Prensas

Monthly
Ecumenical
Letters from
Laboratories
Of
N—M—R

No. 59

אולי יש לך של מכתבים כרטיסים ולנו רשימי
מאמצות של תולים מיוחד נרשמת.
כפי שאתה רואה כולל כאן, כל שאמו הקודם פנאי של 6163
אולי, ואתה נותר הקו יציר פם אחר מכתב הבאה, וי פרטים
פם אותו נגמון כרטיב פרטים.

Please address any reply to
THE DIRECTOR
and quote: BP. 5/6/01
Your reference: 25th July, 1963

Dear Dr. Bothner-By,

ENHANCED DOUBLE QUANTUM SPECTRA

Although double quantum techniques (1,2) have the advantage that no audio-frequency lock-in detector or field-frequency ratio lock is necessary in contrast with more sophisticated double resonance techniques (3), the double quantum transitions are observable only in strongly or moderately coupled systems. Consideration of an AX system composed of two isotopic nuclei with spin $\frac{1}{2}$ indicates how the double quantum signal goes to zero for weakly coupled systems. The double quantum signal has a maximum peak height at the magnetic field H_0 defined by

$$(1) \qquad 2\omega = \gamma(2 - \sigma_A - \sigma_X)H_0$$

where ω is the angular frequency of the radio frequency field H_1, γ is the magnetogyric ratio for the nuclei, and σ_A and σ_X are the magnetic shielding constants for the A and X nuclei, respectively. Using the results of Yatsiv (4) the observed D.C. signal at H_0 is

$$(2) \qquad P = \frac{k\,T_2\,L\,(\gamma H_1)^3}{1 + T_{ab}\,T_2\,L\,(\gamma H_1)^4}$$

where k is a constant of the system and includes instrumental factors, T_2 is the transverse relaxation time for the double quantum process, T_{ab} is directly proportional to the longitudinal relaxation time for the double quantum process, and

$$(3) \qquad L = (4\pi J_{AX})^2 \left[\delta_{AX}^2 - (2\pi J_{AX})^2\right]^{-2}$$

where $\delta_{AX} = \gamma H_0(\sigma_A - \sigma_X)$ and is in <u>angular frequency</u> units, and J_{AX} is the spin-spin coupling constant in c/s. As L becomes small the maximum value of P goes to zero because saturation occurs before the signal is observable.

Formally L can be written as

$$(4) \qquad L = \left[\frac{-2(\delta_{AX} + 2\pi J_{AX})}{(\delta_{AX} + 2\pi J_{AX})^2 - z^2} + \frac{2(\delta_{AX} - 2\pi J_{AX})}{(\delta_{AX} - 2\pi J_{AX})^2 - z^2} \right]^2$$

where $z = \omega_A - \omega_X$ in which ω_A is the frequency of the radio frequency field H_A perturbing nucleus A and ω_X is the frequency of the radio frequency field H_X perturbing nucleus X. Furthermore a radio frequency signal at ω_A is observed owing to nucleus X being perturbed and a radio frequency signal at ω_X is observed owing to nucleus A being perturbed when

$$(5) \qquad \omega_A + \omega_X = 2\omega$$

/if

NATIONAL PHYSICAL LABORATORY

if $\omega_A - \omega = \omega - \omega_X$. In the ordinary double quantum case it is evident that $H_A = H_X = H_1$ and also $\omega = \omega_A = \omega_X$ giving z = 0. In essence Yatsiv (4) realized that a more favourable value of z could be chosen if H_A and H_X were supplied by separate radio frequency fields whose separation was about δ_{AX} so that ω_A and ω_X lay much nearer the A and X single quantum transitions when the magnetic field was at H_o. The signals now observed at ω_A and ω_X when the magnetic field is at H_o are called enhanced double quantum signals (although two quantum signals maybe a more appropriate name for them). Yatsiv (4) developed the theory for the case of amplitude modulation of the radio frequency field to supply the radio frequency fields H_A and H_X at more favourable frequencies.

This theory has been adapted firstly for two separate radio frequencies (for use with systems containing more than one isotopic species) and secondly for the more usual audio-frequency modulation of the radio frequency field or audio-frequency modulation of the steady magnetic field (for use with systems containing one isotopic species). Throughout the work the treatment has been applied to the AX case since the AX theory can be easily modified to apply to any weakly coupled system. (In systems where both strong and weak coupling occur - the simplest of these being the ABX system - the theory can be modified to accomodate variations in relative intensity of single quantum lines and combination lines.) In particular the enhanced double quantum signals from the olefinic AX system of maltol ($\delta_{AX}/2\pi$ = 99.6 c/s at 60 Mc, J_{AX} = 5.4 c/s) have been studied under a variety of conditions using field modulation and are in quantitative agreement with the theory. The enhanced double quantum signals were easily observed and, in this case, at their maximum for the condition z = δ_{AX} the enhanced double quantum signal was only a factor of about 2.3 down on the maximum observed for the single quantum signals and 8 times as strong as the optimum unenhanced signal. It should be noted that the conditions could be varied to give a larger enhanced double quantum signal by a more favourable choice of z but that the 'best' choice of z gives

$$\omega_A = \gamma H_o (1 - \sigma_A) \pm \pi J_{AX}$$
$$(6) \qquad \omega_X = \gamma H_o (1 - \sigma_X) \pm \pi J_{AX}$$

which excites the single quantum transitions and thus invalidates the theory.

The appearance or non-appearance of an enhanced double quantum signal at a given position relative to the single quantum lines enables the ralative energy scheme to be constructed in a manner similar to that using unenhanced double quantum spectra in spectral analysis (5).

Yours sincerely,

A. P. Cohen

A. D. Cohen and D. H. Whiffen,
Basic Physics Division.

References

(1) K. A. McLauchlan and D. H. Whiffen, Proc. Chem. Soc. 144 (1962)

(2) B. Dischler and G. Englert, Z. Naturforsch , 16a 1180 (1961)

(3) R. Freeman and W. A. Anderson, J. Chem. Phys., 37 2053 (1962)

(4) S. Yatsiv, Phys. Rev., 113, 1522 (1959)

(5) W. A. Anderson, R. Freeman and C. A. Reilly, J. Chem. Phys. (to be published)

Monthly

   Ecumenical

      Letters from

        Laboratories

          Of

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HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT   **P. O. BOX 4255**

July 19, 1963

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

Dear Barry:

Recently we have obtained and interpreted the NMR spectra of approximately one hundred API certified paraffins using our A-60 spectrometer. The paraffins were run as fifty volume per cent solutions in carbon tetrachloride using TMS as an internal standard. Solvent shifts, relative to TMS, were found to be negligible by determining the spectra of several paraffins in various concentrations of carbon tetrachloride.

The chemical shifts derived from these spectra are correlated according to proton types in charts I to V. These chemical shifts have proven to be exceedingly useful in elucidating the structures of polymers, other paraffins, and the paraffinic portion of olefins and aromatics. By way of illustration, it is obvious from inspection of charts III and IV that, in most instances, a clear differentiation can be made between t-butyl methyls and internal geminal methyls solely on the basis of chemical shifts. In addition, the chemical shifts of methyls attached to quaternary carbon atoms are sensitive to alkyl substituents located α and/or β to the quaternary carbon atom. (Note: In Chart III, fourth division, the bracket should only enclose the t-butyl group.)
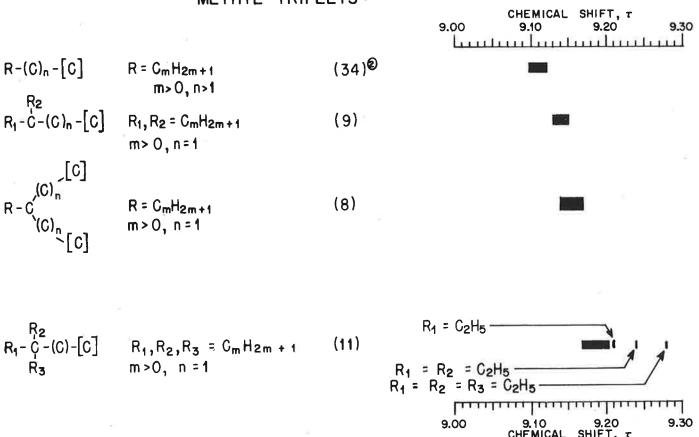
As of yet, we do not have an adequate explanation for the chemical shifts but we plan to publish a more detailed paper concerning paraffinic chemical shifts and their corresponding spin-spin multiplicities in the near future.
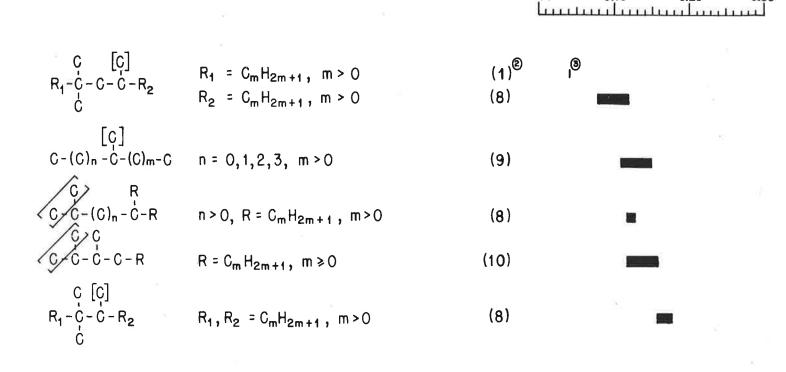
Very truly yours,

Kenneth W. Bartz

Kenneth W. Bartz

KWB:vt

Chart I

CHEMICAL SHIFTS OF $[CH_3]-CH_2-$ METHYL TRIPLETS[1]

CHEMICAL SHIFT, τ

9.00　9.10　9.20　9.30

$R-(C)_n-[C]$ $R = C_mH_{2m+1}$ 　 (34)[2]
$m > 0, n > 1$

$R_1-\overset{R_2}{\underset{|}{C}}-(C)_n-[C]$ $R_1, R_2 = C_mH_{2m+1}$ 　 (9)
$m > 0, n = 1$

$R-C\overset{\diagup[C]}{\underset{\diagdown(C)_n}{\overset{(C)_n}{}}}_{\diagdown[C]}$ $R = C_mH_{2m+1}$ 　 (8)
$m > 0, n = 1$

$R_1-\overset{R_2}{\underset{\underset{R_3}{|}}{C}}-(C)-[C]$ $R_1, R_2, R_3 = C_mH_{2m+1}$ 　 (11)
$m > 0, n = 1$

$R_1 = C_2H_5$

$R_1 = R_2 = C_2H_5$
$R_1 = R_2 = R_3 = C_2H_5$

9.00　9.10　9.20　9.30
CHEMICAL SHIFT, τ

[1] Chemical shifts are measured from the middle band of the triplett.

[2] Numbers in parenthes　refer to the number of compounds used to determine the chemical shift range.

Chart II

CHEMICAL SHIFTS OF $[CH_3]-C'-H$
METHYL DOUBLETS[1]

CHEMICAL SHIFT, τ

9.00   9.10   9.20   9.30

$R_1-\overset{\overset{\text{C}}{|}}{\underset{\underset{\text{C}}{|}}{C}}-C-\overset{[C]}{\underset{}{C}}-R_2$ $R_1 = C_mH_{2m+1}, \; m > 0$ $(1)^{[2]}$ [3]

$R_2 = C_mH_{2m+1}, \; m > 0$ (8)

$C-(C)_n-\overset{[C]}{\underset{}{C}}-(C)_m-C$ $n = 0,1,2,3, \; m > 0$ (9)

$\overset{C}{\underset{C}{}} \diagup C-(C)_n-\overset{R}{\underset{}{C}}-R$ $n > 0, \; R = C_mH_{2m+1}, \; m > 0$ (8)

$\overset{C}{\underset{C}{}} \diagup C-\overset{C}{\underset{}{C}}-C-R$ $R = C_mH_{2m+1}, \; m \geqslant 0$ (10)

$R_1-\overset{\overset{\text{C}}{|}}{\underset{\underset{\text{C}}{|}}{C}}-\overset{[C]}{\underset{}{C}}-R_2$ $R_1, R_2 = C_mH_{2m+1}, \; m > 0$ (8)

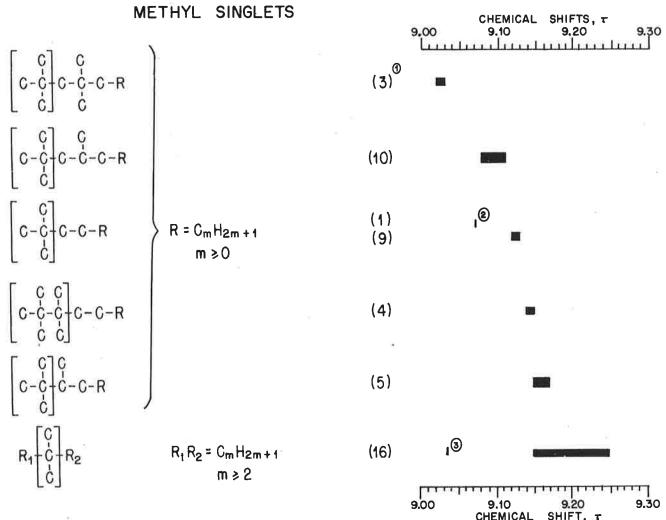9.00   9.10   9.20   9.30
CHEMICAL SHIFT, τ

[1] Chemical shifts are measured from the doublet center.

