

Mailed: OCT 28 1960

Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R
No. 25

A monthly collection of informal private letters from laboratories of nmr.
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Basle, October 12, 1960

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

Dear Dr.Bothner-By:

Your letter (MELLONMR No.9) and P.R.Shafer's (MELLONMR No.18) convinced me that it would be worthwhile to build the magnet shim coils for the Varian V-4012A-SM electromagnet by ourselves. We have done so successfully, following more or less the path described by P.R.Shafer.

As a further accessory we added a set of two pairs of coils (in the plane of the x-, y- and z-coils) in order to be able to correct for an overdishd or dome-shaped field. The theory underlying this is simple. One has to take a pair of coils with a larger radius and a pair with a smaller one. The latter has to produce a field in the opposite direction (Fig.1). As each pair has a different radial distribution of the field strength in the median plane (where the tube is sited), a resulting field can be obtained which is zero in the center of the median plane and which has a finite value farther out.

Plotting the field strength differences in the x-direction between a more and a less dishd field, one gets an idea of the radial distribution of the field strength which has to be produced by the difference in the fields of the two pairs of shim coils. The values we obtained were roughly the following (Fig.2):

Table 1

Radial distance from center				
in mm	4.4	11.0	17.6	22.0
in parts of a	0.2	0.5	0.8	1.0
Percent of maximum field strength difference	20	67	94	100
Theoretical value obtained with our shim coils (%)	15	67	94	85

where a (=22mm) is the radial distance from the center of the maximum field strength difference.

The radial distribution of the field strength in the median plane for a pair of coils may be calculated with the help of tables given by C.L.Bartberger (J.Appl.Physics 21, 1108 (1950)). The distance of the two coils is 44 mm (=1.75") or 2a. As each pair of coils with a different radius has a different radial field distribution, one has to find out which set of two pairs would best fit the values given in row 3 of table1(Fig.3). It turns out that the two pairs with a radius of 0.3a (=6.6mm = 0.26") and 1.1a (=24.2mm = 0.95"), resp., best fit the desired variation of the field strength. The lack of fit far out does not bother us much, for those nuclei do not contribute much to the signal anyhow.

Experimentally we proceeded along the lines proposed by P.R.Shafer, except that we chose a radius of 2a (=44mm = 1.75") for the x-, y- and z-coils (Helmholtz arrangement). The concentric 1.1a-coil has 21 turns and the 0.3a-coil 100 turns (Fig.4). The 1.1a-coils are interconnected, so that the current passes through them in the same direction, and so are the 0.3a-coils inter se but with the field reversed. With this arrangement one should obtain a field strength of 7 mgauss with a current of 5 ma through each coil at a distance of 0.5a (=11mm = 0.43") from the center. The average drain is around 0.5 ma.

The coils are placed upon the pole face covers and protected with a PVC cover. The resistances L,M and N are 100, 10K and 100 ohms, resp. (See MELLONMR No.18, p.4). In order to have exactly opposite field strengths at the center a further potentiometer of 100 ohms is necessary (Fig.5). The correct position of this potentiometer is found by trial. The signal on the scope has to stay put at full variation of the current through the coils.

We are planning to simplify the arrangement so that we need only one potentiometer instead of the coarse and fine one and so that the polarity does not have to be changed separately. The y-gradient and curve shape correction coils are a real help to us. They apparently are independent of each other.

I am indebted to Drs.E.Ganz and St.Hubbard for reading the manuscript and to Mr.Längin for doing the experimental work.

In closing this letter I should like to thank you for including me on the mailing list of MELLONMR - an extremely useful journal.

