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Mailed: **DEC 5 - 1960**

Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R
No. 26

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National Physical Laboratory

TEDDINGTON · MIDDLESEX

Please reply to the DIRECTOR and quote our reference Telegrams: Physics, Teddington Telephone: 276000, Ext. 199

OUR REF: BP.A.A.1.
BP.A.F.1.

BASIC PHYSICS DIVISION

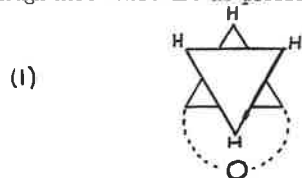
YOUR REF:

10th November, 1960.

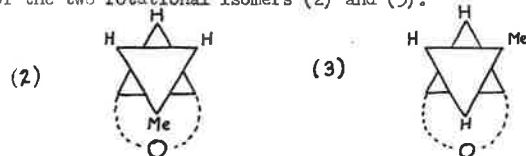
Dear Dr. Bothner-By,

My apologies for the delay in contributing to your excellent news letter. We have been concerned with the usual magnet teething troubles. However, now all is well and here is our contribution.

One of the subjects we are investigating here is the rotational isomerism of aldehydes. Acetaldehyde is known to have the staggered configuration (I), though here there are no possibilities for rotational isomerism.



It is not unreasonable to suppose that Propionaldehyde will consist of the two rotational isomers (2) and (3).



The $\text{CHO}-\text{CH}_2-$ proton-proton coupling constant in (2) has the value J , and in (3) the value $\frac{1}{2}(J + J_n)$ where J and J_n are the gauche and trans coupling constants respectively. However, neither J , J_n nor ΔH , the energy difference between the isomers (2) and (3) is known. In such a case in which all the parameters which determine the variation of the observed coupling constant with temperature are unknown, it is usually only possible to obtain estimates of the values of these parameters by studying the variation of J with temperature. However, if we assume that J_n and J are the same in acetaldehyde and propionaldehyde then we have the additional equation $\frac{1}{3}(2J + J_n) = 2.86 \text{ c.p.s.}$, the acetaldehyde coupling constant, and we can now obtain more accurate values of the three unknowns. These values are of course only valid to the extent that the assumption of constant J 's is valid. Figure 1 shows the variation of J with temperature for liquid acetaldehyde and propionaldehyde, measured by the wiggle beat technique. The acetaldehyde coupling constant (2a) is essentially independent of temperature and from this we assume that J_n and J_c

/are



- 2 -

Dr. Bothner-By.

10th November, 1960.

are themselves independent of temperature. The propionaldehyde coupling constant (2b), however, varies considerably over the temperature range investigated and from this curve we obtain $J = 0.1 \text{ c.p.s.}$, $J_n = 8.3 \text{ c.p.s.}$ and $H = 1.0 \text{ kcal/mole}$ in favour of II. These values of the coupling constants are only slightly lower than those found in substituted ethanes, despite the change from tetrahedral to trigonal hybridisation of one of the carbon atoms.

A full account of this work has been given elsewhere (1).

Also in collaboration with Dr. A.H. Jackson and Prof. G.W. Kenner of the University of Liverpool, we have been studying the P.M.R. of the porphyrins in trifluoroacetic acid, in which solvent they exist as the dication (fig. 2). These compounds are of some interest due to the large ring current they possess. It is possible to give a semi-classical calculation of the ring current which is in good agreement with the observed ring current shifts. Also one can in many cases distinguish different porphyrin isomers by P.M.R. and an example of this is shown in fig. 2. The P.M.R. spectrum of mesoporphyrin II dimethyl ester ($R_{3,6,7} = \text{Me}$, $R_{4,8} = \text{Et}$, $R_{2,6} = \text{Pe}$ where Pe stands for the methyl propionate side chain) is given in 2a and that of the IX isomer ($R_{1,3,5,8} = \text{Me}$, $R_{2,4} = \text{Et}$, $R_{6,7} = \text{Pe}$) in 2b. The values given are τ values (T.M.S., $\tau = 10.00$).

The spectra are easily distinguished by the peaks due to the meso and N-H protons.

Finally we were very interested to read Dr. Jackson's letter (Mellon No. 21) and his description of proton double irradiation experiments. Dr. Freeman has done some proton spin decoupling experiments here with a Varian 60 Mc/s spectrometer using only a very simple lock-in detector as ancillary equipment. This works well in situations where the decoupling frequency is not too close to the measuring radiofrequency. A short note describing the method will shortly be published (2).

Yours sincerely,

R.J. Abraham
Basic Physics Division

References: (1) R.J. Abraham & J.A. Pople. Mol. Phys. (in press)
(2) R. Freeman Mol. Phys. (in press)

