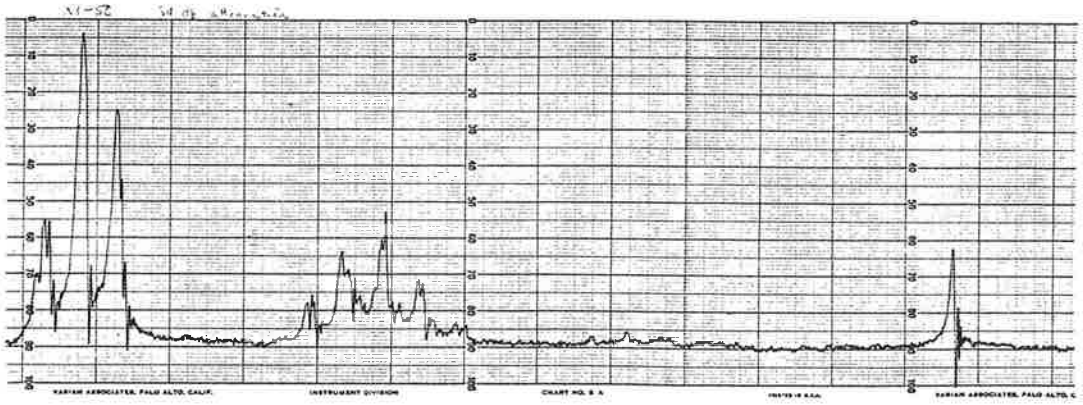
7

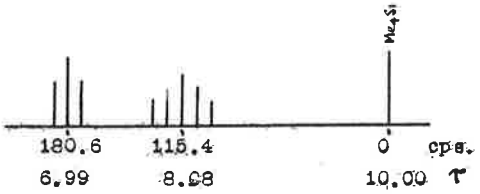
Monthly Ecumenical Letters from Laboratories Of N-M-R

No. 6



Compound: Cyclobutanone (Purified by v.p.c)
15% solution in CCl_4, degassed
Int. ref. Me_4Si(1%) No ext. ref.
R.F. = 60mc.

J_{ab} = 9.5 cps



K. B. Wiberg and B. J. Nist
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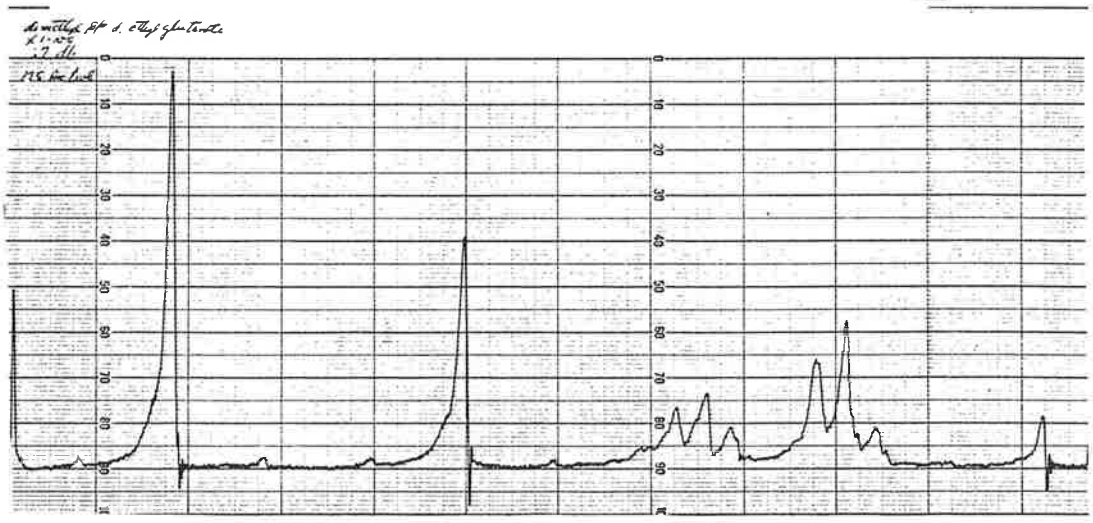
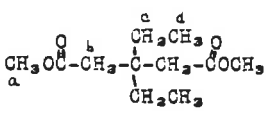
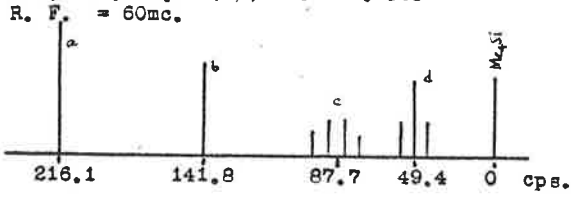


Compound: Dimethyl β,δ-diethylglutarate
15% solution in CCl_4, degassed
Int. ref. Me_4Si (1%) No ext. ref
R. F. = 60mc.