Sincerely yours,

R. Zürcher

R.F.Zürcher

RFZ:am

FIG.1

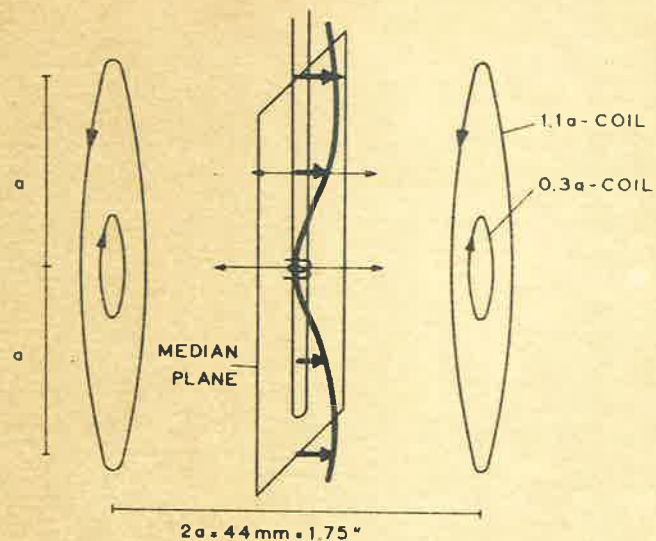


FIG.2

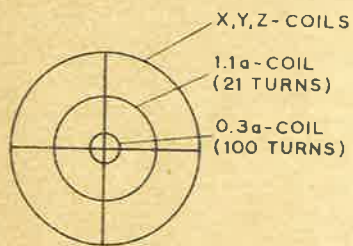
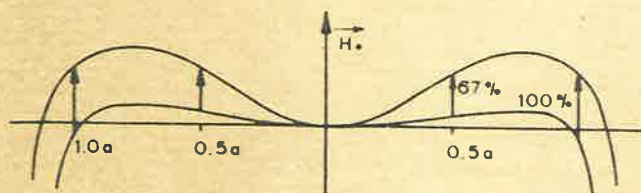


FIG.4

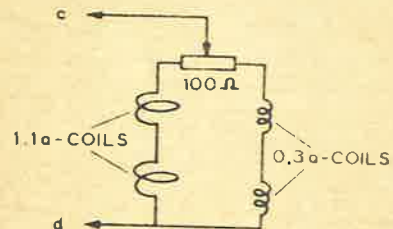
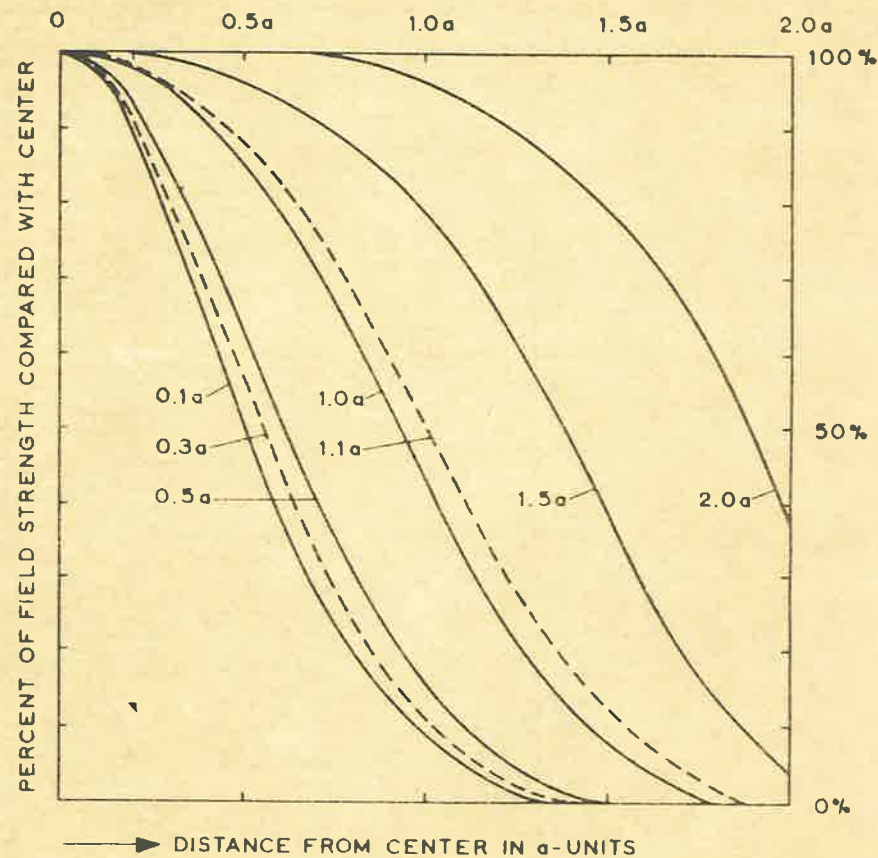