[2] Numbers in parentheses refer to the number of compounds used to determine chemical shift range.

[3] Chemical shift of CH_3 doublet in 2,2,4,6,6-pentamethylheptane.

Chart III

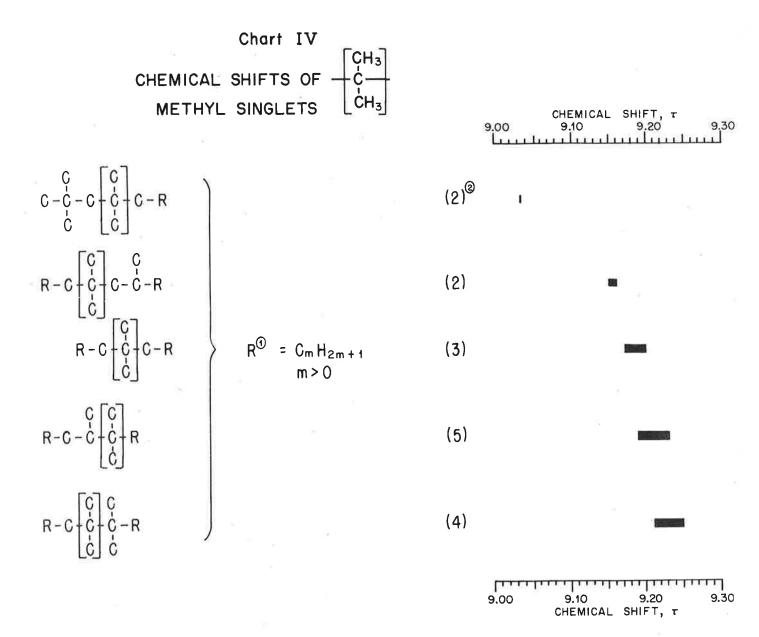## CHEMICAL SHIFTS OF "t-BUTYL" METHYLS

METHYL SINGLETS

$R = C_mH_{2m+1}$

$m \geqslant 0$

$R_1R_2 = C_mH_{2m+1}$

$m \geqslant 2$

[1] Numbers in parentheses refer to the number of compounds used to determine the chemical shift range.

[2] 2,2-dimethylpropane.

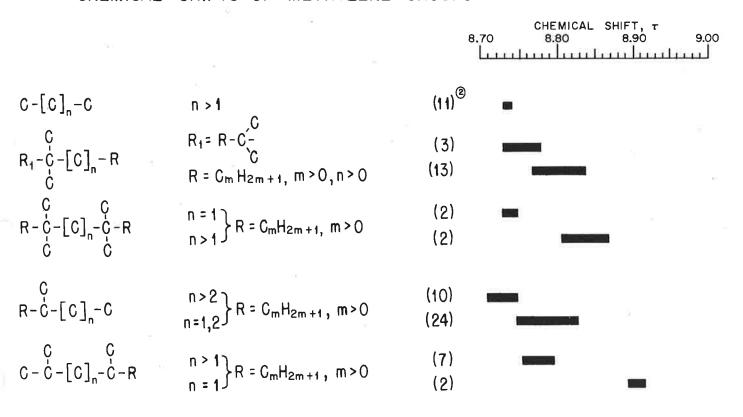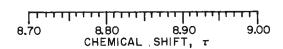[3] Internal gem methyl singlet in 2,2,4,4,6-pentamethylheptane.

Chart IV

CHEMICAL SHIFTS OF $\begin{bmatrix} CH_3 \\ | \\ -C- \\ | \\ CH_3 \end{bmatrix}$ METHYL SINGLETS

CHEMICAL SHIFT, τ

9.00   9.10   9.20   9.30

$R^{①} = C_m H_{2m+1}$
$m > 0$

(2)②

(2)

(3)

(5)

(4)

9.00   9.10   9.20   9.30
CHEMICAL SHIFT, τ

① R ≠ t-butyl.

② Numbers in parentheses refer to the number of compounds used to determine the chemical shift range.
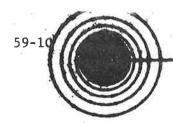
Chart V

CHEMICAL SHIFTS OF METHYLENE GROUPS[1]

CHEMICAL SHIFT, τ

8.70   8.80   8.90   9.00

$C-[C]_n-C$ $n > 1$ (11)[2]

$R_1-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-[C]_n-R$ $R_1 = R-C\overset{C}{\underset{C}{\diagup}}$ (3)

$R = C_m H_{2m+1},\ m > 0,\ n > 0$ (13)

$R-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-[C]_n-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-R$ $\left.\begin{array}{l} n = 1 \\ n > 1 \end{array}\right\} R = C_m H_{2m+1},\ m > 0$ (2) (2)

$R-\overset{\displaystyle C}{C}-[C]_n-C$ $\left.\begin{array}{l} n > 2 \\ n = 1,2 \end{array}\right\} R = C_m H_{2m+1},\ m > 0$ (10) (24)

$C-\overset{\displaystyle C}{C}-[C]_n-\overset{\displaystyle C}{C}-R$ $\left.\begin{array}{l} n > 1 \\ n = 1 \end{array}\right\} R = C_m H_{2m+1},\ m > 0$ (7) (2)

8.70   8.80   8.90   9.00
CHEMICAL SHIFT, τ

[1] Chemical shifts were measured from the centers of the methylene resonance patterns.

[2] Numbers in parentheses refer to the number of compounds used to determine the chemical shift range.

VARIAN AG · SWITZERLAND

HEAD OFFICE   GUBELSTRASSE 17   ZUG   PHONE 042/4 46 55   TELEX 58 444

THE RESEARCH LABORATORY   ZÜRICH 6
KLAUSSTRASSE 43   TELEPHONE 051/47 24 20

8 August, 1963

Dr. B.L. Shapiro
The Mellon Institute
Pittsburgh 13, Pennsylvania
U.S.A.

Dear Dr. Shapiro,

I would like to make a contribution from the Varian AG Research
Laboratory, which concerns the measurement of the Ge^{73}-proton
spin-spin coupling in $Ge(CH_3)_4$.

The splitting of the methyl proton magnetic resonance line in pure
liquid $Ge(CH_3)_4$ has been measured with an A-60. Only the outside
six lines of the "decaplet" due to the isotope G^{73} (J=9/2, natural
abundance 7.6%) are observed, three symmetrically on each side of
the strong central non-split line which contains the other four.
The Ge^{73}-proton spin-spin coupling was not found in Ge_2H_5,
GeH_3PH_2, GeH_3AsH_2, because of the quadrupole relaxation broadening
in these unsymmetrical molecules. The measured Ge^{73}-proton spin-
spin coupling is J=2.94 cps, and the J_{C13_H} is 124.5 cps. The
chemical shift CH_3 is 0.135 ppm. downfield from $Si(CH_3)_4$. It
was previously measured by Allred and Rochow as 0.2 ppm.

It is interesting to mention that J/γ_M for compounds of the type
$M(CH_3)_4$ plotted against the atomic number Z, is a smooth increasing
curve, very close to the formula $J/\gamma_M = aZ^{1.3}$ The table and
Figure 1 show that the Ge^{73} point falls perfectly on this curve.
From the equation $J/\gamma_M = c/\Delta E$, where γ is the gyromagnetic
ratio of M, c is a constant and ΔE the mean triplet exitation energy[3],
one should be able to observe a relation between the spin-spin
coupling and the optical phosphorescence bands, such as was reported[4]
for the chemical shift of Co^{59} and the lowest frequency optical
absorption maximum.

One can expect in $Ge(C_2H_5)_4$ a stronger spin-spin coupling J_{Ge-CH_2}.
However, the complicated A_3B_2X system and the low natural abundance
of the Ge^{73} isotope make this measurement impossible. The proton
N.M.R. spectrum of tetraethyl germanium is only very slightly
different from that of the main multiplet of tetraethyl tin[5],
where $J_{CH_2-CH_3}$ and $J_{CH_3-CH_2}$ = 0.390 ppm.

$$\frac{J_{CH_2-CH_3}}{J_{CH_3-CH_2}} = 0.350$$

Yours sincerely,

A. Tzalmona *
VARIAN AG.
Zurich
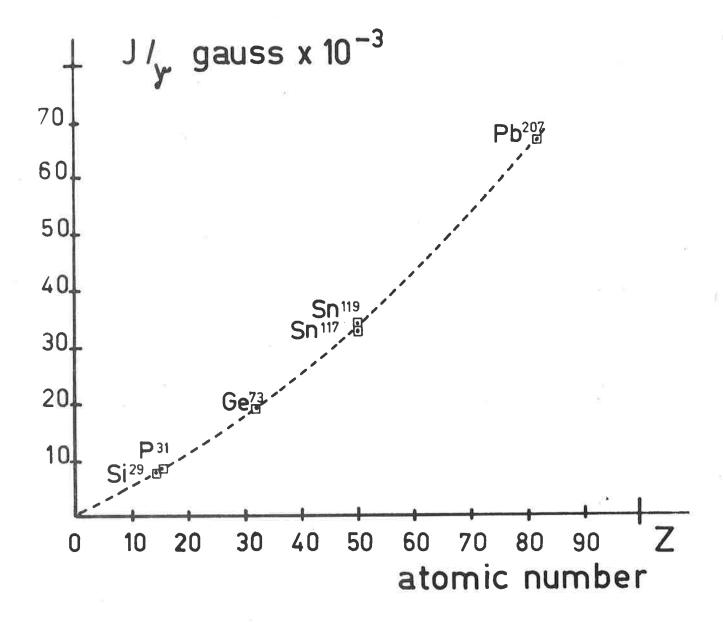
* On leave of absence from the Electronics Department, The Weizmann
Institute of Science, Rehovoth, Israel.

T A B L E

Atomic No.	Isotope	Spin No.	/2 (cps/gauss)	J (cps)	J/ (milligauss)
14	Si^{29}	$\frac{1}{2}$	846.0	6.7	7.93
15	P^{31}	$\frac{1}{2}$	1723.5	14.6[6]	8.48
32	Ge^{73}	9/2	148.5	2.94	19.5
50	Sn^{117}	$\frac{1}{2}$	1577.0	51.9	33.0
50	Sn^{119}	$\frac{1}{2}$	1587.0	54.3	34.1
82	Pb^{207}	$\frac{1}{2}$	889.9	60.5[7]	68.0

References

1. Drake and Jolly, J. Chem. Phys. 1963,38,1033.

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3. Pople, Schneider and Bernstein, "High Resolution Nuclear Magnetic Resonance" McGraw-Hill, New York, 1959, p. 185-189.

4. Freeman, Murray and Richards, Proc. Roy.Soc.(London), 1957, A242, 455.

5. Narasimhan and Rogers, J. Chem. Phys. 1961, 34, 1049.

6. Martin and Avel, Compt. Rend. 1961, 253, 644.

7. Flitcroft and Kasesz, J.Am.Chem.Soc: 1963, 85, 1377.

J/γ gauss x 10⁻³ vs atomic number Z, showing data points for Si²⁹, P³¹, Ge⁷³, Sn¹¹⁷, Sn¹¹⁹, and Pb²⁰⁷.

August 3, 1963

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

Dear Dr. Shapiro

     I have found mistakes in the numerical values
given in the letter which was recently sent to you. The
relative saturation parameters for the lines $\omega_{\alpha\beta}$ of a two-
spin system IS, $\underline{S}(\alpha\beta) = (T_1)_{\alpha\beta}(T_2)_{\alpha\beta}$, should be changed as

$$\underline{S}(12) = .2619 \quad \text{and} \quad \underline{S}(34) = .3067$$
$$S(13) = .2327 \quad \text{and} \quad \underline{S}(24) = .1025$$

in units of $(\gamma_I \gamma_S \hbar R^{-3} \tau_c)^2$. Fortunately no conclusions
obtained in the former letter are ~~not~~ changed.

Yours sincerely

H. Shimizu

H. Shimizu
Department of Chemistry
College of Arts and Sciences
Chiba University
Chiba, Japan

The Structure of Loliolide. A Terpene from Lolium Perenne.