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

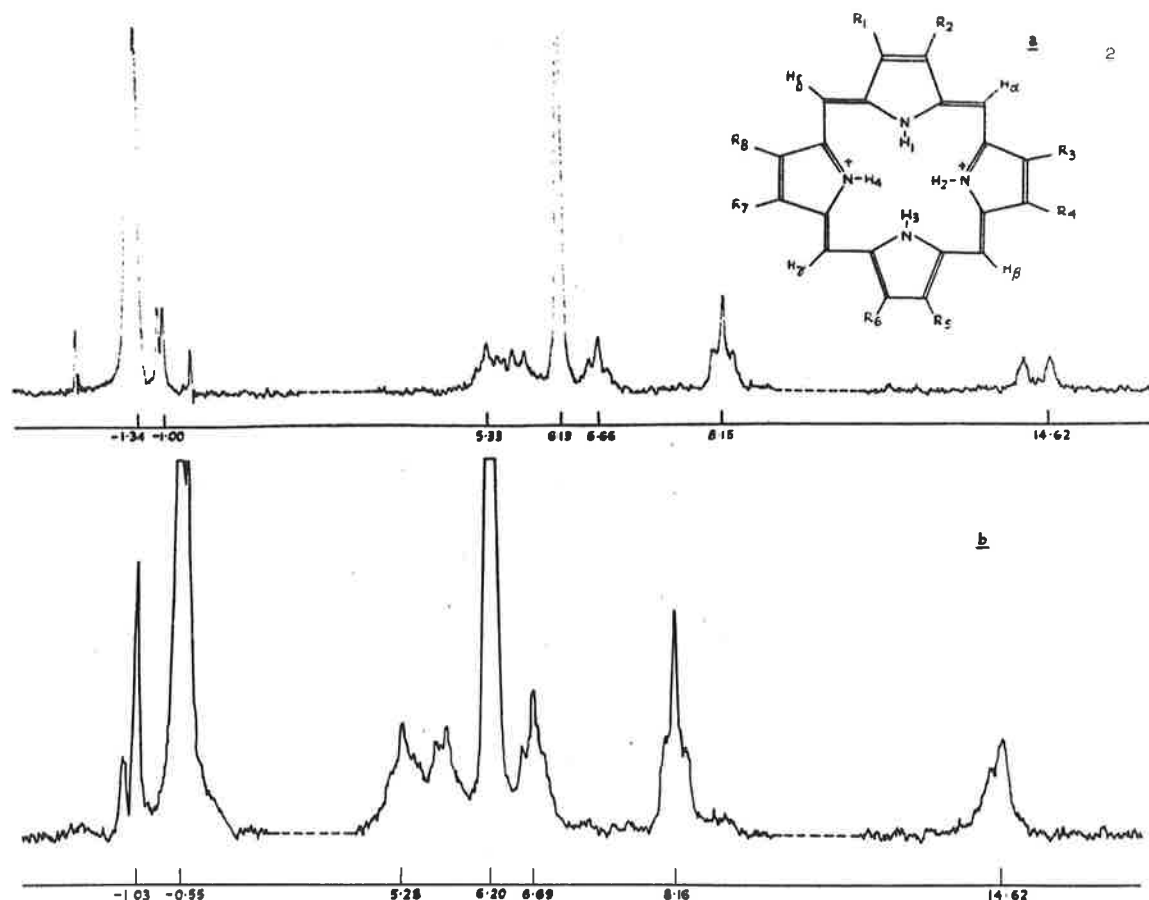


Fig. 2. The P.M.R. spectrum of (a) Mesoporphyrin II dimethyl ester and (b) Mesoporphyrin IX dimethyl ester in Trifluoroacetic acid solution at 60 Mc/s. Assignment (a) -1.34 T.F.A.; -1.07 α, γ -1.00 β, δ ; 5.33 $\text{CH}_2\text{-CH}_2\text{-CO}_2\text{Me}$; 5.71 $\text{CH}_2\text{-CH}_3$; 6.19 Me; 6.66 $\text{CH}_2\text{-CO}_2\text{Me}$; 8.15 $\text{CH}_2\text{-CH}_3$; 14.36 2,4; 14.62 1,3. Assignment (b) is identical save -1.18 γ ; -1.03 α, β, δ .

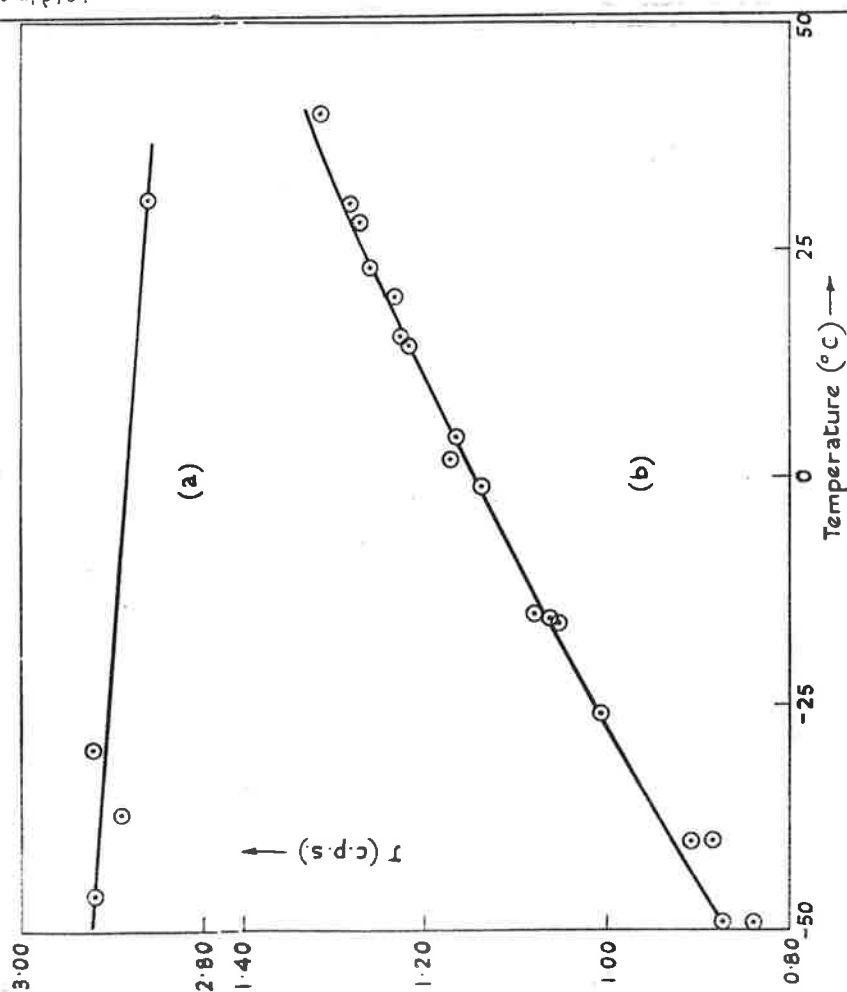


Figure 1. The temperature dependence of the coupling constants $J_{\text{CH-CHO}}$ in Acetaldehyde (a) and Propionaldehyde (b).

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 18, PA.

H^1 NMR Spectra of Deuterated Azulenes and Azulinium Ions

In connection with the preparation of deuterated azulenes for study of their C^{13} NMR spectra, the H^1 spectra of azulene, azulene-1,3- d_2 , 4,6,8-trimethylazulene and 4,6,8-trimethylazulene-1,3- d_2 in CS_2 solution, and of the corresponding ions in CF_3COOH and CF_3COOD solutions, have been obtained. Several of the spectra are shown in the Figures. Comparison with the spectra of Danyluk and Schneider⁽¹⁾ will show that the doublet at lower field in the spectrum of the five-membered ring of the azulinium ion arises from the proton at position 2. A trace of the doublet from the hydrogen at position 3 remains, as does a peak from the CHD and CH_2 groups.

The 4,6,8-trimethylazulene spectrum is identical with that given by Hoffmann⁽²⁾. As expected, the doublet from the 1,3-protons nearly vanishes in the deuterated material and the triplet from the 2-proton becomes a singlet. In the spectrum of the ion we find two slightly broadened peaks from the non-equivalent 5- and 7-protons and a singlet from the 2-proton, along with some residual peaks from partially deuterated molecules. The methyl peaks have become nearly coincident and the 4- and 8-methyls are no longer equivalent. The near-equivalence of the methyls is consistent with the suggestion of Danyluk and Schneider⁽¹⁾ that the

2.

ionic charge is spread rather evenly around the seven-membered ring.

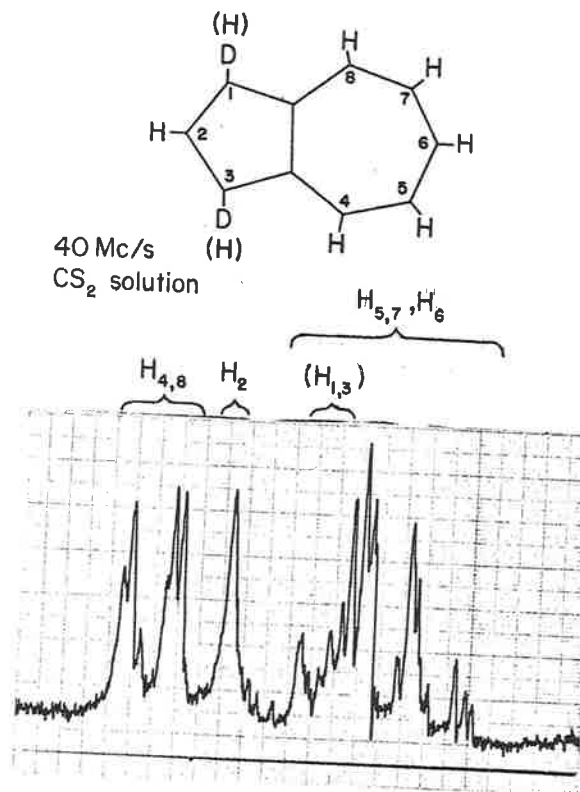
No chemical shift measurements were made on these spectra, which were used only to check on the progress of the deuterium exchange, and it is unlikely that they will be published, since others are undoubtedly carrying out similar experiments in more detail.

