical systems and in pentadiene-1, 3, where the acetylenic and methyl protons are nearly degenerate and form an AB_3 system, was determined from ^{13}C-satellite spectra.

Compound	x	J_{1x} (c.p.s)
$(CH_3)_2C{=}C{=}CH_2$	4	3.1
$(CH_3)_2C{=}C{=}CHCl$	4	2.1
$CH_3CH{=}C{=}CHCl$	4	+2.4
$HC{\equiv}C{-}C{\equiv}CH$	4	2.2
$CH_3C{\equiv}C{-}C{\equiv}CH$	5	1.3
$CH_3C{\equiv}C{-}C{\equiv}C{-}CH_3$	6	1.3
$ClCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2Cl$	6	1.0
$CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OH$	8	0.4
$HC{\equiv}C{-}CH{=}CHOC_2H_5$	J_{13} = 2.4	J_{14} = 0.8

The presence of long-range coupling in polyacetylenes can be quite nicely accounted for, at least qualitatively, on the basis of cumulenic contributing structures, e.g., $CH_3C{\equiv}C{-}C{\equiv}C{-}CH_3 \leftrightarrow \overset{H}{C}H_2{=}C{=}C{=}C{=}C{=}\overset{H}{C}H_2$. One can also calculate hyperfine constants from n.m.r. data by utilizing in reverse the procedure of Karplus [J. Chem. Phys., 33, 1842 (1960)]. In this way one obtains the following values (unpaired electrons in a p orbital, σ-bond sp hybridized):

	A_H (c.p.s.)
$CH{-}C{=}C\cdot$	$+37 \times 10^6$
$HC{\equiv}C{-}C\cdot$	22×10^6
$CH{-}C{\equiv}C{-}C\cdot$	$\sim 14 \times 10^6$

I hope you find the above work of sufficient quality and interest to warrant a subscription.

Sincerely,

Eugene I. Snyder

Eugene I. Snyder

EIS:jmm

Dear Dr. Bothner-By!

Thank you for your letter of 5th march. I send you a reprint of our last article in Double Resonanse field.

Our group of physicists conducts so theoretical as experimental work in Electron and Nuclear Magnetic Resonanse field. Particulary, at present we are interested in magnetic resonanse phenomena in a weak magnetic fields; in Double Electron and Nuclear Resonance; in Optical Pumping.

I shall inform you of our following work.

Glad to be of any use to you.

Sincerely

20/VI 61.

G. B. Skrotskii

Ural Polytechnic Institute
Sverdlovsk, Russia

um Reprint geschrieben 18.8.61 R

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Editor's Corner

The July issue of Bulletin du Groupement d'informations mutuelles Ampère contains the program of the 10th Colloque Ampère which will take place in Leipzig, East Zone, in September. There are many papers dealing with electron spin and nuclear magnetic resonance. The largest representations are from the French, Swiss, and East German schools.

Dr. Skrotskii (see last letter in this issue) has sent several reprints including К теории двойного электронного и ядерного резонанса в системах со сверхтонким взаимодействием' and "Применение преобразования Лапласа в теории магнитного резонанса и релаксации"

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DEADLINE FOR NEXT ISSUE

Monday, 28 August

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