The compound formulated $C_{20}H_{30}O_6$ was first isolated[1] from ether extracts of New Zealand pasture. This same compound, now called loliolide, has now been obtained from Lolium perenne (perennial ryegrass) in a yield of $8 \times 10^{-4}\%$. We have revised the molecular formula to $C_{11}H_{16}O_3$ and on the basis of U.V., I.R. and P.M.R. investigations have shown that the compound is 1,3-dihydroxy-3,5,5-trimethylcyclohexylidene-4-acetic acid lactone (I). This has been confirmed by the chemical reactions which the compound undergoes.

If the six membered ring exists in the less sterically hindered chair form then loliolide is II, and its dihydro derivative, obtained by reduction with Adams' catalyst, is III. The large number of substituents have quite an effect on the chemical shifts of the six membered ring protons, and one "long range" coupling constant involving these protons has been observed.

The actual shifts and coupling constants obtained from loliolide are given in the enclosed table.

Loliolide

Functional Group	τ value	Functional Group	τ value
C(1)H	5.65	C(5)CH$_3$ (α; β)	8.52; 8.72
C(2)H$_2$ (α; β)	7.48; 7.94	C(6)H$_2$ (α; β)	8.0 ; 8.5
C(3)CH$_3$	8.21	C(1)OH	7.73
C(4)=CH	4.32		

Coupling constants (c/sec., all $\pm$ 0.3 c/sec.)

J[C(1)H-C(2)H(α)] = 3.6   J[C(2)H(α)-C(2)H(β)] = 14.4

J[C(1)H-C(2)H(β)] = 3.6   J[C(6)H(α)-C(6)H(β)] = 13.8

J[C(1)H-C(6)H(α)] = 3.6   J[C(2)H(α)-C(6)H(α)] = 2.7

J[C(1)H-C(6)H(β)] = 3.6

[1] E.P. White, N.Z. J. Agric. Res., 1, 859 (1958)

Andrew L. Porte,
Department of Chemistry,
The University,   and
Glasgow, W.2., SCOTLAND

R. Hodges,
Ruakura Animal Research Station,
P.B. Hamilton,
NEW ZEALAND.

Dr B.L. SHAPIRO

Mellon Institute

4400 Fifth Avenue

PITTSBURG 13 Pa.

U.S.A.

GRENOBLE, LE **1er août 1963**
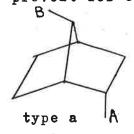
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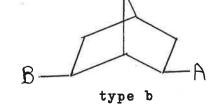G/ COP I
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VOTRE RÉF. :

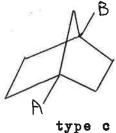VOTRE LETTRE DU

Cher Docteur Shapiro,

Couplages ^4J de composés bicycliques

Dans une étude de dérivés de synthèses dieniques avec le furanne (ref 1) des couplages ^4J ont été déterminés par analyse complète des spectres de R.M.N.

En série bicyclo –2-2-1 heptanique, la théorie de MEINWALD (ref. 2) prévoit des couplages ^4J de type a, b, et c

type a   type b   type c

Or si les couplages de type a et b sont observés, il n'en est plus de même du type c (cf par exemple ref. 3). En série <u>oxa-7</u> ou <u>oxa</u>-2 on trouve des couplages de type a et c, comme dans les exemples suivants (spectres dans le DMSO deutéré).

$$J_{12} = 0 \quad J_{23} = 3,2 \quad J_{34} = 5 \quad J_{45} = 0$$

$$J_{56} = 7 \quad J_{61} = 0$$

<u>et</u> $J_{14} = 1,1$ cps (type c)

.../...

$$J_{12} = 0 \quad J_{23} = 1,4 \quad J_{34} = 3 \quad J_{35} = 4,5$$

$$J_{56} = 10,2 \quad J_{16} = 1,4$$

et : $\quad J_{13} = 1,4$ cps (type c)

$\qquad\qquad J_{45} \quad 0,8$ cps (type a)

A noter, que dans tous les dérivés de la série, J **exo-exo** est supérieur à la théorie (10 à 11 cps) classique, à géométrie et électronégativité de groupements voisins, comparables. Jendo-endo est conforme à la théorie (7 cps). Comme dans des cas non hétérocycliques voisins, (ref. 4), il ne semble pas que électronégativité et géométrie suffisent à déterminer exactement un couplage (voir cependant ref. 5)

Dans un ordre d'idée comparable, nous avons trouvé un couplage ^3J dans le composé suivant :

$$J_{BD} = 2,9 \quad J_{AB} = 3,1 \quad J_{AC} = 4,5 \quad J_{AD} = 1,3$$

$$(J_{BC} = 0)$$

et : $\quad J_{CD} = 0,8$ cps

Le rôle de l'oxygène et de la double liaison semblent importants, le couplage disparaissant par hydrogénation du composé.

(1) D. GAGNAIRE et E. PAYO-SUBIZA, Bull. Soc. Chim. (à paraître) -

(2) J. MEINWALD et A. LEWIS, JACS **83** 2769 (1961) -

(3) P. LASZLO et P. SCHLEYER, Mellon. M.R. **57**, 2 -

(4) J.I. MUSHER Mol. Phys. 1963, 93 -

(5) O. JARDETZKY, Mellon M.R. **57**, 46 -

D. GAGNAIRE   E. PAYO-SUBIZA

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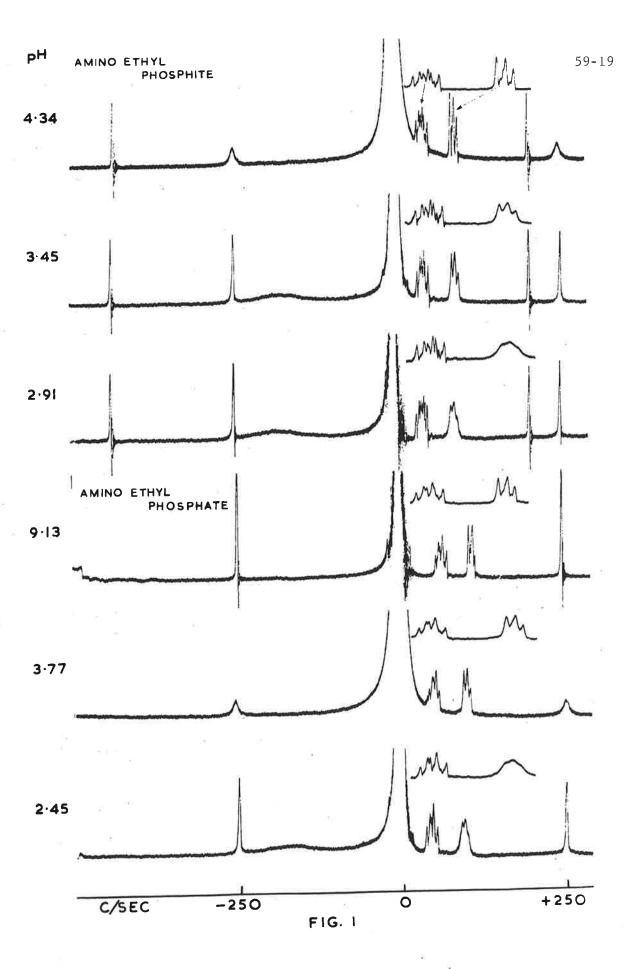| OUR REF.	YOUR REF.	DATE
Res/G.2050/ACC/JB.		13th August, 1963.

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

Dear Dr. Shapiro,

We offer our apologies for the delay in making this our first contribution to MELLONMR. We have been greatly delayed by the late delivery of our instrument and a variety of annoying faults. However, our AEI RS2 spectrometer is now working quite well.

We have examined the spectra of aminoethyl phosphite ("aminite", I) and aminoethyl phosphate ("aminate", II), with a view to confirming the presence of a P-O-C linkage in the aminite, as found crystallographically in the aminate[1], rather than a P-NH-C linkage.

<div align="center">

(a)   (b)   (c)   (d)

</div>

$$\text{I} \quad \overset{H}{HOP(O)OCH_2CH_2NH_2} \rightleftharpoons \overset{H}{{}^-OP(O)OCH_2CH_2NH_2} \rightleftharpoons \overset{H}{{}^-OP(O)OCH_2CH_2NH_3^+} \rightleftharpoons \overset{H}{HOP(O)OCH_2CH_2NH_3^+}$$

$$\text{II} \quad \overset{H}{\overset{O}{HOP(O)OCH_2CH_2NH_2}} \rightleftharpoons \overset{H}{\overset{O}{{}^-OP(O)OCH_2CH_2NH_2}} \rightleftharpoons \overset{H}{\overset{O}{{}^-OP(O)OCH_2CH_2NH_3^+}} \rightleftharpoons \overset{H}{\overset{O}{HOP(O)OCH_2CH_2NH_3^+}}$$

The 60 Mc/sec proton spectra at 24°C of 2.13 M aqueous solutions of both materials at various pH values are shown in Fig. 1. The pH values of the equimolar solutions of the aminite and aminate in the slightly acid water used as solvent are 4.34 and 2.45 respectively. The aminite proton spectrum reveals $^{31}P - {}^{1}H$ couplings with $J_{P-H} = 642.2 \pm 1.0$ c/sec and $J_{PCH_2} = 7.3 \pm 0.1$ c/sec of which the latter appears as a doublet splitting on one half of a system approaching the A_2X_2 limit. The 25 Mc/sec ^{31}P spectrum has the expected doublet of triplet form. The fact that J_{PCH_2} appears on the more deshielded methylene proton resonance, considered with the greater deshielding influence of oxygen over nitrogen, strongly suggests the presence of the $-P-O-CH_2-$ system. Furthermore, because the more deshielded methylene proton resonance occurs as a doublet split A_2X_2 band, irrespective of solution pH, it is evident that rotation about the C-C bond is restricted. This appears to be due to the formation of an intramolecularly bonded cyclic molecule because dilution gives no indication of free rotation.

pH   AMINO ETHYL
         PHOSPHITE

59-19

4·34

3·45

2·91

AMINO ETHYL
      PHOSPHATE

9·13

3·77

2·45

C/SEC   −250   0   +250

FIG. 1

The more shielded methylene proton signal broadens at low pH and sharpens to the original pattern as the pH is subsequently raised, showing the existence of some pH-dependent equilibrium. This variation of band shape with pH can be explained by the nitrogen relaxation, which at high pH is sufficiently rapid to completely decouple this nucleus from the nearest methylene protons, whose resonance is therefore sharp and shows coupling only to the other methylene protons. At low pH the nitrogen relaxation evidently slows so that the coupling with the adjacent methylene protons is not completely collapsed, producing the observed band broadening. Such a large change in the nitrogen relaxation time implies a change in the electric field gradient at this nucleus, as given by a change from an $-NH_2$ to an NH_3^+ group, the latter being close to cubic symmetry, giving a lower field gradient and hence slower relaxation at low pH. The results therefore provide strong evidence for the transition a (or b) $\rightleftharpoons$ c (or d), both forms being held in cyclic configurations by intramolecular hydrogen bonds. Forms c or d predominate below about pH 2.9.

The protons on the nitrogen give, at low pH, a single broad band, showing that the NH triplet has been collapsed; this band disappears at higher pH because of exchange with the solvent. The nitrogen relaxation at low pH is evidently too slow to account for much of the triplet collapse, which is probably a result of proton exchange between the nitrogen atoms of solute molecules.

The aminate behaves similarly to the aminite showing analogous changes with pH (Fig. 1) as well as the persistent tendency to exist in the intramolecularly bonded cyclised form.

Because of the limitations of an aqueous solvent with a molecule having labile hydrogens, nothing can be said about the presence or otherwise of hydroxyl protons at the phosphorus end of the molecule. However, the increase of water line width and the disappearance of the NH band (Fig. 1) show that slow solute solvent exchange takes place at intermediate pH. At higher pH the exchange is evidently rapid and the water line sharpens. Further work is being carried out on both these compounds.

We have been troubled by 50 c/s sidebands which always appeared in our spectra. Most of the effect appeared to be coming from modulation of H_0 by stray 50 c/s fields in the laboratory. We have been able to nullify this by feeding a 50 c/s correction signal to a 90 : 1 stepdown transformer with the secondary in series with the modulation coils; this arrangement enables us to leave the correction signal on while feeding A.F. to the modulation coils for calibration purposes. About 50 μA, suitably phased, was required in the modulation coils. When the H_0 correction signal was optimised there was a weak sideband still remaining, which appeared to be coming from 50 c/s modulation of H_1, either by stray fields at the sample coil, or by modulation of the R.F. carrier or both. We have eliminated this by fitting a small coil (250 turns of 2.6 cm. diam.) parallel to the sample coil and 5.75 cm. below it. This was fed with a suitably phased 50 c/s current of around 15 mA. Fig. 2a shows typical 50 c/s sidebands and Fig. 2b the effect of the compensation.