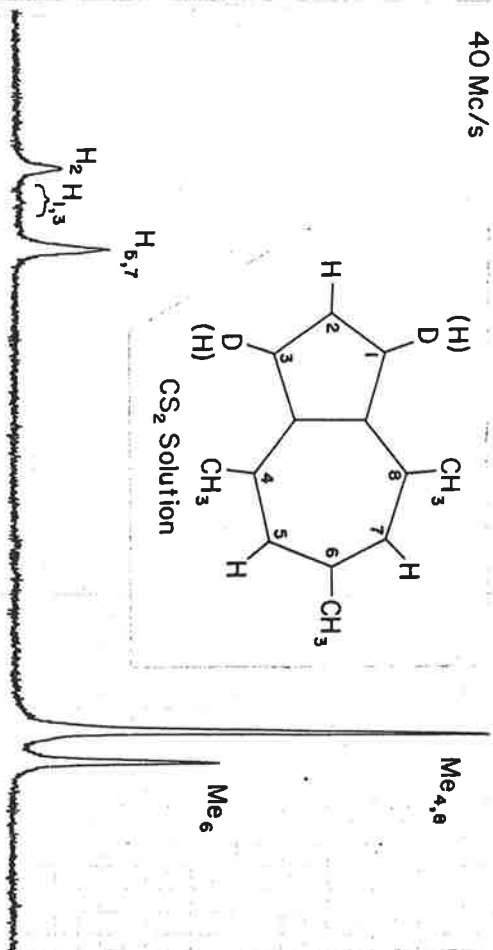
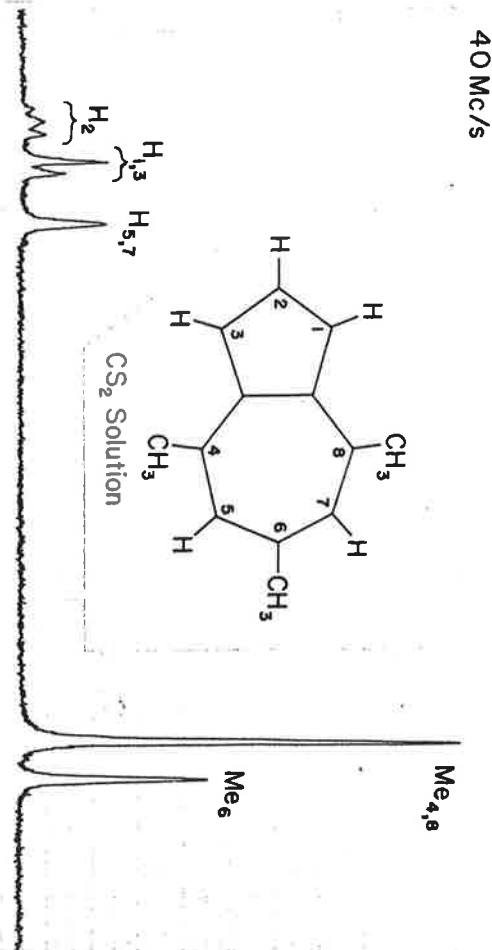
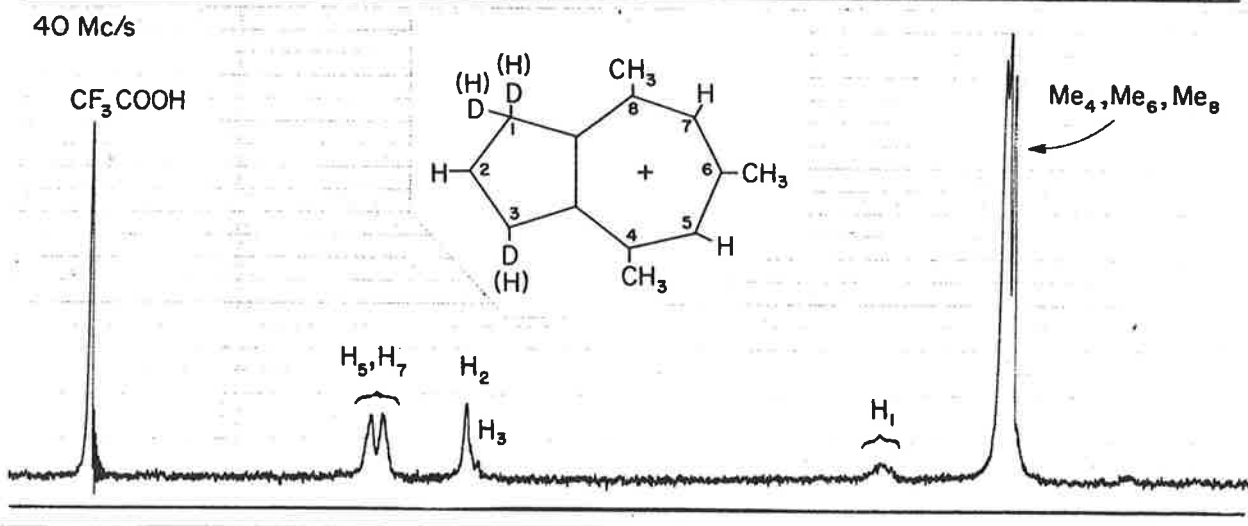
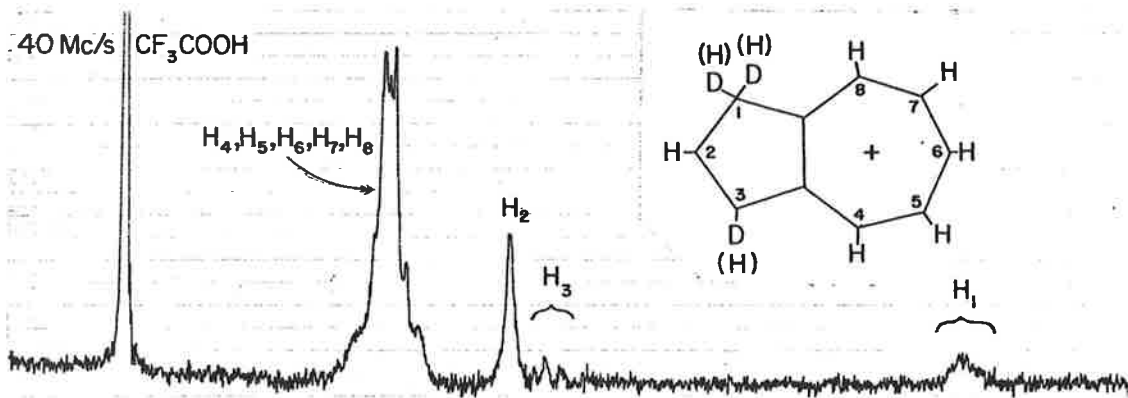
Paul C. Lauterbur
Paul C. Lauterbur

Mellon Institute

(1) S. S. Danyluk and W. G. Schneider, J. Am. Chem. Soc. **82**, 997 (1960).

(2) E. G. Hoffmann, Z. Anal. Chem. **170**, 177 (1959); Ann. **624**, 47 (1959).





UNIVERSITY OF WASHINGTON
DEPARTMENT OF CHEMISTRY
SEATTLE 5

October 27, 1960

KENNETH B. WIBERG

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

Dear Aksel:

We also have the problem of trying to assimilate the data which pours from our computer using your seven-spin program. We are not as fortunate as John Waugh in that we do not have a scope display attached to our computer. Therefore, we have written a program which takes the output tape from your program, produces an ordered list of frequencies, and then prepares a list of summed intensities based on Gaussian curves at 0.05, 0.1, 0.2, 0.5 or 1.0 cycle intervals, depending on the frequency range for the particular case.