FIG.5

FIELD STRENGTH OF A COIL PAIR IN THE MEDIAN PLANE



DISTANCE OF COILS : $2a = 44 \text{ mm} = 1.75''$

PARAMETER : RADIUS OF THE COIL IN a -UNITS

FIG.3

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TUXEDO, NEW YORK

UNION CARBIDE RESEARCH INSTITUTE

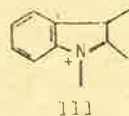
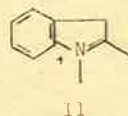
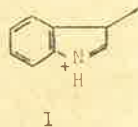
October 11, 1960

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

Dear Dr. Bothner-By:

Thank you for the reminder that my subscription to M.E.L.L.O.N.M.R. is in arrears. Following are two items which I hope are worth five months apiece.

Through the suggestion of Dr. R. L. Hinman of our physical biology group, I have examined some proton resonance spectra of methylindoles in aqueous H_2SO_4 in order to help determine the position at which protonation occurs. At acid concentrations in the range of 12M exchange is slow enough to give resolved multiplets which show rather clearly that the proton adds to the 3-position. In skatole, for example, the methyl group in the protonated form I is shifted (relative to the aromatic hydrogen) to higher field by about 1.2 ppm and split into a 7.5 sec^{-1} doublet. A quartet corresponding to the added proton in the 3-position is observed, and at lower field than the aromatic line(s) a doublet is assigned to the hydrogen in the 2-position. This splitting is due to the otherwise unobserved N-H proton, and demonstrates that exchange processes involving either of these hydrogens are slow. In 1,2-dimethylindole (II) the line corresponding in shift to the quartet in I

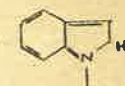
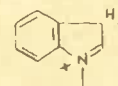


Dr. Aksel A. Bothner-By

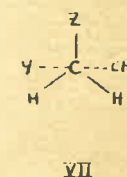
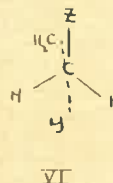
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October 11, 1960

is single and twice as intense. In the trimethylindole III we have observed the disappearance of multiplet structure in the methyl group and the broadening of the 3-ring proton resonance on dilution of the acid. I am doing further work on the exchange rates, while Dr. Hinman has submitted a paper dealing with the structural evidence. The contrast between the 3-protonation of indoles and the 2-protonation of pyrroles is not too surprising when one considers that there are two unexcited structures corresponding to IV and only one for V. C_3 rather than N protonation of indole is analogous to the existence of acetaldehyde and ethylene imine rather than vinyl alcohol and vinyl amine.



A second problem in which I've been interested is the correlation of long-range coupling constants and molecular information in dihalopropenes. Assuming an angular dependence $J = J_0 \cos^2 \phi$ on the dihedral angle between a methylene C-H bond and the π axis of the central carbon as suggested in the recent letter by Karplus; and further assuming that the constant term J_0 is unaffected by allylic substitution, one obtains a relation between the long range couplings J_3 and J_2 in the systems $R-CH_3$ and $R-CH_2E$ ($R = \text{vinyl}$) of the form $J_2 \approx J_3 (1/2 + \sin^2 \phi')$, where ϕ' applies to the allylic substituent. Combining this with appropriate IR intensity data for doubled bands in some dihalopropenes has pointed to the existence of the two forms VI and VII. Their relative proportions vary with the solvent in a predictable manner, the slope in Figure 1 being that calculated from a point



Dr. Aksel A. Bothner-By

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October 11, 1960

dipole-Onsager cavity model. The extrapolated data suggest that, in the vapor, form VI of 2,3 dichloropropene is lower in energy by some 900 cal/mole than VII. This correctly predicts the temperature dependence of the dipole moment although the calculated moments are low by about 0.18 D both in vapor and (benzene) solution.

I am in process of writing up some of this work and hope to have preprints available for anyone interested. In the meanwhile, I would appreciate anyone else's thoughts or comments on the subject.