Fig. 2

Yours sincerely,

A. C. Chapman   John Homer.

[1] Kraut, Acta Cryst. 14, 1146, (1961).

UNIVERSITY OF COLORADO

BOULDER, COLORADO

August 7, 1963

ᴚTMENT OF CHEMISTRY

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

Dear Barry:

Mr. Alan Ashbaugh and I have recently completed an n.m.r. study of π-molecular complexes between various aromatic donors and 7, 7, 8, 8-tetra-cyanoquinodimethane (TCNQ). By a modification of a treatment recently reported in hydrogen-bonding studies [Berkeley and Hanna, J. Phys. Chem., 67, 846 (1963)] it is possible to derive an n.m.r. analogue of the Benesi-Hildebrand Equation [Benesi and Hildebrand, J. Am. Chem. Soc., 70, 2832 (1948)] for spectroscopic determination of molecular complexes. This analogue is

$$\frac{1}{\Delta^A_{OBS}} = \frac{1}{K\Delta^A_{AD}}\frac{1}{\xi_D} + \frac{1}{\Delta^A_{AD}}\qquad (1)$$

where

Δ^A_{OBS} is the observed shift of acceptor protons relative to their position in a non complexing solvent

Δ^A_{AD} is the shift of acceptor protons in pure complex

K is the formation constant for the complex, AD.

ξ_D is the concentration of donor in some convenient concentration units.

A similar equation may be written for the observed donor shift by interchanging the A's and the D's. Equation 1 assumes that the concentration of donor is much larger than that of the acceptor and that the solution is ideal. If Equation 1 holds, a plot of $1/\Delta^A_{OBS}$ vs. $1/\xi_D$ should give a straight line whose slope is $1/K\Delta^A_{AD}$ and intercept is $1/\Delta^A_{AD}$, enabling one to calculate both K and Δ^A_{AD}. An example of some of the plots for systems of TCNQ and donor in dioxane is shown in Figure 1. The resulting values of K and Δ^A_{AD} are given in Table 1.

DONOR	K_m by n.m.r. at 37°	Δ_{AD}^{A} in cps	K_m(spectroscopic)
Benzene	0.061	77	
Toluene	0.085	63	
O-Xylene	0.12	55	
Mesitylene	0.16	48	
Durene	0.33	40	0.47[+]
Pentamethylbenzene	0.55	35	
Hexamethylbenzene	1.15	33	1.03, 1.22[+]

Table 1

[+]Values calculated from data of L. R. Melby, et al, J. Am. Chem. Soc., 84, 3374 (1962). They reported K_x values at 24° in methylene chloride.

In a way the results were disappointing because the shifts Δ_{AD}^{A} turned out to be so small. It was hoped that these shifts might shed more light on the structure of molecular complexes. It does appear that we are measuring a property of the complex and not a general solvent effect, however. The order of the K's as well as the reasonable agreement between n.m.r. and spectroscopic K's when both are available dictate against the effect being a general solvent effect.

It should be pointed out that it is impossible to make spectroscopic measurements of equilibrium constants for the first four donors in Table 1 because the charge-transfer band is apparently buried in the absorption of the acceptor. It may well be that n.m.r. will provide a valuable supplement to the Benesi-Hildebrand method for measuring formation constants of molecular complexes when such a situation exists.

The direction and order of the Δ_{AD}^{A}'s can be rationalized. It should be noted that all donors give an upfield shift, but that the upfield shift becomes smaller as the complex gets stronger. A consideration of the geometry of molecular complexes with a 3.1 - 3.5 Å separation between parallel rings indicates that the protons of the acceptor lie in the shielding region of the donor ring currents. The smaller upfield shift as the complex gets stronger could be due to the extra term in the paramagnetic part of the chemical shift from the charge-transfer excited state. As the charge-transfer band is shifted to longer wave lengths this term should make a greater contribution to the downfield shift giving rise to the observed order. Perhaps this is too much speculation for shifts differing by only a small amount, but an interesting prediction can be made from this theory. If the complex could be made strong enough, the sign of the shift should reverse and a downfield shift of the acceptor protons should be observed.

We are currently investigating other n.m.r. ways of studying π-molecular complexes.
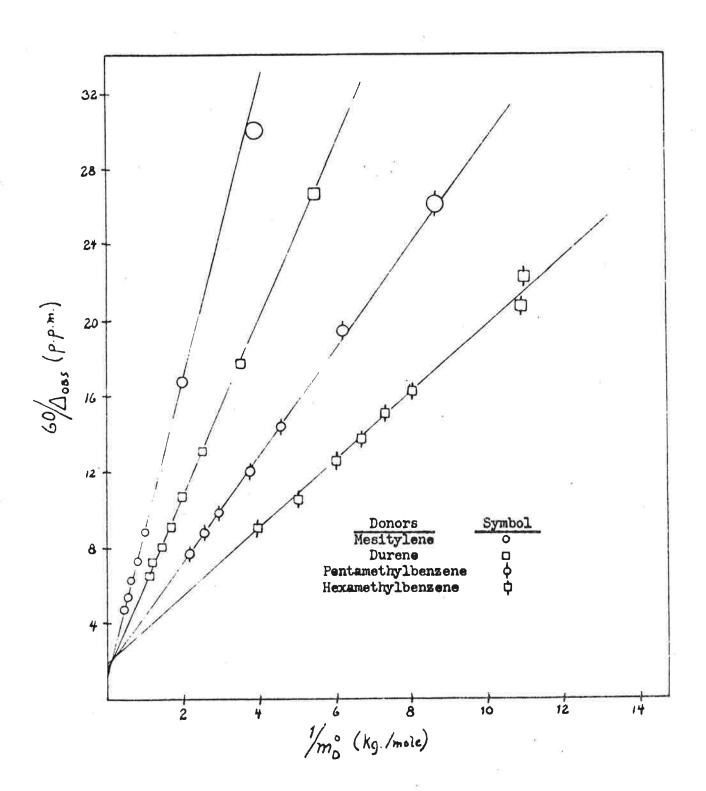
Sincerely yours,

Melvin W. Hanna
Assistant Professor of Chemistry

MWH/gb

FIGURE ⬛I., System: TCNQ-Donors-Dioxane with Internal Reference.
Plot of $60/\Delta_{obs}$ against $1/m_D^o$.

Donors	Symbol
Mesitylene	○
Durene	□
Pentamethylbenzene	⬭
Hexamethylbenzene	⬓

y-axis: $60/\Delta_{obs}$ (p.p.m.)

x-axis: $1/m_D^o$ (Kg./mole)

THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN

August 13, 1963

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

Dear Dr. Shapiro:

A new subroutine has been written to replace subroutine "BEQUAL" in the NMR programs of J. D. Swalen.[1] This new routine makes it possible to handle symmetry cases with the programs in addition to those possessing magnetic equivalence. Thus, for example, an AA'BB'C spin system may be run as well as an A_2B_2C spin system.

The routine uses the original values of the parameters to decide whether to average the corrections to them which arise in the course of an iteration. If none of the original values of the chemical shifts are identical, no averaging is done by the subroutine. If one or more sets of equal chemical shifts are given as input data, the routine will average corrections to each shift in each set, as does the original routine. The important difference is that when the routine looks at the coupling constants, it averages corrections for any set or sets whose original values were set equal. The Swalen routine only averaged sets for magnetically equivalent protons. The new routine does not examine the couplings if no two shifts are originally equal.

Additional advantages of the new routine are:

1. It is shorter by almost 300 decimal locations.

2. It cannot err if two shift values happen to become accidentally identical during iteration. Although unlikely, this is possible in the Swalen routine.

Differences in running time cannot be obtained from runs that I have made, but I don't expect that there is much.

The changes required in the present series of programs are only two:

1. Replacement of "BEQUAL" by the new routine (which I have named "BEQUIV" to distinguish it from the former - such a name change is, of course, unnecessary).

2. Replacement of the statement "CALL BEQUAL (B,BB,A
AA,N)" in "NMRIT" by the statement "CALL BEQUIV
(or BEQUAL) (BB,HB,AA,AB,N)". One would hope that
only a binary change would be required in NMRIT.

I will be happy to provide listings and decks of this
routine to interested parties. Anyone who wishes to have
these may obtain them by writing to me at the address below.

Would you please count this contribution toward the sub-
scription of J. P. Heeschen since he and I share an office
and his subscription to MELLON Letters.

A. W. Douglas
The Dow Chemical Company
Chemical Physics Research Laboratory
1603 Building
Midland, Michigan

AWD:jvh

cc: J. D. Swalen

REFERENCE

1. Swalen and Reilly, J. Chem. Phys.; 37, 21-29 (1962).

LABORATORIUM FÜR PHYSIKALISCHE
CHEMIE UND ELEKTROCHEMIE DER
TECHNISCHEN HOCHSCHULE, STUTTGART, Germany

STUTTGART N
Wiederholdstraße 15
Telefon 29 97 83 93

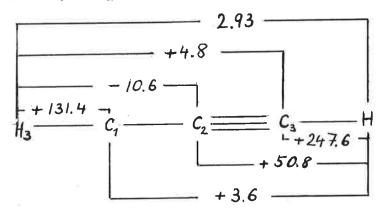Dr. H. Dreeskamp   August 12, 1963

Dr.B.L.Shapiro
Mellon Institute
1400 Fifth Ave.
Pittsburgh 13, Penna.
U. S. A.

Re.: The relative signs of C-H coupling in Propyne

Dear Dr. Shapiro:

Ever since Shoolery, Johnson and Anderson [J.Mol.Spectr. 5
(1960) 110] published the complete set of absolute values
of C-H coupling constants in a molecule we felt this would
be a particularly good example to investigate the relative
signs. Our technique has been published [Z.Phys.Chem. NF. 34
(1962) 263] and consists essentialy in the following: By
appropriate substitution, dilution or change of frequency
(or a combination of these) one can decrease the value of
the effective chemical shift between C^{13}-sattelites to a
value small enough that a determination of signs becomes
possible. If furthermore a substitution does not drastically
change the absolute value of a coupling constant one feels
safe that the sign does not change on changing the substituent.
This seems to be true in those cases we investigated. See how-
ever the paper by Freemann and Anderson to be published in
J.C.P. Aug. 1st. (Private communication).

To investigate the coupling over three bonds in propyne we

took at C_1 monosubstituted propynes: X = Cl for a C_1 carbon being a C^{13} (see above paper) and X = $O-\overset{O}{\overset{\|}{C}}-CH_3$, $O-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{\overset{\|}{C}}-C\equiv CH$ for a C_3 carbon being a C^{13}. In all cases a final adjustment of the optimal chemical shift was done by dilution and the coupling constants were found to have the same sign as the one-bond coupling. For C_2 being a C^{13} we took propyne itself dissolved in Dimethylsulfoxyd. Here the two couplings showed to have opposite sign. This means the simple rule: one inter- vening carbon reverses sign is wrong. This of course had been clear by other arguments already. Recently Frei and Bernstein (J.C.P. 38 1216 (1963)] showed that it is the coupling of the acetylenic proton to the C_2 carbon which has the same sign as the one-bond coupling. This makes the other constant negative so that finally we get:

Once again I like to stress that our assignments rely on the fact that a one-bond C-H coupling is always positive and the chemical substituents did not change the coupling to such an extend that the sign was reversed. For this we will give good reasons in a paper to be submitted to "Berichte der Bunsenge- sellschaft für Physikalische Chemie". The remaining sign of the H-H coupling we are investigating by double frequency ex- periments.

Sincerely yours,

H. Dreschamp

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA
August 9, 1963

Dr. Bernard Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

<u>The Time Weighted Average
Approximation in Ethanes</u>

Dear Dr. Shapiro:

I thought for once we were going to get our subscription paid before you had to bill us. Unfortunately we were a couple days too late. We certainly do appreciate MELLONMR.

It is frequently assumed that the coupling constants and chemical shifts of substituted ethanes at high temperatures are the weighted averages of the values for the individual rotamers: If the energies of the three rotamers are 0, E_2 and E_3, then

$$(F)_{AVE} = (F_1 + e^{-E_2/RT} \cdot F_2 + e^{-E_3/RT} \cdot F_3)/(1 + e^{-E_2/RT} + e^{-E_3/RT}) \tag{1}$$

where F is a chemical shift or coupling constant and the subscripts refer to the three rotamers. Recently Ramey (MELLONMR 55:29) reported the low temperature spectrum of $CF_2BrCFBrCl$ in which the three rotamers are resolved. He pointed out that the coupling constants observed at low temperatures were not equal to those calculated by Gutowsky, Belford, and McMahan, [J. Chem. Phys. <u>36</u>, 3353 (1962)] from high temperature spectra using equation 1, thereby throwing some doubt on the validity of equation 1. We have redetermined the spectra of this compound at several temperatures in order to test equation 1.