Since you might find this to be useful, I have sent a set of Fortran statement cards to you. Our program was compiled on an IBM-709 and therefore the object program would probably not be of value to you. The program uses the tape assignments: 5 = input, 6 = output, 9 = NMR program output tape. It requires two data cards, copies of which are enclosed with the other cards. The first has some masking constants and the second has the band width in columns 1-10, and either 0 or 1 in column 20. With a zero in column 20, the program operates normally, and with a one, the frequency range may be specified using additional cards. A sample program output (from the first set of data you included with the program you gave me) is enclosed.

If anyone who has received your program is interested in the one described here, I would be glad to send him a copy also.

I am planning to try to write a program similar to yours, but with the ability to use symmetry in factoring the secular equation, thus making it possible to conveniently go to 8-10 spin cases where there is some symmetry. It would help me considerably if I could obtain a listing of the Fortran statement cards from which your program was compiled since I could probably use the subroutines without much alteration.

Sincerely,

KWB

KWB:jlp



Telephone KOYal 8221

Head of Department
A. J. LINDSEY, D.Sc., Ph.D.,
F.R.C., M.I.E.E.

SIR JOHN CASS COLLEGE,
DEPARTMENT OF CHEMISTRY,
JEWRY STREET, ALDGATE,
LONDON, E.C. 3.

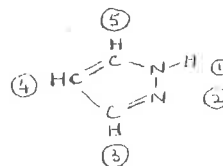
22nd. November, 1960.

The N.M.R. Spectra of Pyrazole and N-Methyl Pyrazole.

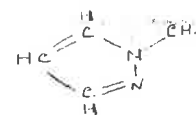
As part of a general study of the orientation of substitution reactions in heterocyclic molecules we have recently examined the N.M.R. spectra of Pyrazole (I) and N-Methyl Pyrazole (II). Several points of interest have shown up in the preliminary experiments.

The spectrum of pyrazole dissolved in NaOD-D₂O consists of the expected triplet due to the proton in the 4 position and a doublet due to the protons in the 3 and 5 positions, the 3 and 5 positions being equivalent as pyrazole exists mainly as the conjugate base in this solvent. The spectrum of pyrazole dissolved in sulphuric acid has a broad peak at low field indicating that protonation of a nitrogen atom occurs in this solvent. The peaks due to the -CH groups show more fine structure than in the spectrum of pyrazole in an alkaline medium, at present our incomplete measurements suggest that the conjugate acid formed in sulphuric acid solution has the symmetrical structure (III).

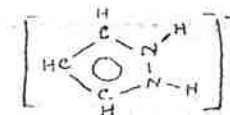
The spectrum of the ring protons of liquid N-methyl pyrazole consists of three groups of lines (IV), the 3 and 5 protons being non-equivalent in this compound. One line is sufficiently broadened for the fine structure to be lost. Broadening of lines has been observed in the spectrum of thiazole (V) (Taurins and Schneider, Canadian Journal of Chemistry 1960 38, 1237.) accordingly the broadened peak in the spectrum of N-methyl pyrazole has been tentatively assigned to the proton in the 3 position. The spectrum of N-methyl pyrazole dissolved in D₂O is simpler than that of the pure liquid, the ring protons giving a spectrum consisting of a triplet and a doublet (similar to the spectrum of pyrazole itself). Apparently solvent-solute interaction is such that (a) the 3 and 5 protons become equivalent in solution and (b) the effects of quadrupole broadening are eliminated.



(I)



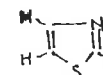
(II)



(III)



(IV)



(V)

R. White
R. White.

UNION CARBIDE CHEMICALS COMPANY

RESEARCH DEPARTMENT

SOUTH CHARLESTON 3, W. VA.

November 22, 1960

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

Dear Dr. Shapiro:

Thank you very kindly for adding my name to your mailing list of MelloN-M-R. You are rendering a very fine service with MelloN-M-R, and I congratulate you people for it.

Some of your readers may be interested in a simple modification of--or, more accurately, addition to--the R-F unit of the Varian N-M-R Spectrometer which makes possible a convenient measurement of thermal relaxation time, T_1 , using the "saturation curve" method of Bloembergen, Purcell, and Pound. I have used this arrangement with quite satisfactory results for the past 3 years with the V-4310 40 Mc R-F unit, and for the last 3 weeks with a new V-4311 40 Mc R-F unit.

Figure 1 shows the block diagram of the system used with the Varian V-4310 or V-4311 R-F units. Except for a very simple aluminum junction box (Figure 2) which can be assembled and wired in a matter of minutes, all parts are commercially manufactured equipment. The Daven Model 651-93 R-F attenuator boxes cover the range of 0-100 db in 1 db steps, have characteristic impedances of 93 ohms, and are manufactured by the Daven Company, Livingston, N. J., selling for about \$150 each. The Model IF31M supplementary R-F amplifier is a low-noise-figure (1.5 db), fixed-gain (60 db), fixed-frequency (40 Mc) unit custom built for us by LEL, Inc. of Copiaque, N. Y., for about \$385; its bandwidth is about 0.5 megacycle, and both input and output impedances are 93 ohms. (It is essentially a slight variation of LEL Model IF31, which is

Dr. B. L. Shapiro
Page 2
November 22, 1960

priced near \$200). An external power supply is required for the IF31M amplifier; we use a Hewlett-Packard Model 712B.

The junction box (Figure 2) utilizes 4 type BNC coax receptacles, 4 half-watt carbon resistors (not wire-wound), and 5 disc ceramic capacitors. Its function is to supply plate voltage from the Varian Receiver input terminal to the plate of the Varian Preamplifier, while keeping this plate voltage off both the LEL amplifier input and the Daven attenuator, and while channeling the signal through the LEL amplifier-Daven attenuator circuit.

In running a "saturation-curve", the sum of the attenuation in transmitter and receiver attenuator boxes is kept constant (usually at values of 60 to 70 db) as the transmitter attenuation is changed in, say, 5 db steps over the range from, say, 55 db to 0 db. The amplitude of absorption line-shape (or, alternatively, its derivative) can then be observed as a function of transmitter attenuation; when this amplitude "saturates" to half the amplitude obtained at very high transmitter attenuation, then it will be true (under certain conditions) that $\nu^2 H_1^2 T_1 T_2 \cong 1$. Knowing H_1 from previous calibration, and obtaining T_2 from the linewidth, T_1 can then be computed, if desired. While this is a rather indirect measurement, it often is quite valuable. Particularly is this true when one wants to be sure that a (weak) signal is not suffering line-shape distortion due to excessive transmitter power.

Although this modification was primarily intended for use in wide-line N-M-R studies, it has occasionally been very useful in high-resolution work. One of its principal virtues is that the new "saturation-curve" circuit ^{may} be brought into (or removed from) the normally operating Varian Spectrometer by the simple reconnection of 2 or 3 coax cables, a procedure that takes less than 30 seconds.