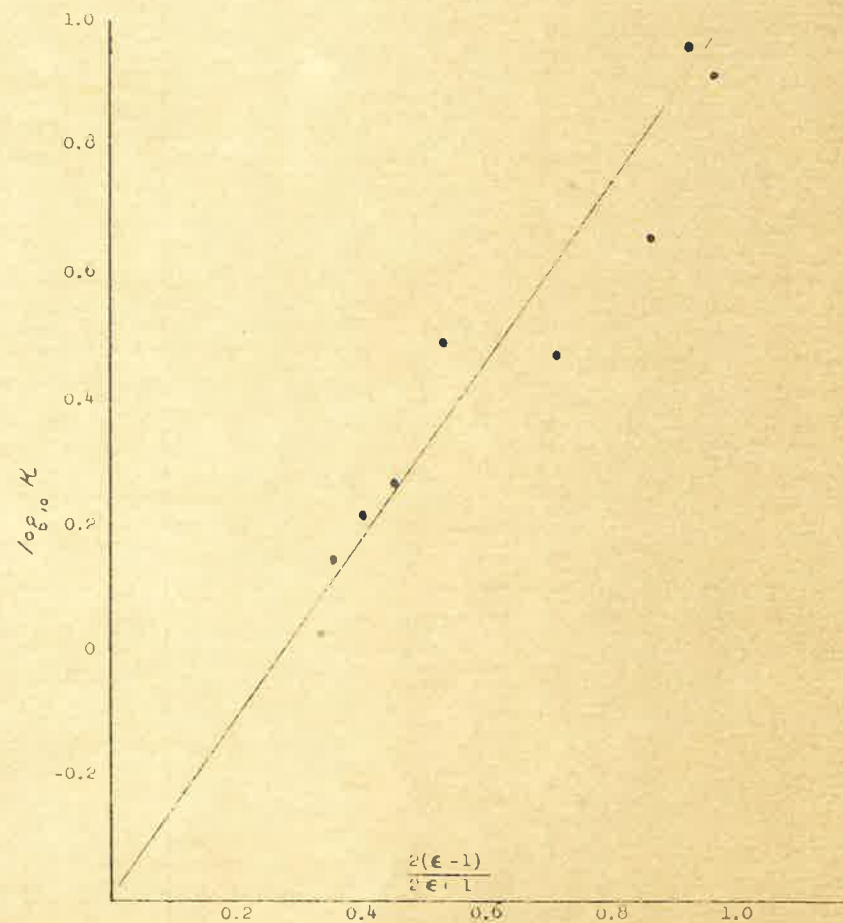
I continue to enjoy your excellent newsletter, both as a service to and forum for people interested in the NMR field.

Sincerely yours,

E. B. Whipple
E. B. Whipple

EBW/gh

Variation of Rotational Isomer Equilibrium Constant in
2, 3 Dichloropropene with Solvent Dielectric Constant



CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

WATER AND SPECTROSCOPY LABORATORIES OF CHEMISTRY

October 14, 1960

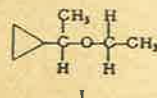
Dr. A. A. Bothner-By
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel,

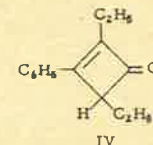
The recent letter to MELLONMR by John Waugh regarding nonequivalence of ethyl methylene hydrogens in acetaldehyde diethyl acetal caught us with a manuscript written but lacking the final numbers from calculations by your 704 computer program needed to compare calculated and observed line positions and intensities for the n.m.r. spectra of acetaldehyde diethyl acetal and several related compounds having ethyl groups attached to asymmetric centers.

The present work follows up our previous observations [P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957)] that the methylene protons of systems of the type $R-CH_2-CR_1R_2R_3$ may be magnetically nonequivalent and display AB rather than A_2 -type spectra. We have several examples of this type of behavior with ethyl groups ($R=CH_3$), particularly ethoxy groups, knowledge of which could be important to anyone using n.m.r. for organic qualitative analysis. This work has been carried on by Paul R. Shafer, Donald R. Davis, M. Vogel, and K. Nagarajan. We are much indebted to S. L. Manatt and the Jet Propulsion Laboratory Computer Group for aid with the calculations.