The spectrum of a 50% solution of $CF_2BrCFBrCl$ in $CFCl_3$ at 56.4 Mc is given in Fig. 1. We assign peaks 1-6, 10-11, and 16-18 to an ABX spectrum for rotamer I; peaks 9, 12-15 and 22-24 as an ABX spectrum for rotamer III (the other three peaks of the two outer doublets were not resolved), and peaks 7-8 and 19-21 as forming essentially an A_2X spectrum for rotamer II. (See Ramey's note for drawings of the three rotamers.) Our assignment was verified by the obvious double resonance experiments.

Because of the near degeneracy present $(\nu_A - \nu_B)_{II}$ can not be determined from the low temperature spectrum. However, we can calculate it, and prove the validity of equation 1 for the quantity $(\nu_A - \nu_B)$ by the following line of reasoning. Equation 1 is certainly valid to $\pm$ 40 cps. This fact establishes that $(\nu_A - \nu_B)_{III}$ is negative assuming $(\nu_A - \nu_B)_I$ to be positive.

$(\nu_A - \nu_B)_{II}$ is now the only unknown quantity necessary to calculate $(\nu_A - \nu_B)_{AVE}$ at any elevated temperature using eq. (1). It is therefore possible to determine the values of $(\nu_A - \nu_B)_{II}$ necessary to make eq. (1) accurately predict the value of $(\nu_A - \nu_B)_{AVE}$ at each of several elevated temperatures. These values are -9.7, -12.3, -11.6, and -10.3 at 242, 300, 322, and 371°K, respectively. The near equality of these four values strongly support the validity of eq. (1) for the quantity $\nu_A - \nu_B$ and establish the value of $(\nu_A - \nu_B)_{II}$ as -11 ± 2 cps. This value has been used for the rest of the calculated values, which are given in Table 2. The experimental results are given in Table 1.

It is seen that the calculated coupling constants are .6 to 1.3 cps above the experimental ones. The low and high temperature data on $\nu_A - \nu_B$ fit very well with equation 1 with one arbitrary parameter. All other calculated chemical shifts are significantly different from the observed values. These deviations are nearly linearly proportional to the temperature. We believe that at least some and possibly most of these deviations from equation 1 are due to temperature dependent molecular associations. Since A and B fluorine atoms in $CF_2BrCFBrCl$ are almost equivalent chemically, and therefore likely to have identical intermolecular effects, this explanation would predict the experimental good fit for the quantity $\nu_A - \nu_B$, but no other. This explanation can give rise to deviations of the proper order of magnitude as is shown by the observation that the chemical shift between $CFCl_3$ and CF_3Br in a 50-50 mixture varies linearly with the temperature, changing 31 cps in 150°.

A more complete report on this work has been transmitted to the Journal of Chemical Physics. Preprints are available.

Sincerely,

C.H. Sederholm   R.A. Newmark

P.S. Hot off the spectrometer - the barriers to internal rotation in $CF_2Cl-CFCl_2$ are approximately 9.25 kcal measured by same technique as was used in D. S. Thompson, R. A. Newmark and C. H. Sederholm, J. Chem. Phys. 37, 411 (1962)(or MELLONMR 40-7). This barrier fits very well on the empirical curve of barriers vs. size of substituents which appears in the J.C.P. article above.

Table I. Experimental chemical shifts and coupling constants of the three rotamers (I, II and III) of $CF_2BrCFBrCl$ at 150°K, and of the averaged spectrum at higher temperatures. $\nu_{AB} = \frac{1}{2}(\nu_A + \nu_B)$; chemical shifts are measured from the solvent, $CFCl_3$. All values in cps.[a]

	J_{AX}	J_{BX}	$\frac{1}{2}(J_{AX}+J_{BX})$	J_{AB}	$\nu_A-\nu_B$	$\nu_X-\nu_{AB}$	ν_A	ν_B	ν_X
I	-11.8	-14.8	-13.3	170.0	244.6	605.3	3438.8	3194.2	3921.8
II			-14.0		-11.0[b]	500.2	3474.5	3485.4	3980.2
III	-20.3	-21.3	-20.8	160	-210.3	552.6	3639.9	3859.2	4297.6
242°K	-13.48	-14.42	-13.95	168.0	112.31	536.5	3450.6	3338.3	3930.0
300°	-13.40	-14.14	-13.77	167.26	94.57	522.7	3436.2	3341.6	3911.6
322°	-13.61	-14.07	-13.84	167.15	89.13	517.0	3429.9	3340.7	3902.3
371°	-13.44	-13.96	-13.70	167.13	80.22	507.6	3417.8	3337.6	3885.3
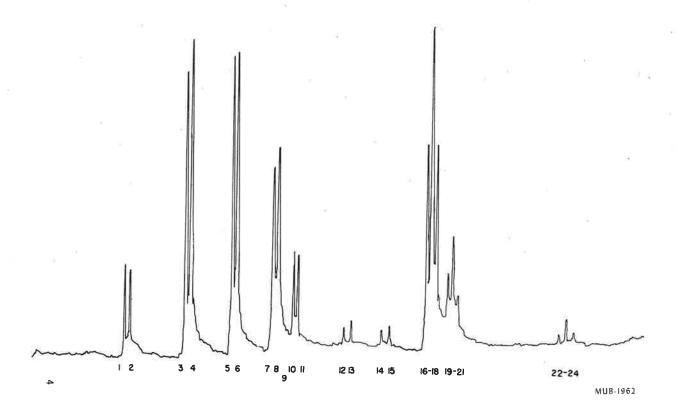
[a] J_{AX} and J_{BX} are accurate to ± 0.25 cps at 150°K and 242°, ± 0.20 cps at 300°, and ± 0.15 cps at 322° and 371°. Except for rotamer III, J_{AB} is accurate to better than 0.4 cps. $\nu_A - \nu_B$ at 300° and above is accurate to ± 0.40 cps; all other chemical shifts have a standard deviation less than 0.5 cps.

[b] This number is calculated using Eq. (1), see text.

Table II. Calculated chemical shifts and coupling constants at high temperatures using weighted averages of the low temperature data, and the deviations from the experimental quantities. $\Delta X = X_{cal'd} - X_{observed}$. Chemical shifts are measured from the solvent, $CFCl_3$, in cps.

	$\frac{1}{2}(J_{AX} + J_{BX})$	$\Delta\frac{1}{2}(J_{AX} + J_{BX})$	$\nu_A - \nu_B$	$\Delta(\nu_A - \nu_B)$
242°K	14.55	0.60	112.10	-0.21
300°	14.77	1.00	94.77	0.20
322°	14.84	1.00	89.55	0.42
371°	14.98	1.28	79.79	-0.43

	ν_A	$\Delta(\nu_A)$	ν_B	$\Delta(\nu_B)$	ν_X	$\Delta(\nu_X)$
242°K	3474.8	24.2	3362.7	24.4	3986.1	56.1
300°	3480.7	44.5	3385.9	44.3	3997.5	85.9
322°	3482.7	52.8	3393.2	52.5	4001.2	98.9
371°	3485.9	68.1	3406.1	68.5	4007.6	122.3

1 2   3 4   5 6   7 8 10 11   12 13   14 15   16-18 19-21   22-24
              9

4

MUB-1962

NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF PURE CHEMISTRY

OTTAWA 2,   August 12, 1963

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

Dear Barry,

I have sent along a few spectra[*] of
some C^{13} doubly enriched compounds which may be
of interest to M.E.L.L.O.N.M.R. readers.   There
is about 25% of each of the species I, II, III and
IV in the material whose spectrum is shown.   These
species are the molecules with C^{12}-C^{12}, C^{12}-C^{13},
C^{13}-C^{12} and C^{13}-C^{13} carbon bonds respectively.

The theoretical spectra are also
shown.