Yours truly,

Charles W. Wilson III

Charles W. Wilson, III

CWW/mhw

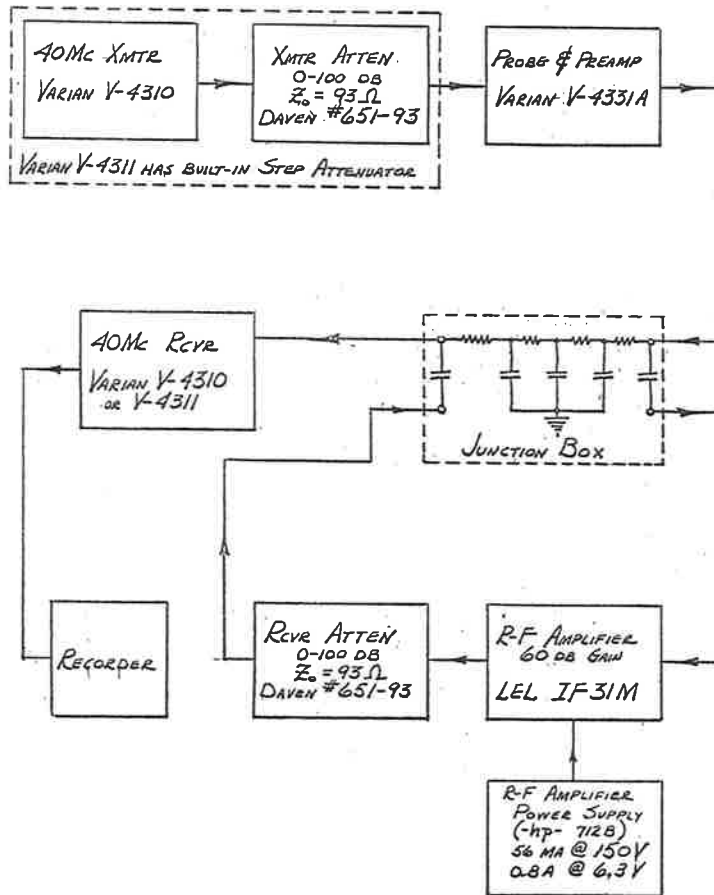
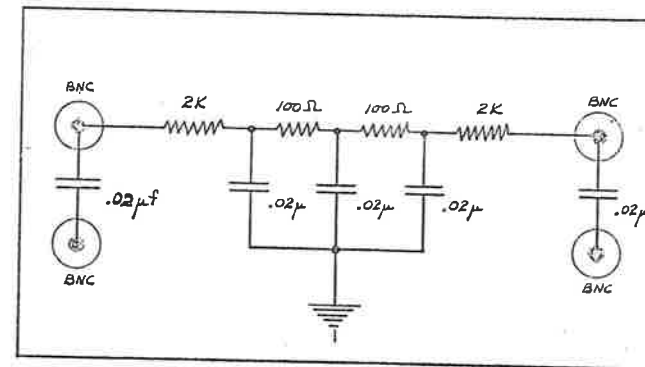


FIG. 1: BLOCK DIAGRAM OF "SATURATION CURVE" MODIFICATION

CWV III
11/22/60



ALL RESISTORS $\frac{1}{2}$ WATT CARBON
ALL CAPACITORS 0.02 μ F DISC CERAMIC
ALL TERMINALS TYPE "BNC" COAX RECEPTACLES

FIG. 2: JUNCTION BOX

CWV III
11/22/60

AMERICAN CYANAMID COMPANY
STAMFORD RESEARCH LABORATORIES
1837 WEST MAIN STREET, STAMFORD, CONN.
FIRESIDE B-7931

November 18 1960

Dr. B. L. Shapiro
MELLONMR News Letter
Mellon Institute
Pittsburgh, Pennsylvania

Dear Barry:

I would like to report the results of some work done recently at these Laboratories under the direction of Dr. R. W. Young in connection with O,O-diethyl methylphosphonothioate, $\text{CH}_3\text{P}(\text{S})(\text{OCH}_2\text{CH}_3)_2$. Finegold (J.A.C.S. 82, 2641 (1960)) recently observed sixteen lines for the CH_2 proton resonance instead of the usual eight (two overlapping quartets). He proposed the explanation that the two ethoxy groups were somehow not equivalent. Dr. Young, with the assistance of Miss G. Peters, has synthesized this compound, as well as some related ones, and I have observed their H^1 NMR spectra at 60 mc.

The spectrum obtained for the CH_2 groups in O,O-diethyl methylphosphonothioate shows more detail than that reproduced in Finegold's paper, with considerably more than sixteen lines appearing. I am enclosing one of the traces of the CH_2 multiplet that we obtained. The extra lines are the weak lines which appear at both the low and high field side of the strong lines. (Incidentally, x and z field gradients were minimized with the Varian electric shims to remove spurious side-bands). These weak lines are no doubt the outer lines of the familiar AB pattern with large J/6 (Pople, Schneider and Bernstein, p. 122, figure 6-1 (c)), and it is this pattern which appears eight times to give the observed spectrum. Thus, the spectrum arises from the non-equivalence of the two protons in each CH_2 group, and not from any difference between the two ethoxy groups.

A more direct proof was furnished by the isomer, O,S-diethyl methylphosphonothioate, $\text{CH}_3\text{P}(\text{O})(\text{SEt})(\text{OEt})$, which was also prepared by Dr. Young and Miss Peters. The same type of spectrum for the $-\text{OCH}_2$ group was observed even though there is only one ethoxy group present. The S- CH_2 resonance, which appears at higher field than the O- CH_2 resonance, gives only the normal spectrum of eight lines.

- 2 -

The explanation of the non-equivalence of the CH_2 protons appears analogous to the explanation of the similar phenomenon in substituted ethanes of the type CH_2RCXYZ (J.A. Pople, Mol. Phys. 1, 3 (1958)), even with rapid rotation about the C-C bond.

Here we have the structure $\text{CH}_2\text{R-O-PXYZ}$, where, although we have replaced the C-C bond by a bent C-O-P bond, the situation remains formally the same as in the ethane case. The criterion for non-equivalence of the CH_2 protons is also the same, that is, none of the possible rotational isomers contains a plane of symmetry. Evidently the degree of asymmetry produced in these two isomeric phosphonothioates, where $\text{X}=\text{C}$, $\text{Y}=\text{O}$, $\text{Z}=\text{S}$, is sufficient to produce the required non-equivalence at the CH_2 protons. The normal eight-line pattern might be expected for $\text{CH}_3\text{P}(\text{O})(\text{OEt})_2$, since Y and Z are now both oxygen, and this is observed. This also accounts for the normal spectrum of the -S- CH_2 - resonance in $\text{CH}_3\text{P}(\text{O})(\text{SEt})(\text{OEt})$. One might expect the -S- CH_2 group in $\text{CH}_3\text{P}(\text{O})(\text{SEt})_2$ to show non-equivalence, but we observed the normal spectrum here. The lack of a plane of symmetry is, of course, only a necessary condition for the appearance of the non-equivalent spectrum, not a sufficient one.

Finegold observed a temperature independence of the spectrum. We would conclude that the energy differences of the three possible rotational isomers must be very small.

We also observed non-equivalence of the OCH_2 group in the compound O-ethyl-N,N-diethyl methylphosphonamidate, $\text{CH}_3\text{P}(\text{O})(\text{OEt})(\text{NEt}_2)$, where the sulfur atom is replaced by nitrogen.

In the enclosed spectrum, the H-H coupling is observed to be 10.3 cps., which is the correct order of magnitude. The regular progression of increasing spacings in the strong peaks as one goes to lower field can be accounted for only by assuming that the rotationally averaged couplings to both the P and CH_3 groups are very slightly different for each of the two methylene hydrogens.

We are planning to publish a complete discussion of the work.