J_{cd} = 7.2 cps.



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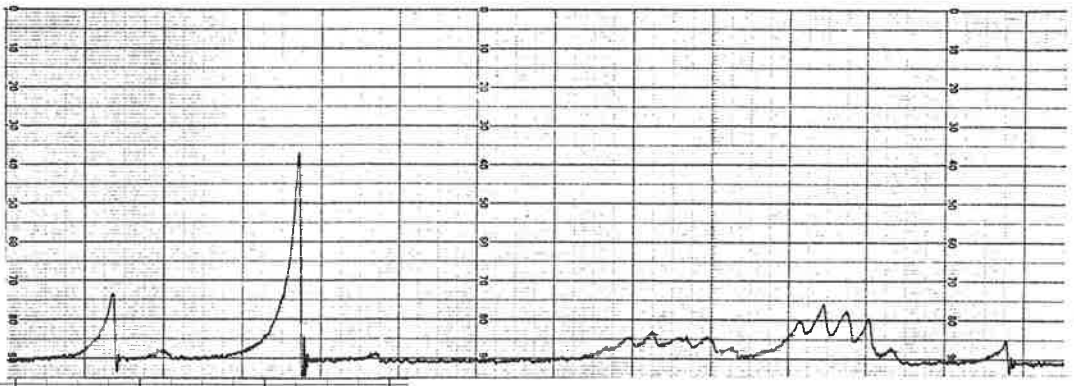
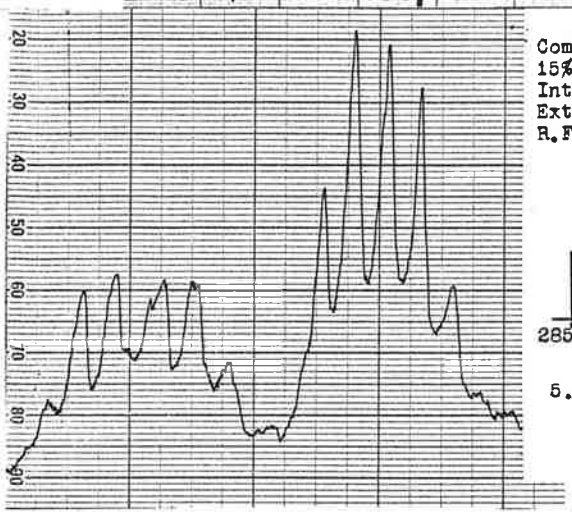
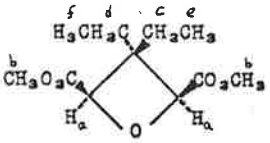
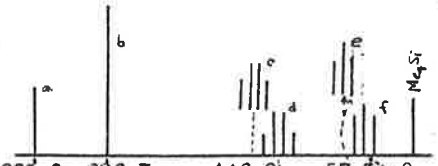




Compound: Dimethyl 3,3-diethyloxetane-cis-2,4-dicarboxylate
15% in CCl_4, degassed
Int. ref. Me_4Si (1%)
Ext. ref. none
R.F. = 60mc.