Yours sincerely,

H. J. Bernstein
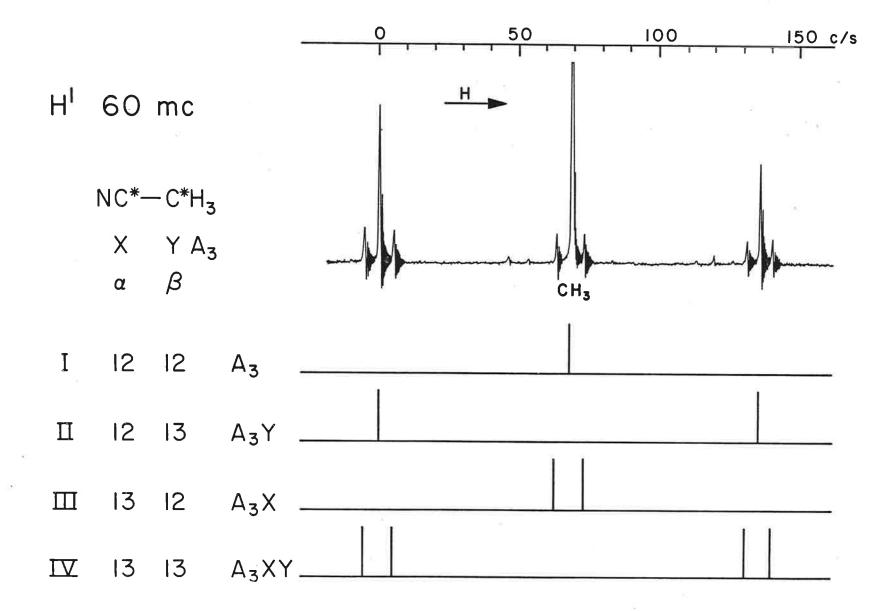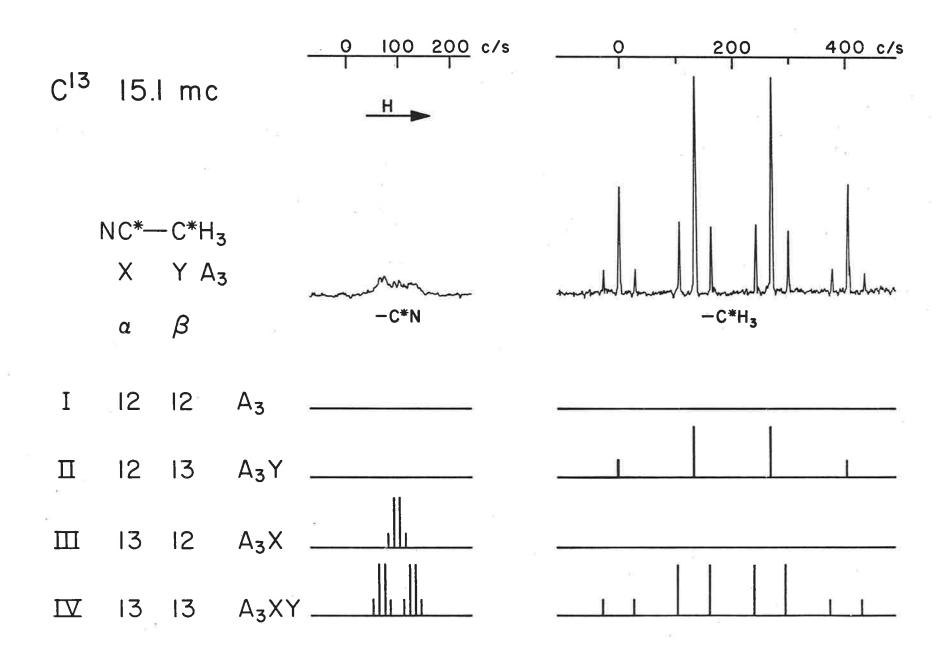
HJB/amd

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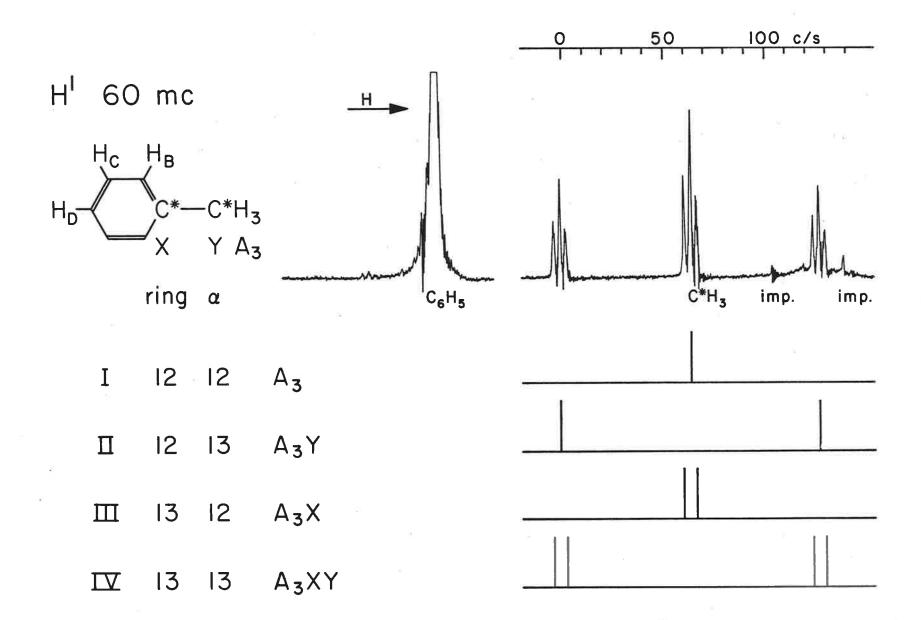
[*]With the kind permission of the author, only a few of these spectra have
been reproduced on the following pages.   Copies of additional examples
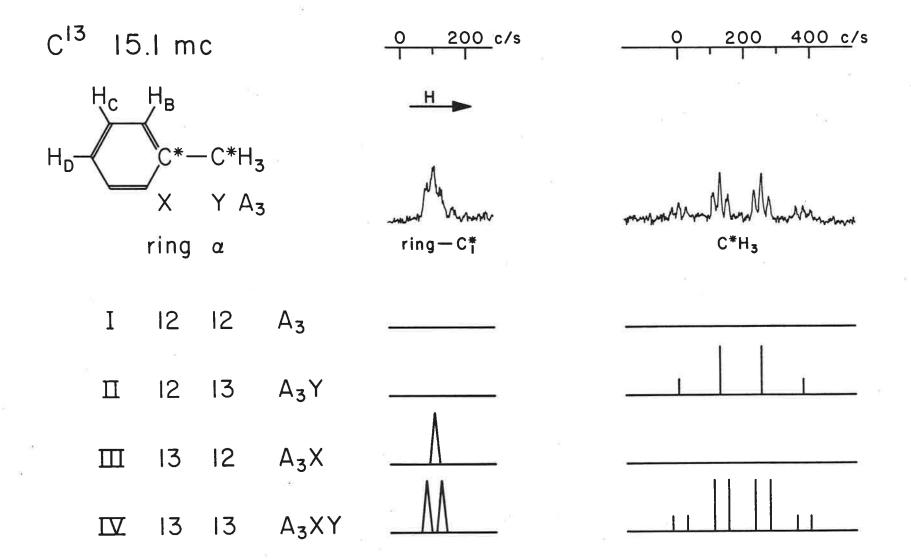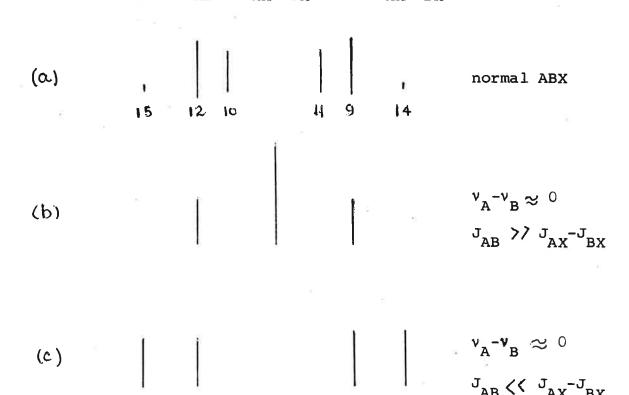can be obtained directly from Dr. Bernstein.

BLS

H¹ 60 mc

NC*—C*H₃

	X	Y A₃	
	α	β	

I	12	12	A₃
II	12	13	A₃Y
III	13	12	A₃X
IV	13	13	A₃XY

C^{13} 15.1 mc

$NC^* - C^*H_3$

X   Y A_3

α   β

	X	Y	A_3		
I	12	12	A_3		
II	12	13	A_3Y		
III	13	12	A_3X		
IV	13	13	A_3XY		

H^I 60 mc

H_C H_B

H_D — C*—C*H$_3$

X   Y A$_3$

ring α

I	12	12	A$_3$
II	12	13	A$_3$Y
III	13	12	A$_3$X
IV	13	13	A$_3$XY

0   50   100 c/s

H →

C$_6$H$_5$ C*H$_3$ imp.   imp.

C^{13} 15.1 mc

0   200 c/s

$\xrightarrow{\text{H}}$

ring—C_1^*

0   200   400 c/s

C^*H_3

	X	Y	A_3		
I	12	12	A_3		
II	12	13	A_3Y		
III	13	12	A_3X		
IV	13	13	A_3XY		

ring   α

NATIONAL RESEARCH COUNCIL

CANADA

DIVISION OF PURE CHEMISTRY

OTTAWA 2, August 13, 1963

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

Dear Barry,

I recall that the question has been raised about the utility of the labelling AA'X for an ABX type spectrum for which $\nu_A - \nu_B \approx 0$ or coincidentally equal to zero. I present here an argument which I hope will (i) discourage people from using this nomenclature or (ii) encourage the introduction of additional nomenclature, perhaps AA''X, to distinguish yet another special case of the ABX type.

There are two very different types of spectral pattern arising from the ABX type system for which $\nu_A - \nu_B \approx 0$ depending on whether $J_{AB} \gg J_{AX} - J_{BX}$ or $\ll J_{AX} - J_{BX}$.

(a)	normal ABX

15 12 10   11 9 14

(b)	$\nu_A - \nu_B \approx 0$ $J_{AB} \gg J_{AX} - J_{BX}$

(c)	$\nu_A - \nu_B \approx 0$ $J_{AB} \ll J_{AX} - J_{BX}$

- 2 -

(b)

The first case has been observed and gives rise to a so-called deceptively simple spectrum with a 1:2:1 triplet for the X spectrum and a 1:1 doublet for the AB spectrum. However, if $J_{AB} \ll J_{AX}-J_{BX}$ it is readily seen that the central pair of lines (10, 11) in the X spectrum (see Fig.) collapse and have zero intensity whereas the outer pair (14,15) due to the combination lines become as intense as the middle pair (9,12) giving a 1:1:1:1 quartet symmetrically disposed about the center. This type of spectrum has been observed for $H-C \equiv C^{13}-C \equiv C-H$, for example, and could be encountered quite often when X is a nucleus different from hydrogen. The question now arises whether the labelling AA'X serves any useful purpose. Both (b) and (c) of Fig. 1 are merely special cases of ABX (a). If one retains the AA'X labelling one has always to bear in mind that depending on the values of the coupling constants, two different spectral patterns are obtained. If on the other hand the labelling AA'X is reserved for (b) only, then one is justified in looking for a new type of labelling for (c), for example AA" X or what have you. I would like to suggest that only the labelling ABX be retained since it seems unnecessary to invoke new labelling every time a special case is encountered. In any event if AA'X is retained then perhaps AA" X will also prove useful.

Yours sincerely,

Harold

H. J. Bernstein

HJB/amd

August 19, 1963

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

Dear Barry:

Over the past few months, a group of us at the National Institutes
of Health have been studying the spectra of polycyclic aromatic
compounds. We were able to identify the normal aromatic AB and ABC
systems but found that little had been done on the analysis of
ABCD systems found in fused rings. Using the Frequint III computer
program, we have been able to develop a general analysis of the
spectra of this common group of protons and these generalizations
have been successfully applied to provide solutions for phenanthrenes,
benzphenanthrenes, benzanthracenes and a number of more complex
polycyclic aromatics.

The first interesting discovery was that the coupling constants
within these groups are symmetrical, as shown in Figure 1, regard-
less of the nature of substituents in the adjacent ring. Computation
showed that the gross features of the spectra are controlled by
the relative chemical shifts of A and B and are little affected by
changes in the chemical shifts of C and D. Thus the arrangement
approximates an R-AB-X system and calculations based on this assumption
allowed the assignment of computed peaks to specific transitions.

The effects of changes in the various coupling constants were
studied. Because these parameters vary so little in aromatic
systems, they do not have a great influence on the overall spectral
patterns but do vary the interline distances slightly in a predictable
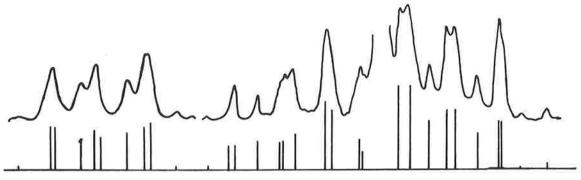manner.

To ease the application of this data to practical problems, nomograms
of typical spectra with the AB chemical shift as the only variable
were drawn up. Using these and the coupling constant trends, spectra
of such compounds as phenanthrene can be quickly analyzed and a
correct solution obtained with relatively few computations.

Figure 2. compares observed and computed spectra for phenanthrene
and gives the respective chemical shifts and coupling constants.

With best wishes,

Yours sincerely,

T. J. Batterham

T. J. Batterham
Laboratory of Physical Biology, NIAMD

$J_{AC} = J_{BD}.$ $J_{AD} = J_{BC}.$

Figure I

NMR spectrum of phenanthrene showing only peaks from the
fused ring ABCD systems. The full scale (not continuous)
covers 60 cps.

Calculated parameters.

ν_A= 63cps, ν_B = 66.5 cps., ν_C= 0cps., ν_D= 48.5cps.,
where ν_C is actually 536.0 cps. downfield from tetramethylsilane.

J_{AB}= 7.3 cps., J_{AC}= 8.4 cps., J_{AD}= 1.6 cps., J_{BC}= 1.6 cps.,

J_{BD}= 8.4 cps., J_{CD}= 0.5 (?)cps.

(Esso) **ESSO RESEARCH AND ENGINEERING COMPANY**
CENTRAL BASIC RESEARCH LABORATORY   P. O. BOX 45, LINDEN, N. J.

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

August 20, 1963

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

Dear Barry:

     Partly in response to Prof. Sheppard's call for additional examples of stereospecific long range couplings (No. 56), we would like to mention some observations we have recently made upon examining the spectra of 7-substituted norbornadienes and norbornenes. It was found that only one of the two vinyl proton pairs of the norbornadienes was coupled to the bridge hydrogen. That the vinyl-bridge hydrogen had to be anti-oriented was demonstrated in the isomeric 7-syn- and 7-anti-substituted norbornenes (A and B resp.) for a long range coupling of 0.8 cps. was observed in only the A series.

     Regarding the nature of the coupling, the symmetry of the compounds examined does not allow a distinction between 4-bond coupling in the fragment H-C-C-C-H or 5-bond coupling in the fragment H-C-C-C=C-H. What is clear is that the rigidity of the ring system does not allow a "planar zig-zag path" in either fragment.

     On the basis of the magnitude of P_{23} (see figure), the known magnitude of J_{12}, and the line width of the central, unresolved line of the low field vinyl pattern observed in several derivatives, we have concluded that J_{12} and J_{13}, the vicinal and allylic couplings, are of the same sign, which is in stark contrast to the situation in acyclic compounds. Although Laszlo and Schleyer mention this sign relation in No. 57, Mortimer had arrived at this same conclusion upon analysis of the norbornadiene spectrum in 1959 (J. Mol. Spect. 3, 528). What seems surprising is that, to our knowledge, no one has commented on this anomaly heretofore. If no anomaly is present, except in our minds, perhaps someone can correct us. A preprint of a manuscript dealing with the spectra of 7-substituted norbornadienes and norbornenes is available to any interested parties.