A typical example is cyclopropylmethylcarbinyl ethyl ether (I). The n.m.r. spectrum of the ethyl CH_2 group of I appears as the AB part of the ABX_3 type.

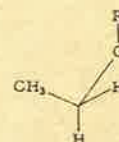
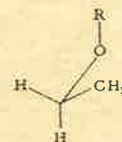


with $\nu_A - \nu_B = 9.0$ cps and $J_{AB} = 9.4$ cps. The nonequivalence of the CH_2 hydrogens is due to the asymmetric center at the carbinyl group of the cyclopropylmethylcarbinyl moiety, which acts to favor one of the possible rotational conformations about the C-O bonds over the others. Similar behavior has been noted with acetaldehyde diethyl acetal (II) and acetophenone diethyl ketal (III), and with ethyl-substituted cyclobutenones such as IV. With IV the effect is



observed with CH_2 of the ethyl located directly at the asymmetric 4 position and is further complicated, of course, by spin-spin interaction involving the 4 hydrogen.

As noted by Waugh the spectrum of II (and of I and III) shows a very interesting effect in that the methylene hydrogens of the ethyl groups are not equally coupled to the methyl hydrogens. We find the respective couplings to be 7.35 cps and 6.68 cps for I and II. Since the splittings result from electron coupling of nuclear spins, these differences in J values speak for induction of asymmetry in the bonding of the methylene protons to their carbon. Such would be expected to be the case if the effect of R were to make either V or VI a more favorable conformation about the C-O bond than VII. Predominance of



either V or VI would fit well, of course, with the considerable chemical shift difference between the methylene hydrogens. One conformation must be highly favored because no significant change in the spectrum of II was noted at temperatures as low as -80° .

The asymmetry observed by Finegold [*Proc. Chem. Soc.*, 283 (1960)] for the ethyl groups of diethyl sulfite may well arise from the same causes as those discussed here. We have noted changes in the methylene resonance of acetophenone diethyl ketal (III) when the material is diluted with carbon tetrachloride. These changes are analogous to those observed by Finegold for diethyl sulfite.

With all good wishes,

Very truly yours,

John D. Roberts

John D. Roberts

Professor of Organic Chemistry



NATIONAL INSTITUTES OF HEALTH
U.S. GOVERNMENT PRINTING OFFICE

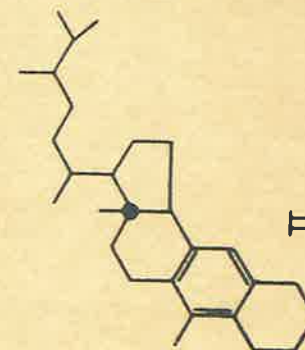
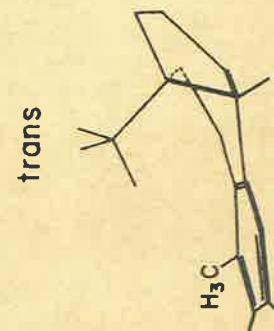
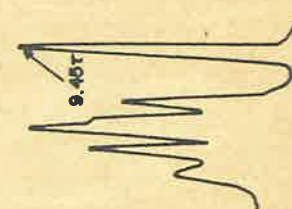
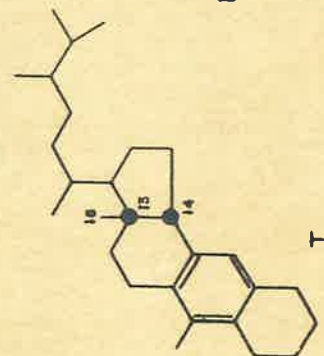
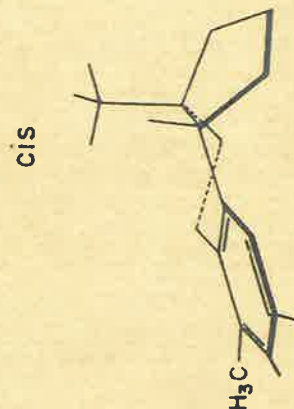
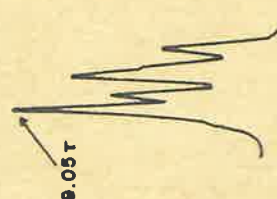
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
BETHESDA 14, MD