285.8 226.7 116.0 57.3 0 cps
96.9 42.2

5.24 6.22 8.07 9.04 10.00 τ
8.39 9.30

$J_{ce} = J_{df} = 7$cps

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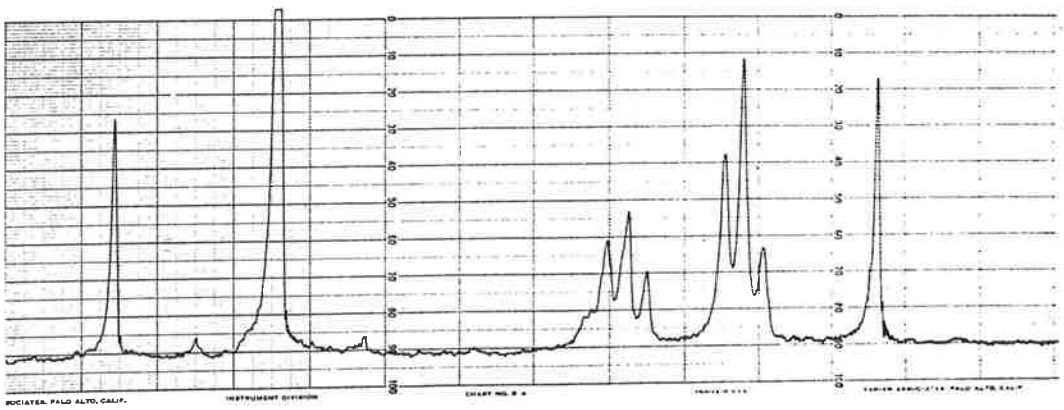
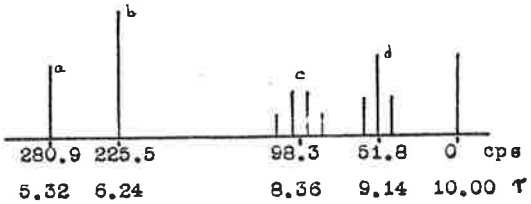
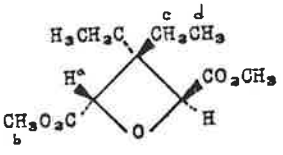


Compound: Dimethyl 3,3-diethyloxetane-trans-2,4-dicarboxylate
15% solution in CCl_4, degassed
Int. ref. Me_4Si (1%) No ext. ref.
R.F. = 60mc.



280.9 225.5 98.3 51.8 0 cps

5.32 6.24 8.36 9.14 10.00 τ



J_{cd} = 7.2cps

K. B. Wiberg and B. J. Nist
University of Washington

Lincoln College,
Oxford,
England.

March 5th, 1959.

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

Dear Aksel,

During recent months we have in our laboratory here at Oxford been using a simple procedure for measuring small quantities of organic materials in spherical samples. The use of this method is convenient when small amounts are available and it also is useful when accurate calibrations with respect to an external standard are required. I have written a short account of the method for the Proceedings of the Chemical Society, but thought you might like to hear about the method first.

A cylindrical sample tube is filled with a suitable gel which we have been making from normal laboratory gelatine in boiled out distilled water. A glass syringe is calibrated by weighing. The sample tube of gelatine is warmed to 35°C and held horizontally, and a calculated volume (about 0.03 ml.) of the sample is injected into the gelatine at about the correct height from the bottom of the tube forming a bubble in the gelatine matrix. The tube is then rotated slowly while the gel cools and the tube tilted so as to obtain a perfectly spherical bubble at just the correct position. If the sample and gel are of the same density, it is easy to adjust the position of the bubble in the tube by adding or removing gelatine from below the bubble by means of a second glass syringe. When the gel has cooled, the sample tube can be used in the ordinary way except that only low spinning speeds can be permitted to avoid distortion of the bubble. We find that using this method the amount of material required for a given signal to noise ratio is about one third of that required using a cylindrical sample tube with a nylon plug as suggested in the Varian Technical Bulletin. The resolving power obtained is always at least as good as that obtainable by the use of long cylindrical samples provided that care is taken to maintain perfectly spherical bubbles.

The water in the gel provides a very convenient external standard, and because of the spherical shape of the sample, there are no corrections for susceptibility necessary. In the Table below, I have listed the uncorrected shifts from Mellon Newsletter No. 2 given by C.A. Reilly, the same values corrected for the susceptibilites of the material to benzene as a zero, the values we have obtained using bubbles of those compounds in gelatine matrix, and the shifts using cyclohexane as an internal reference in cylindrical tubes. The last two columns represent figures obtained on our spectrometer at 29.92 Mc. corrected to a value corresponding to 40 Mc. You will see that the agreement between the bubble values and the corrected values is certainly as good as the accuracy of the magnetic susceptibilities would warrant.