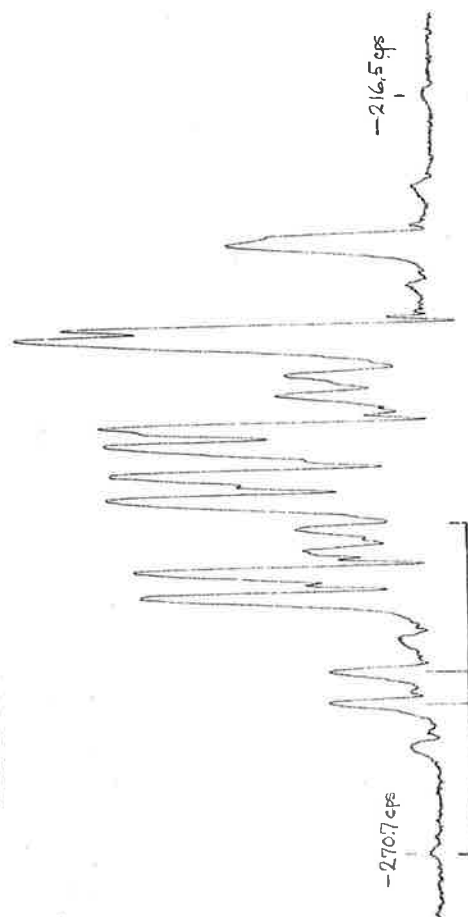
Very truly yours,

John E. Lancaster
John E. Lancaster, Group Leader
Magnetic Resonance Group
Research Service Department

JEL/dm
enclosure

Lancaster, continued,

The proton NMR spectrum of the CH_2 groups in 0,0'-diethyl methylphosphonothioate, taken as a 40% solution in CCl_4 . A typical AB pattern is indicated at the low field side. This spectrum was taken at 60 mc. and the calibration is referred to TMS.



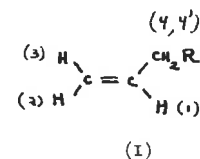
MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

Rotational Isomerism in Alkylethylenes

Pursuing the idea that the coupling constant $J_{1,4}$ in alkylethylenes (I)

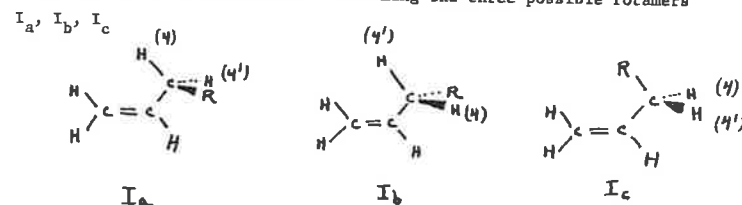


might be used as a measure of rotamer populations in alkylethylenes, we have made preliminary measurements of the constants in a number of olefins (Table I)

Table I

	J _{1,4} (cps)
Propene	6.40
Butene-1	6.22
3-methylbutene-1	6.41
Hexene-1	6.55
4-methylpentene-1	7.01
4,4-dimethylpentene-1	7.48

It appears that $J_{1,4}$ increases sharply with substitution of larger and larger groups as R in formula I. Assuming the three possible rotamers



a ready explanation is found if one supposes that the trans arrangement ($J_{1,4}$ in I_a , or $J_{1,4}'$ in I_b) is characterized by a large coupling constant and the gauche by a small. Then I_c is less and less favored as R becomes larger. The figures as found indicate $J_{\text{gauche}} \approx 3.7$, $J_{\text{trans}} \approx 11.3$ cps, as limits.

Paranthetically, we note that the pattern observed for the allylic protons in 4,4-dimethylpentene-1 is asymmetric, as expected for an ABCX₂ case (cf. N. Sheppard MELLONMR #25), and leads to the assignment +7.48 cps for J_{1,4}, if J_{1,2} and J_{1,3} are taken as positive. The asymmetry is not as pronounced in the methyl signal from propylene, but in that case also, the sign for J_{1,4} appears to be the same as J_{1,2} and J_{1,3}.

A. Bothner-By

C. Nagar-Colin



SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

November 25, 1960

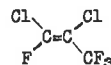
TELEPHONE OLYMPIC 3-2100

A DIVISION OF
SHELL OIL COMPANYDr. A. A. Bothner-By
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel:

The readers of MELLONMR may be interested in some work that Jerry Swalen and I have completed recently.

Following up the suggestion of Fessenden and Waugh (J. Chem. Phys. 30, 944 (1959)) that signal "X" in the spectrum of $\text{CF}_3\text{CCl}=\text{CFCl}$ arises from one of the isomers, we have definitely proved that such is the case by analyzing both the 40 Mc/sec and 60 Mc/sec spectra. The more abundant isomer has the cis configuration



and signal "X" belongs to the spectrum of the trans isomer. We have also analyzed the spectra of the related propenes $\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_3\text{CCl}=\text{CF}_2$. The NMR parameters are collected in the following table.

NMR Parameters for

X ₁ X ₂ X ₃ X ₄	ppm from Ext. Reference: CF ₃ group in CF ₃ CF ₂ COOH				cps						
	δ ₁	δ ₂	δ ₃	δ ₄	J ₁₂	J ₁₃	J ₁₄	J ₂₃	J ₂₄	J ₃₄	
F F F CF ₃	11.6	25.1	110.6	-13.0	60.0	40.3	8.7	120.2	22.0	13.2	
F Cl Cl CF ₃	-25.0			-23.7			10.4				
Cl F Cl CF ₃		-18.4		-23.5					24.3		
F F Cl CF ₃	-6.2	-5.9		-18.6	16.65		9.20		23.83		

The parameters for $\text{CF}_3\text{CF}=\text{CF}_2$ were obtained by first order perturbation theory, those for the two isomers of $\text{CF}_3\text{CCl}=\text{CFCl}$ were obtained from the traces of the sub-matrices ($F_2 = \pm 1, 0$) for an AB₃ system of spins and those for $\text{CF}_3\text{CCl}=\text{CF}_2$ were obtained by iteration to the experimental energy levels for an ABC₃ system of spins.

Preprints of a paper describing this work are available from either Jerry or me.

Sincerely yours,

C. A. Reilly

CAR:je1

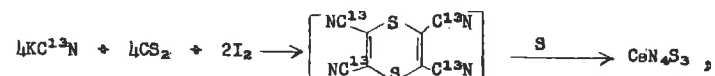
MELLON INSTITUTE

4400 FIFTH AVENUE

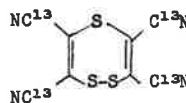
PITTSBURGH 13, PA.