     Effective with the present issue one of us (E.I.S.) would appreciate having his copies of MELLON-M-R sent to the University of Connecticut, Department of Chemistry, Storrs, Connecticut.
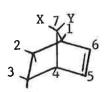
Sincerely,

Boris Franzus

Eugene I. Snyder

COUPLINGS IN NORBORNADIENES AND NORBORNENES

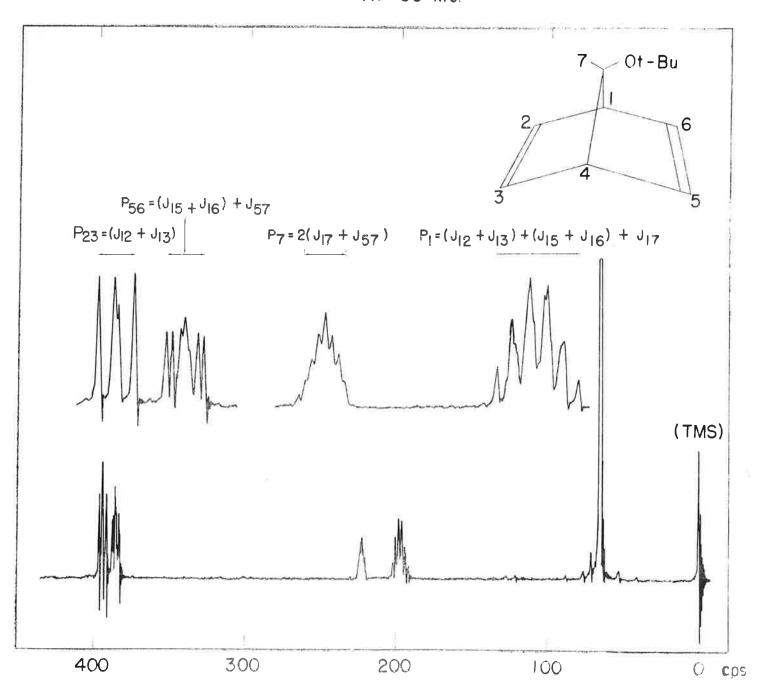| Y	Solvent	J_{17}	J_{57}	$(J_{12} + J_{13})$	$(J_{15} + J_{16})$
$-O_2C\emptyset$	$CHCl_3$	1.74	0.76	4.52	3.93
-OAc	-	1.85	0.83	4.73	4.09
	CCl_4	1.78	0.86	4.82	4.02
-Ot-Bu	-	1.75	0.78	4.81	4.29
	CCl_4	1.66	0.76	4.92	4.24
-OH	-	2.10	0.70		
-Cl	$CDCl_3$	1.66	0.69	4.40	3.87

X	Y		J_{17}	J_{57}	$(J_{12} + J_{13})$	$(J_{15} + J_{16})$
H	$-O_2CCH_3$	-	1.77	0.83	2.98	3.63
		$CDCl_3$	1.66	0.96	3.46	3.50
$-O_2CCH_3$	H	CCl_4		0		4.40
H	-OH	$CDCl_3$		0.92		3.57
-OH	H	$CDCl_3$	1.86		3.50	4.38

59-44

Figure I

N.m.r. SPECTRUM OF 7-tert-BUTOXYNORBORNADIENE
AT 60 Mc.

CARNEGIE INSTITUTE OF TECHNOLOGY

SCHENLEY PARK

PITTSBURGH 13, PENNSYLVANIA

DEPARTMENT OF CHEMISTRY
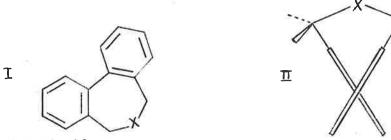
TELEPHONE: 621-2600
AREA CODE 412

August 22, 1963

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

Dear Barry:

We'd like to report some work which we presented at the I.U.P.A.C. Congress, and which also relates to work by Mislow (MELLONMR No. 57).

We have been carrying out variable temperature proton resonance studies of the singly bridged biphenyl systems shown in I:

I

II

$X = O, S, SO_2, CO$

If the differential chemical shift of the methylene protons is due only to aromatic ring current effects (not a likely supposition for R = SO_2 or CO) and if the molecule is not inverting, one will see an AB quartet for the methylene protons. When the molecule inverts the methylene protons H_a and H_b (as in II, and end-on view of the molecule) interchange. If the inversion rate is sufficiently great, only a single, sharp methylene line will be seen. For the dibenzoxepin (R=O in I), 10% wt. % in CS_2, we observed an AB quartet at -105°C, the lines of which broaden, the pattern coalescing to a single line at about -85°C, this line sharpening as the temperature is raised; similar behavior was observed for thiepin (R=S in I) in CS_2; here the coalescence temperature is +42.3°C. In order to analyze this behavior we have programmed Alexander's density matrix treatment[1] for the Bendix G-20 here at Tech. (Anyone interested is welcome to this program. However, it is written in GATE not Fortran.)

The computer output was a series of plotted line shapes, each pattern corresponding to a particular inversion lifetime, τ (these lifetimes taken at logarithmic intervals), and to the particular n.m.r. parameters for the AB system. From the computer prepared plots we then took $\delta \nu$, the separation of the inner pair of lines in the AB system, at given values of τ and prepared a plot of this separation vs. $-\ln \tau$. The experimental values of $\delta \nu$ at various temperatures yielded $-\ln \tau$ by interpolation from the above plot. The usual Arrhenius plot of $\ln k$ versus $1/T$ yielded

59-46

E_{act}, where k, the inversion frequency, is $1/\tau$. We might note that similar procedures attempted for various line-width parameters gave line-widths outside the range of those observed or inconsistent with those obtained from the $\delta\nu$ vs. $-\ln\tau$ plot. (The computer plots were essentially independent of T_2). Whether this latter state of affairs reflects an inadequacy in the theory or is the result of experimental difficulties in line-width measurements we don't know, and would appreciate any comment.

The n.m.r. parameters and the activation parameters for dibenzoxepin and dibenzthiepin are given in Tables I and II.

Table I - N.M.R. Parameters

Oxepin - CH$_2$	$\bar{\nu}_0^*$	$\delta\nu$(cps)	J (cps)
~300°K	4.105	---	---
165°K	4.130	24.0	10.6
Thiepin - CH$_2$			
294°K	3.262	15.0	12.4
203.5°K	3.253	13.1	12.4

*(center of AB pattern)

Table II - Activation Parameters

	ΔE (kcal/mole)	ΔA (kcal/mole)	ΔS (cal/mole °K)	E_{Act} calcd[a] (kcal/mole)
Oxepin (188.7°K)	9.6 ± 0.6	9.2 ± 0.2	70	11
Thiepin (298.2°K)	16.2 ± 0.3	16.5 ± 0.3	~-1.0	18.5

It is of interest to note that the derived activation energies agree rather well with those estimated by Mislow.[2]

The estimated ring-current chemical shifts for H_a and H_b for different values of the dihedral angle φ are given in Table III. These were calculated by the simple point dipole model for an assumed interannular C-C distance of 1.50 Å, C-O distance of 1.41 Å, a C-S distance of 1.82 Å, and typical aromatic bond-distances and angles and, implicitly, variable O-C-O and S-C-S angle.

Table III - Calculated Ring Current Shifts

φ	$\bar{\nu}_A^*$(cps)	$\bar{\nu}_B^*$(cps)	δ^*(cps at 60 Mc/s)
2:7-dihydro-3:4, 5:5-dibenzoxepin			
30°	-33.4	-25.4	8.0
40°	-31.0	-13.5	17.5
50°	-18.8	- 3.8	15.0
2:7-dihydro-3:4, 5:6-dibenzthiepin			
40°	-31.2	-12.2	19.0
50°	-26.4	- 2.5	23.9
60°	6.0	- 4.2	10.2

*$\bar{\nu}_A$ is the ring current shift of proton H_a, $\bar{\nu}_B$ that of proton H_b.

Mislow[3] has also estimated the dihedral angles for the oxepin and thiepin to be about 44° and 56°, respectively. The ring current shifts obtained by interpolation in Table III yield, for these dihedral angles, differential shifts which agree remarkably well (perhaps, fortuitously well) with the experimentally derived ones. We'd hesitate to predict the dihedral angle from the observed shifts, however, for a number of reasons: (1) solvent effects, as Mislow has demonstrated, may play an important part: (2) the point dipole model is only approximate: (3) anisotropy in the C-O or C-S bonds may also possibly contribute to the differential chemical shifts.

The effect of anisotropic shielding from other than the aromatic rings is probably demonstrated by the behavior of the SO2 and CO compounds in CH2Cl2. The CH2 lines of these compounds do not break up into a quartet at temperatures as low as -60°C and -80°C, respectively. The oxepin in CH2Cl2 shows qualitatively the same behavior as it does in CS2 but we have not yet studied it or the thiepin in a variety of solvents.

One last point should be noted. As indicated in Table I, there is a continous shift with temperature of both the average CH2 frequency, ν_0, and of the differential chemical shift, δ . The aromatic portion of the oxepin spectrum also shows a marked change, going from a broad pattern at ~360°K to a much narrower group of lines at 165°K. This effect we believe to be due to the temperature dependent change in the average (over vibrational states) dihedral angle, ϕ . The same behavior is observed in biphenyl (i.e. 4,4' dideutero-biphenyl). We hope to be able to contribute our results on this last compound to MELLONMR soon.

We'd like to thank Dr. Mislow for the precursor of the CO compound and for a stimulating discussion.

Sincerely,

Robert J. Kurland
Mordecai B. Rubin
William B. Wise

1. S. Alexander, J. Chem. Phys., 37, 971 (1962) with special reference to eqs. 57a, 57b, 58. Several minor points might be worth noting for those who may use this treatment. (a) the "τ" used in equations 57a, 57b is not the mean life time, nor the same as the τ used in the Boltzmann and following equations. Evidently a factor of two has been dropped between equations 56 and 57. The τ used in eq. 57 is the same as that used in the Gutowsky, McCall and Slichter treatment of uncoupled interchanging spins; (b) one can show explicitly (in the case $1/\tau_L = 0$) [by setting the first and second derivatives of the absorption with respect to frequency equal to zero at ν_0, the center frequency of the AB pattern] that the lifetime at coalescence, τ_0 , is the same as that given by G.M.S., that is,

$$\tau_0 = \frac{2\sqrt{2}}{2\pi(\nu_A - \nu_B)}$$

2. K. Mislow, J. Am. Chem., 84, 1449 (1962). The values here are one-half those estimated by Mislow for the analogous doubly bridged compounds.

3. K. Mislow, Private communication.

CANISIUS COLLEGE
BUFFALO 8, N.

July 31, 1963

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

Dear Dr. Shapiro:

I would like to begin to receive the Mellon
NMR letters and am contributing the following sug-
gestions as my first letter.

For several years at various meetings, I have
mentioned our use of arsenic trichloride as a solvent
for both NMR and IR work. This material is probably
similar to such solvents as liquid sulfur dioxide,
etc. except I believe extremely simple to handle.
Our first use of it as a solvent was to study water
at concentrations near 0.5%. In these ranges a
strong water signal is seen somewhere between that
of liquid water and water vapor and a weak signal on
the low field side of liquid water which we attribute
to the hydronium ion. Both signals can be displaced
by changing water concentration or adding acid and
our assignment of these signals appears correct.

Assuming we had a solvent which seemed capable
of breaking H-bonding we investigated many other sub-
stances. I am enclosing two spectra to illustrate
its solvent properties. The first is an organo-phos-
phorus acid which has been extensively studied in
other solvents. We can easily move the OH signal by
varying the concentration. The low solubility of
this material in most solvents makes arsenic trichlo-
ride a very useful solvent.

The second spectra is that of a phenolic resin
which simply would not give us good NMR spectra in
the solvents we tried. Excuse the poor intergration
curve, as we took very little time in running this
particular spectra. Infrared spectra of the compound
in arsenic trichloride convinces us we have not des-
troyed the polymer by dissolving it in arsenic tri-
chloride.

I hope my letter will be of service to some.

Sincerely,

Herman A. Szymanski, Chairman
Department of Chemistry

HAS/mam

60 MC NMR
SPECTRUM NO. #12

OPERATOR: .... DATE ......

SAMPLE: ....

$(ETHYL\ HEXYL-O)_2\ P{\overset{O}{\underset{OH}{\diagup}}}$

SOLVENT: $AsCl_3$

FILTER BANDWIDTH:	2	cps
R. F. FIELD:	0.4	mG
SWEEP TIME:	250	sec
SWEEP WIDTH:	1000	cps
SWEEP OFFSET:	0	cps
SPECTRUM AMP:	10	
INTEGRAL AMP:	—	
REMARKS:		

VARIAN associates
PALO ALTO, CALIFORNIA
INSTRUMENT DIVISION

CHART S-60A

PRINTED IN U.S.A.

8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 PPM (δ)

1000
500
250
100
50

400 300 200 100 0 CPS
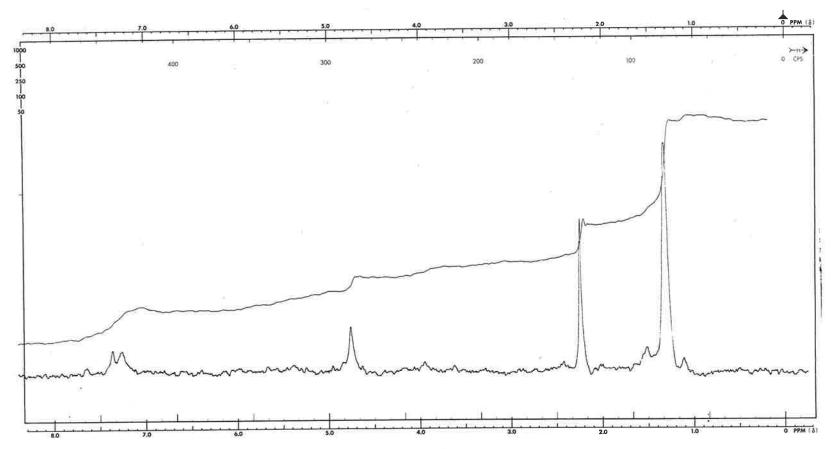
60 MC NMR
SPECTRUM NO.