The big limitation of this method is of course is that the sample must be immiscible with and unreactive to water, and also that there is a strong resonance from the water in the gel which obscures a small region of the spectrum. We have tried quite hard to find suitable matrices for samples which are miscible with water, but so far have not had any success. All the compounds we have tried so far suffer from one of the following disadvantages: (a) it does not wet glass, (b) it sets too sharply, (c) it has a complex spectrum of its own, (d) it melts at too high a temperature. We would certainly welcome any suggestions for a gel matrix which could be used with alcoholic and aqueous materials.

I very much look forward to seeing you in July,

Yours sincerely,

Rex Richards

TABLE I

Compound	Uncorrected shifts from published data.	Corrected values.	Bubble values.	Shifts using cyclohexane as internal reference.
Chloroform	-33.9	-25.0	-23.4	-20.3
Benzene	0	0	0	-16.7
Toluene ring	3.1	3.7	3.2	-11.6
Toluene	199.4	200.0	200.0	183.8
Cyclohexane	212.2	212.5	212.2	212.5

Interpretation of high-resolution NMR-spectra.

The A B case.

by R.A. Hoffman

University of Uppsala, Sweden

In the course of investigation of a series of di-substituted thiophenes [1] it has been necessary to interprete a number of nuclear magnetic resonance spectra of the A B-type [2]. The purpose of the present note is to show that with a simple re-arrangement of the well known formulae pertaining to this case[3], one can obtain equations which are better suited for rapid evaluations from the experimental resonance curve.

The general spectrum from two nuclei of spin $\frac{1}{2}$ with a chemical shift δ and a spin-spin coupling constant J consists of four lines (cf figure 1) with transition frequencies and relative intensities as given in table 1.

It is thus seen that $\nu_1 - \nu_2$ or $\nu_3 - \nu_4$ directly gives J. Further it can be verified that the ratio of the calculated intensities of the strong lines (2 or 3) to the weak lines 1 or 4 equals the ratio $(\nu_1 - \nu_4)/(\nu_2 - \nu_3)$. Finally we obtain the relative chemical shift δ from the equation

$$\delta^2 = (\nu_1 - \nu_4)(\nu_2 - \nu_3).$$

Thus if we measure the frequencies b and a (cf. figure 1) we obtain

$$\left.\begin{aligned} J &= \tfrac{1}{2}(b - a) \\ \delta &= \sqrt{a\,b} \end{aligned}\right\}$$

And the theoretical ratio of the intensities of the strong lines to the weak lines equals b/a.

With these formulae it is also easy to estimate errors in J and δ due to experimental uncertainties in b and a.

References

1. Hoffman, R.A. and Gronowitz, S. to be published.

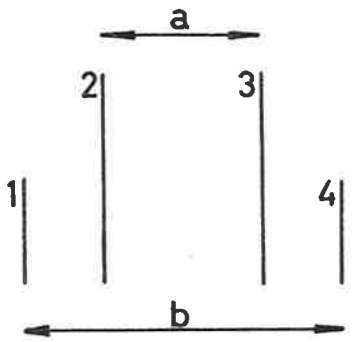
2 Bernstein, H.J., Pople, J.A. and Schneider, W.G. 1957 Canad. J. Chem. 35 65 .

3 Hahn, E.L. and Maxwell, D.E. 1952 Phys. Rev. 88 1070
Banerjee, M.K., Das. T.P. and Saha, A.K. 1954 Proc. Roy.Soc. A 226 490
Anderson, W.A. 1956 Phys. Rev. 102 151
Bernstein, H.J. et al. loc. cit.

Table 1.

Frequency relative to band center	Relative intensity
$\nu_1 = \frac{1}{2}J + \frac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}$	$1 - J/(\delta^2+J^2)^{\frac{1}{2}}$
$\nu_2 = -\frac{1}{2}J + \frac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}$	$1 + J/(\delta^2+J^2)^{\frac{1}{2}}$
$\nu_3 = \frac{1}{2}J - \frac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}$	$1 + J/(\delta^2+J^2)^{\frac{1}{2}}$
$\nu_4 = -\frac{1}{2}J - \frac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}$	$1 - J/(\delta^2+J^2)^{\frac{1}{2}}$