The C^{13} NMR Spectrum ofTricyano-p-dithiino[2,3-d]-2,1-isothiazole (TCS_3)

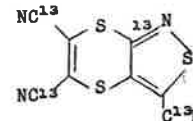
The product of the reactions



believed to have one of the two structures below,



I



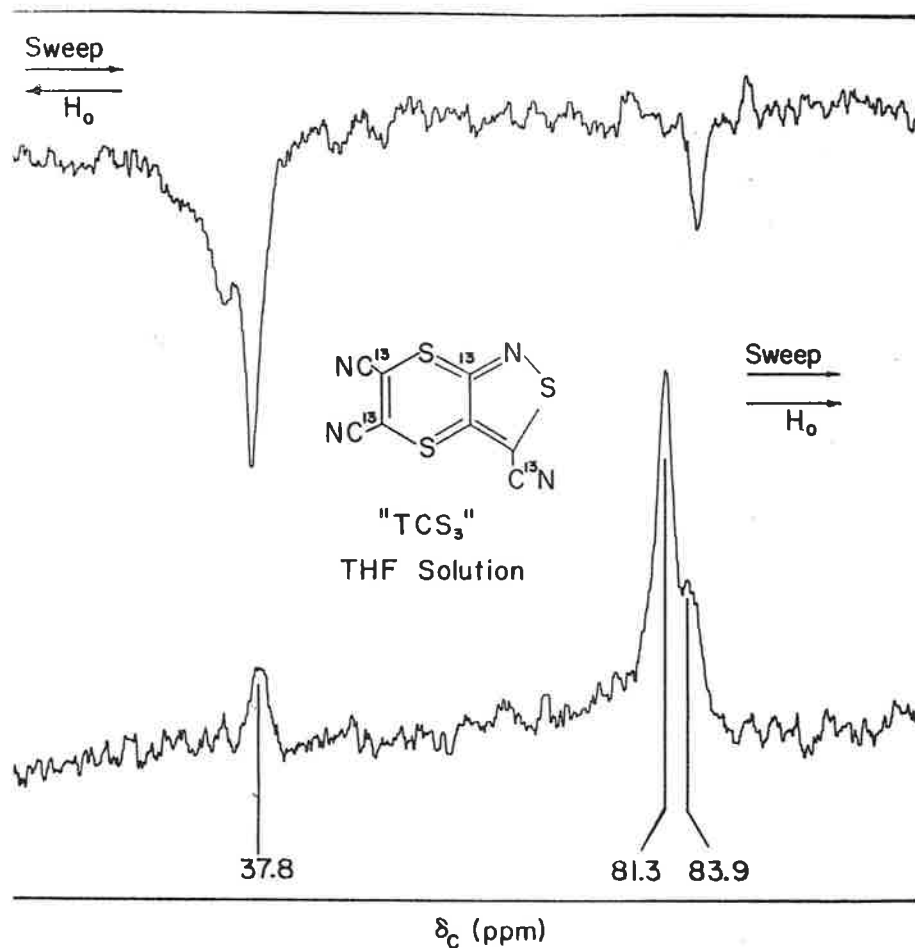
II

was sent to us by Harlan Foster and Howard E. Simmons of duPont. The KCN used was 65% enriched in C^{13} . 80 milligrams of the solid sample was dissolved in THF in a 5 mm. OD sample tube and rapid passage C^{13} spectra shown in the attached figure were run at 8.50 Mc/s. The chemical shifts given are relative to external CS_2 .

There can be no doubt that structure II is preferable to I. The peak at low field is close to the position predicted for the C^{13} in the ring in II (C-2,6' in 2,6-lutidine is at 35.6, and the shifts in thiophene are not much different from those in benzene). No C^{13} shifts of aromatic nitriles have been measured, but acetonitrile has $\delta_c = 73$ ppm. so the observed values are reasonable. The relative peak intensities are also consistent with II rather than I.

Simmons and co-workers plan to publish the details on the chemistry of TCS_3 and related compounds in the near future.

Paul C. Lauterbur



(Contribution from Mellon Institute)

Proton Magnetic Resonance, Structure and Stereoisomerism in Cyclic Sulfites

by J. G. Pritchard and P. C. Lauterbur

Abstract

The proton magnetic resonance spectra and structure of ethylene sulfite, ethylene sulfate, isobutylene sulfite and the two, stable, geometrically isomeric species of propylene sulfite are discussed. The isomerism in the propylene sulfite system is demonstrated for the first time; the isomers are characterized via vapor chromatography, infrared spectrum and refractive index, and a structural assignment is given from an analysis of the proton spectra. The value of 3.7₄ Debye units for the dipole moment of the ethylene sulfite molecule in benzene solution at 25° is reported.

A few preprints of the above paper are available, but some additional information on its contents might be given here for those who will be able to contain their curiosity until it appears in the J. Am. Chem. Soc. In order to decide which isomer of propylene sulfite has the methyl group cis to the >S=O oxygen, an attempt was made to calculate the effects of the dipole moment and the magnetic anisotropy of the S=O group on the shifts of the ring hydrogens. The differential effect of the electric field, using the method of Buckingham [A. D. Buckingham, Can. J. Chem. **38**, 300 (1960)], turned out to be about 0.05 ppm., with the protons cis to the S=O at lower field. Reasonable assumptions about the magnetic anisotropy of the S=O bond lead to a shift in the same direction as that resulting from the electric field (fortunately) and the magnitude of the effect is right if

$$\Delta\chi = \chi_{xx} - \chi_{zz} = +6 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1}$$

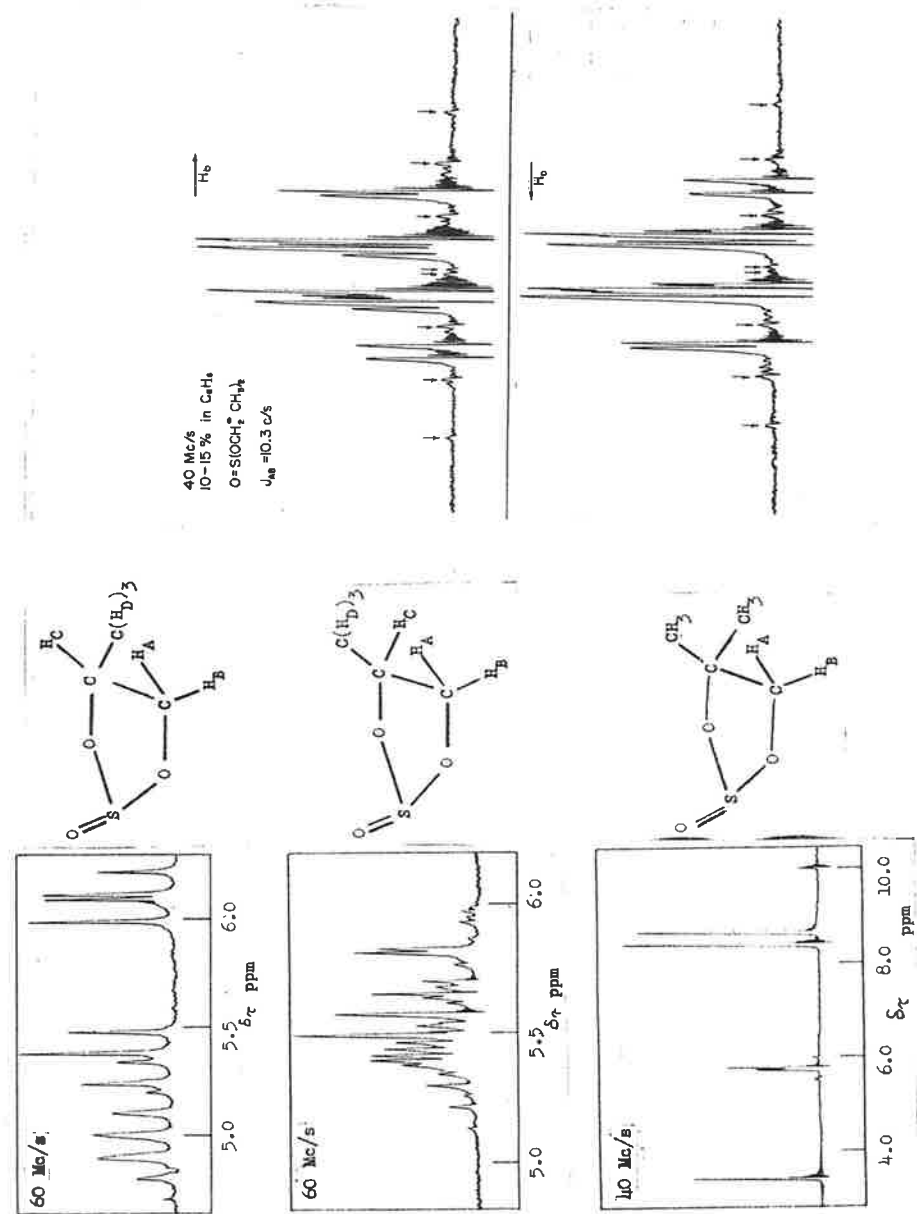
2.