OPERATOR: DATE

SAMPLE:

SUBSTITUTED - MODIFIED
PHENOLIC RESIN HAVING
t - BUTYL GROUPS

SOLVENT: $AsCl_3$
FILTER BANDWIDTH: 0.2   cps
R. F. FIELD: 0.35   mG
SWEEP TIME: 25.0   sec
SWEEP WIDTH: 500   cps
SWEEP OFFSET: 0   cps
SPECTRUM AMP: 10.0
INTEGRAL AMP:
REMARKS:

VARIAN associates
PALO ALTO, CALIFORNIA
INSTRUMENT DIVISION

CHART S-60A

PRINTED IN U.S.A.

8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 PPM (δ)

CZECHOSLOVAK ACADEMY OF SCIENCE
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

Na cvičišti 2,

PRAHA 6

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

August 13, 1963

Dear Dr. Shapiro,

In the last few months we have been mostly doing some routine work and we also had some experimental difficulties and, therefore, this time I have very little to contribute to MELLONMR.

One of the problems which is perhaps worth mentioning is the determination of the number of methyl and methylene groups in a series of compounds isolated from brown-coal tar (Chem. & Ind. 1963, 692). The relative areas were determined by simple planimetry (our spectrometer is not yet equipped with an integrator). The results were good enabling us to confirm the structure proposed for the compounds listed in Table I. The curves were approximated by Lorentz type curves; in the case of the methylene group a correction for overlap with CH group peak was carried out. All spectra were measured on our prototype spectrometer operating at 40Mc/s; (CCl_4 solutions, 10%; TMS used as inner standard; sweep rate 1 cps/s; resolution 1.3×10^{-8}).

In connection with our spectroscopic studies of nucleosides we have investigated the aza-analogues of cytidine and arrived at the conclusion that these compounds exist predominantly in the amino form both in polar and non-polar solutions. The compounds investigated were measured in dimethyl sulphoxide solutions where no chemical exchange took place and the area of the peak due to protons of the NH_2 group was determined. E.g., for 6-azacytidine the NH_2 peak appeared at 217.3 cps (lower field) from dimethyl sulphoxide signal and its area was compared with that of the peak (202.6 cps) due to the proton at the 5 position of the heterocyclic ring.

At this point I would like to mention that in some cases we employed fully deuterated dimethyl sulphoxide as solvent and it proves a very suitable solvent not only for various heterocyclic compounds but we also used it with success for work with sparingly soluble polyhydroxy terpenic compounds. (The only disadvantage of this solvent is that we have to prepare it ourselves).

I would like to end with praising the MELLONMR which is of great value for our work here. Next time I hope to contribute something more valuable as it seems that the proverb "Aller Anfang ist schwer" is still functioning.

   With best regards.

                                        Yours sincerely,

                                        J. Jonás

                                        J. Jonás

TABLE I

| Compound | Number[a] of CH_3 and CH_2 Groups | | | |
| | CH_3 | | CH_2 | |
	Theory	Found	Theory	Found
2,6,10-Trimethyl- undecane	5	4.84	6	6.02
2,6,10-Trimethyl- dodecane (Farnesane)	5	4.91	7	6.92
2,6,10-Trimethyl- tridecane	5	5.12	8	8.07
2,6,10-Trimethyl- pentadecane	5	4.80	10	10.30
2,6,10,14-Tetramethyl- pentadecane (Pristane)	6	6.02	9	9.21

[a]Average values obtained from two spectra.

Department of Chemistry and Department of Pharmacy
University of Washington
Seattle 5

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

Dear Dr. Shapiro:

Recently we investigated the NMR spectra of 4-deuterioxycyclohexanone-2,2,6,6-d_4 in pyridine, chloroform-d and deuterium oxide and have found the following interesting results. The spectra in pyridine and chloroform-d displayed a downfield pentuplet, assignable to the 4-hydrogen, and an upfield doublet attributable to the remaining four hydrogens. These assignments are consistent with the cyclohexanone ring existing in a boat conformation in which the dihedral angles between the 4-hydrogen and each of the adjacent hydrogens are approximately equal, resulting in a firstorder five peak multiplet.

The spectra obtained in deuterium oxide is consistent with the cyclohexanone ring existing in a chair conformation with the -OD group equatorial. The signal of the axial 4-hydrogen is a seven peak multiplet whereas the signals due to the adjacent hydrogens occur as a complex multiplet, indicative of the A_2B_2 portion of an A_2B_2X system.

Intermolecular rather than intramolecular hydrogen bonding is indicated by IR studies in carbon tetrachloride and chloroform at various concentrations.

An interpretation which is consistent with both the IR and NMR data is that the compound predominantly forms dimers in pyridine and chloroform-d but not in deuterium oxide, at the concentrations investigated.

Sincerely,

Bernard J. Nist
Alain C. Huitric
William F. Trager

BJN:ed

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

91109

August 23, 1963

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

Dear Dr. Shapiro:

We have recently used the Reilly-Swallen iteration program (NMRIT and NMREN) in the analysis of several A_2B_2 and AA' BB' type spectra. Frequently the $3\underline{s}_0$ spin-state [$(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$] is not involved in any observable transition and consequently the value of this energy level cannot be determined experimentally. To circumvent this problem we assume an arbitrary (but reasonable) value for this energy level and calculate the experimental energy level matrix using energy sum rules. The value for the energy level obtained after iteration is then used to recalculate the experimental energy level matrix. This process is repeated until a constant value for the $3\underline{s}_0$ energy level is obtained (two or three cycles are usually sufficient).

For example, we have analyzed the AA' BB' spectrum of 2, 2-dibromo-cyclobutanone by this procedure. Only the following set of parameters, $\nu_A = 3.40$ ppm, $\nu_B = 3.12$ ppm, $\underline{J}_{AA} = \underline{J}_{gem} = -15.31$ cps, $\underline{J}_{AB} = \underline{J}_{vic} = +11.16$ cps, $\underline{J}_{AB'} = \underline{J}_{vic'} = +7.67$ cps, $\underline{J}_{BB} = \underline{J}_{gem}' = -10.92$ cps was found to yield a satisfactory fit of all the frequencies and intensities. (The signs of the J's are relative). The average deviation between the observed and calculated spectra (Fig. 1) is 0.04 cps, well within the experimental error. As in many previous cases, opposite signs for the geminal and vicinal coupling constants are found. Although the present system avoids several possible objections to comparison with theoretical predictions, the fact that a strained-ring system is involved means introduction of a variable which removes any claim for generality.
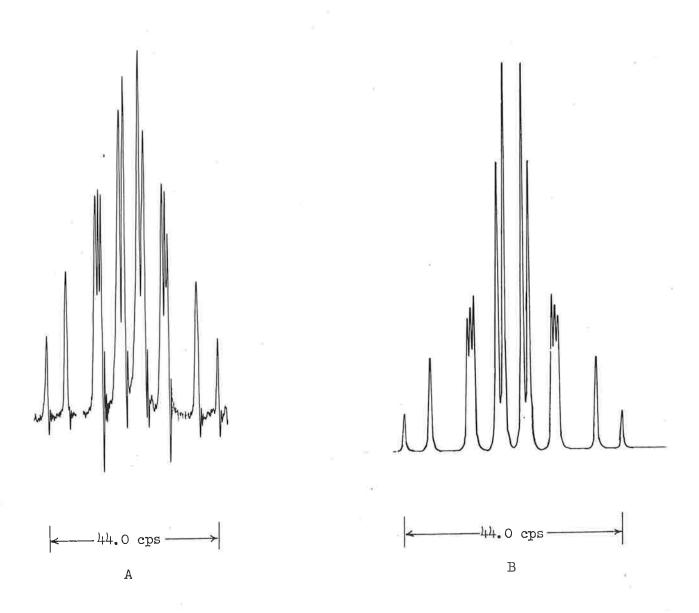
With all good wishes,

Very sincerely yours,

Kenneth L. Servis

John D. Roberts

KLS:jmd

(legend)

Fig. 1. A, The 60-Mcps nuclear magnetic resonance spectrum of
2,2-dibromocyclobutanone; B, calculated 60-Mcps nuclear
magnetic resonance spectrum of 2,2-dibromocyclobutanone.

A

B

BASF

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

IHRE ZEICHEN	IHRE NACHRICHT VOM	UNSERE NACHRICHT VOM	UNSERE ZEICHEN	TAG 17. 9. 1963

BETREFF

Dear Dr. Shapiro,

Nowadays, long range coupling is a favorite subject in the discussions of nmr-spectroscopists. I found a coupling over five bonds in certain naphthalene derivatives unknown hitherto as I believe (it is not included in the compilation by PACHLER and BRASCA in Mello-Back 47). Normally, it is assumed that the protons of the two naphthalene rings do not couple mutually. This seems to be true in naphthalene itself and in all symmetrically substituted naphthalenes, but it is not valid in e.g. 1-substituted naphthalenes. Of course, the spectrum of a 1-substituted naphthalene is complicated and it is difficult to pick out the lines belonging to a certain proton. While the lines of the protons in 3-, 4-, 5-, 6- and 7-position considerably overlap, fortunately the lines of the proton in 8-position are clearly separated at the low field end of the spectrum, the more distinct the more marked the substituent in 1-position is. In this range the spectra of 1-substituted naphthalenes show much more lines than are expected for an ABCD-problem with six different coupling constants, as it corresponds F(including a long range coupling over five bonds between proton 8 and proton 5). The discrepancy is solved if we take into consideration another coupling with one of the protons of the substituted ring with a coupling constant of about 0.8 cps. This can be only the proton in 4-position. For the other two are too far away from the proton in 8-position. Moreover, their lines are in some cases discoverable without difficulty and do not show any unexpected coupling. The lines of the 4-proton itself are overlapped too large in all cases investigated for finding the coupling with the 8-proton clearly. But if the 4-position is substituted the effect disappears as the figure shows. There seems to be a coupling between the 8-proton and the 4-proton, too, but the overlapping is terrible and the coupling constant is much smaller (about 0.4 cps).

I investigated the following substituents in the 1-position: CH_3, C_2H_5, CH_2Cl, F, Cl, Br, NO_2, CHO, $OCOCH_3$, OCH_3, OH, NH_2. This long range coupling with a coupling constant J_{48} of about 0.8 cps is also found in

F to the unsubstituted ring

Badische Anilin- & Soda-Fabrik AG

Empfänger Dr.B.L. Shapiro   Unsere Zeichen   Ludwigshafen am Rhein 17.8.63 Blatt 2
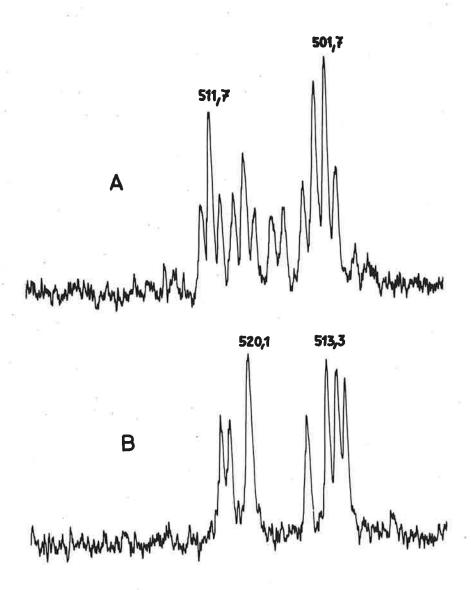
Betreff

1.2-disubstituted naphthalenes. In this moment, I can not say whether or not the same coupling takes place in 2-substituted naphthalenes too. Investigations about that are running still. The completely different character of the spectrum of a 2-substituted naphthalene, especially the less separation of the lines of the 8-proton, makes the decision difficult. Perhaps, this long range coupling appears only if the two naphthalene rings are markedly unsymmetrical as it is by a substitution in the 1-position. If this is true the unexpected coupling is connected with the "peri effect" of DUDEK (Spectrochim.Acta 19, 691, 1963) which I can completely confirm by investigation of 30 compounds. So far this coupling is comparable with the long range 4,8-coupling in 5.7-dichloroquinoline detected by ANET (J. Chem. Phys. 32, 1274, 1960). In this case, too, the reason for the long range coupling may be the marked unsymmetry of the two rings.

A similar effect is found in 9-substituted anthracenes (R = CH_3, OCH_3, Cl, Br, CHO, $OCOCH_3$, NO_2). In this case the lo-proton couples with the 1- and 8-protons (J = o.8 cps) as well as with the 4- and 5-protons (J = o.4 cps). The splitting of the signal of the lo-proton is not resolved, but the line width clearly shows the coupling.

Sincerely Yours

(Werner Brügel)

Low field spectrum (proton in 8-position) of
A: 1-nitronaphthalene, B: 1-nitro-4-methoxy-
naphthalene, 25% by weight in $CDCl_3$, degassed.
The figures are cps from TMS.

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