Fig. 1



March 17, 1959

PROTON NUCLEAR RESONANCE SHIELDING VALUES, τ, FOR SOME ORGANOSILICON COMPOUNDS

Compound	τ-Value[a]	Mult.	Vol.% conc. in CCl_4	J (c.p.s.)[a]
$C_6H_5SiMeCl_2$	2.52	m.	5.	
$C_6H_5SiH_3$	2.64	m.	5., 10.	
$(CH_2=CH)_2SiCl_2$	3.79	m.	5.	ca. 1
$CH_2=CHSiMeCl_2$	3.848		5.	sharp
$HSiCl_3$	3.95		ca.10 in cyclohexane	
	3.937	(b)	0.0 in cyclohexane	
$CH_2=CHSiMe(OEt)_2$	4.092		5.	sharp
$CH_2=CHSi(OEt)_3$	4.102		3.	sharp
$C_2H_5SiHCl_2$	4.539		7.	
$(C_6H_5)_3SiH$	4.57		10.(w/v)	
$(C_6H_5)_2SiH_2$	5.14		5.	197.2 (Si^{29}-H)
$C_6H_5SiH_3$	5.81		5.,10.	200.0 (Si^{29}-H)
$Si(OCH_2CH_3)_4$	6.21	q	5.	7.0
Allyl-$Si(OCH_2CH_3)_3$	6.22	q	5.	7.0
Vinyl-$Si(OCH_2CH_3)_3$	6.23	q	3.	7.1
Vinyl-$SiMe(OCH_2CH_3)_2$	6.27	q	5.	7.0
$Me_2Si(OCH_2CH_3)_2$	6.30	q	4.	6.9
Me_3SiCH_2OH	6.72		2.0	
Me_3Si-C=CF-CF_2-CH_2	7.47	d,t	6.0	12.5 (d), 3.0 (t)
$CH_2=CH$-$CH_2Si(OEt)_3$	8.45	d	5.	7.2
$Si(OCH_2CH_3)_4$	8.80	t	5.	7.0
Allyl-$Si(OCH_2CH_3)_3$	8.81	t	5.	6.9
Vinyl-$Si(OCH_2CH_3)_3$	8.82	t	3.	7.1
Vinyl-$SiMe(OCH_2CH_3)_2$	8.82	t	5.	7.0
$Me_2Si(OCH_2CH_3)_2$	8.83	t	4.	6.9
CH_3-CH_2SiHCl_2	8.850		7.	(v.narrow mult.)
$MeSiCl_3$	8.855	(c)	4.	
$C_6H_5SiMeCl_2$	8.992		5.	

MINNESOTA MINING & MANUFACTURING CO.

March 17, 1959

PROTON NUCLEAR RESONANCE SHIELDING VALUES, τ, FOR SOME ORGANOSILICON COMPOUNDS

Compound	τ - Value[a]	Mult.	Vol.% conc. in CCl_4	J(c.p.s.)[a]
Vinyl-$SiMeCl_2$	9.160		5.	
Me_2SiCl_2	9.199	(c)	2.0	
4-cyclohexenyl-$SiMeCl_2$	9.259		10.	
Me_3SiCl	9.579	(c)	2.0	
Me_3Si-C=CF-CF_2-CH_2	9.79		6.0	
Me_3Si-CH-CCl_2-CF_2-CH_2	9.81		6.0	
Me_3Si-CH-CFCl-CF_2-CH_2	9.83		10.	
Vinyl-$SiMe(OEt)_2$	9.898		5.	
$(Me_2SiO)_4$	9.925		2.0	
$(Me_2SiO)_5$	9.938		2.0	
$Me_3SiOSiMe_3$	9.948		2.0	
$Me_2Si(OEt)_2$	9.958		4.	
Me_3SiCH_2OH	9.962		2.0	
Me_4Si	10.000		1.0, 5.0, etc.	

a) The τ-values given to three decimals have standard deviations averaging + 0.015 and were obtained by the technique of J.Phys.Chem., 62, 1151 (1958); Values given to two decimals were obtained by the less precise method of J. Phys. Chem. 63, 302 (1959). The J-values were obtained by similar methods and appear to have standard deviations of ± 0.1 cps.

b) C. M. Huggins and D. R. Carpenter, J. Phys. Chem. 63 238 (1959). Conversion to τ -values by addition of τ-value for cyclohexane in cyclohexane solution, 8.544 τ (8.564 τ in CCl_4).

c) Measurements also reported by E. Schnell and E. G. Rochow, J. Inorg. & Nucl. Chem, 6, 303 (1958); unfortunately their numerical values appear virtually worthless.

GVDT:bv

Dr. George Van Dyke Tiers

3-18-59