The spectra of the two propylene sulfites, with the structures assigned on the basis of the theoretical calculations, are shown in the figures, along with the spectrum of isobutylene sulfite. The spectrum of ethylene sulfite itself was given some time ago [MELLON-M-R No. 5, p. 8].

The referee of the above paper insisted that we consider the Finegold Hypothesis of "fundamental skewness" in the sulfite group [H. Finegold, Proc. Chem. Soc. (London), 283 (1960)]. We have, therefore, run the H^1 spectra of diethyl sulfite at 40 and 60 Mc/s and found the additional peaks predicted if the methylene shift is between the two gem hydrogens instead of between the two ethoxy groups. 40 Mc/s spectra are shown here; they are very similar to those of acetaldehyde diethyl acetal and can be approximately analyzed as ABX_2 types (see also J. D. Roberts in MELLON-M-R No. 25, p. 5).

Paul C. Lauterbur
Paul C. Lauterbur

John G. Pritchard



THE EFFECT OF MAGNETIC NON-EQUIVALENCE
IN A_2B_2 NMR SPECTRA *

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Salt Lake City, Utah

and
H. S. Gutowsky
Noyes Chemical Laboratory, University of Illinois
Urbana, Illinois

The proton magnetic resonance spectra of β -propiolactone,¹ ethylene monothiocarbonate,² trans-dibromocyclopropane³ and 2,3-dihydrofuran³ have been interpreted by the several workers on the basis of equal cis and trans spin-spin coupling between the A and B nuclei in the A_2B_2 groups. These molecules have cyclic structures such that internal motional averaging about the carbon-carbon bonds is not possible, and, therefore, the cis coupling J is not necessarily the same as the trans, J' . The proposed equality of the coupling constants ($J = J'$) has been explained in each case as accidental. However, the calculations summarized in Fig. 1 demonstrate that such a spectral assignment is not unique and that the magnetically equivalent A_2B_2 spectrum, Fig. 1a, can be duplicated with a magnetically non-equivalent assignment, $|J - J'| \neq 0$, Fig. 1b-1e, provided that $|J_A + J_B| \geq 5|J - J'|$ and $|J_A - J_B| \geq 5|J - J'|$. The calculations in the figure assume that $J_B = 0$; however, the results are similar for $J_B \neq 0$, if the conditions cited at the end of the previous paragraph are met.

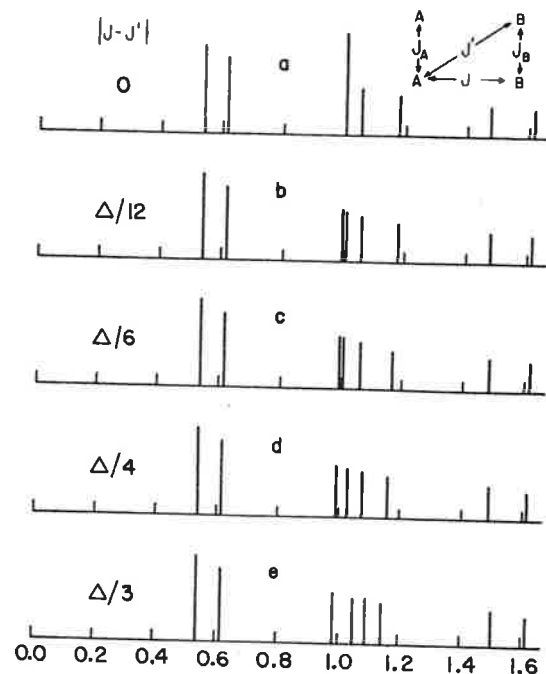


Fig. 1. Calculated high resolution nmr spectra for the A_2B_2 system, exhibiting the effects of magnetic non-equivalence, $J \neq J'$. Only half of the spectrum is plotted; the other half is obtained by reflection at the left. The chemical shift between the A_2 and B_2 multiplets is defined as 2Δ cps, and the abscissa is given in units of Δ . In each of the calculated spectra it is assumed that

$$|J + J'| = |J_A + J_B| = |J_A - J_B| = \Delta.$$

Comparison of the calculated spectra in Fig. 1a-1e reveals that the main effect of increasing $|J-J'|$ from zero is an initially very slow increase in the splitting of the pair of lines centered at $\nu = \Delta$, where 2Δ is the chemical shift in cps between the A_2 and B_2 sets. For $|J-J'| \leq \Delta/5$, this splitting is only about $(1/10)|J-J'|$. Thus, the question of magnetic equivalence is one of degree and experimental resolution. For example, if $|J+J'| = \Delta = 10$ cps, and the resolution were 0.2 cps, $|J-J'|$ could be as large as 2 cps and the non-equivalence would not be apparent in the observed spectrum. In general, if this central pair of lines is not resolved, an upper limit can be placed upon $|J-J'|$, provided that approximate values are available for J_A , J_B and Δ .

Such arguments show that it is unlikely for each pair of AB coupling constants to be identical in all of the above compounds, but there is evidence that they are about equal in some cases. For instance, one would expect the cis and trans coupling constants to have similar values in β -propiolactone because the corresponding constants have been found experimentally to be 4.9 and 5.9 cps in a substituted form of the compound, β -(p-nitrophenyl)- β -propiolactone.⁴ In order for there to be a similar unobserved difference in β -propiolactone itself, it is necessary to have $|J_A - J_B| \geq 5$ cps. The latter is reasonable, because the geminal coupling, J_A , between the α -protons in β -(p-nitrophenyl)- β -propiolactone is 16.6 cps,⁴ and a value of 11 cps or less for the β geminal coupling, J_B , is certainly feasible.

On the other hand, $|J-J'|$ might be of considerable magnitude in trans-dibromopropane because both $|J_A + J_B|$ and $|J_A - J_B|$ could be quite large. By designating the CH_2 group as A_2 , we define J_A as the geminal coupling and J_B as the trans. Both of these can be sizeable yet differ a good bit in magnitude. Of course, a reliable estimate of $|J-J'|$ in this compound would require at least approximate values for J_A and J_B in other substituted cyclopropanes.

The spectra presented here were computed on the Data-tron 205 (University of Utah) and Illiac (University of Illinois) high speed digital computers, using programs based upon an exact solution of the 4-spin system. A more detailed study of the nmr spectra of magnetically non-equivalent A_2B_2 groups is in progress and the results will be presented shortly.

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¹W. A. Anderson, Phys. Rev. **102**, 151 (1956). This case has been cited many, many times as one exhibiting accidentally degenerate coupling constants.

²P. L. Corio, Chem. Rev. **60**, 396 (1960).

³L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry (Pergamon Press, London, 1959), p. 84.

⁴H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys. **31**, 1278 (1959).