October 18, 1960

RING CURRENT EFFECTS IN STEROID SYSTEMS

In the course of their studies on the rearrangement of polyunsaturated steroids, J. A. Steele and E. Mosettig (Steroid Section, Laboratory of Chemistry) obtained a pair of isomeric hydrocarbons which were known from chemical evidence to differ only in stereochemistry at C₁₄. The task was then undertaken to determine which was which. Upon examination of the NMR spectra of both compounds in CCl₄ solution, we were surprised to find a marked difference in chemical shift for the angular methyl protons (C₁₈). It is evident by inspection and superposition that the two NMR curves differ only in the position of the C-CH₃ peak. Since a chemical shift of 9.45 τ is about 0.2 τ higher field than the maximum values generally observed for saturated steroid protons, magnetic shielding of the angular methyl by the aromatic B ring was suspected. Inspection of Dreiding models supported the assumption. In the *cis* isomer, the C₁₃-C₁₈ bond is oriented about 110° away from the aromatic plane; in the *trans* isomer the bond is only 50° from the aromatic plane with one of the methyl protons close enough to fall within the field of π electron density. On this basis, as well as from supporting chemical evidence, II has been assigned the *trans* structure. By comparison, the C₁₈ methyl of estrone (aromatic ring A, C/D *trans*) appears at 9.11 τ while that of neoergosterol (aromatic ring B, C/D *trans*) is at 9.40 τ , again showing the influence of the ring current in a rigid, *trans*-fused system.

Louis A. Cohen
Metabolite Section
Laboratory of Chemistry



(Contribution from The Kedzie Chemical Laboratory,
Michigan State University, East Lansing, Michigan)

September 24, 1960

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

Dear Dr. Bothner-By:

During a recent NMR investigation of internal rotation in some substituted amides,¹ we encountered an interesting phenomenon pertaining to the effects of solvents on barrier heights. The barrier height, E_a , for internal rota-

¹ J.C. Woodbrey, in a doctoral thesis submitted to The School for Advanced Graduate Studies of The Michigan State University, East Lansing, Michigan, 1960; J.C. Woodbrey and M.T. Rogers, in a paper to be presented at The 138th National Meeting of The American Chemical Society, New York, N.Y., September, 1960.

tion about the central C-N bond of N,N-dibenzylacetamide (DBA), 38.0% mole percent in dibromomethane solution, was found to be 7.3 ± 0.7 kcal./mole. The corresponding value for 38.2% mole percent DBA in carbon tetrachloride solution was found to be 6.4 ± 0.7 kcal./mole. Although these two values do overlap, we felt that the two least-squared values differed sufficiently to warrant further study of other systems.

Consequently, barrier heights for internal rotation about the central C-N bond of N,N-dimethylpropionamide (DMP) and of N,N-dimethylcarbamyl chloride (DMCC) were determined for several concentrations of each amide in dibromomethane solutions. Similar determinations were made for several concentrations of each amide in carbon tetrachloride solutions. The values of E_a obtained for DMP in each solvent are plotted in Fig. 1, and the corresponding values obtained for DMCC are plotted in Fig. 2. The errors for the values shown in these two figures, just as those given above for DBA, include the limits of 90 percent confidence.

Each barrier height was calculated from the temperature dependence of the rate of internal rotation. Proton magnetic resonance spectra ($\nu_0 = 60,000$ mcs.) were obtained for each sample at several different temperatures. While sweeping through a given spectrum, the temperature of the sample was usually controlled to better than $\pm 0.15^\circ\text{C}$. Rates of internal rotation were obtained from the ratios of maximum to central minimum v-mode intensities,² for the chemical-shift doublet arising from the protons of the two N-methyl or the two N-methylene groups. This method allowed the calculation of barrier heights with considerably smaller errors than those previously reported for similar studies.³

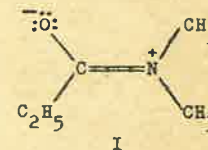
² A. Loewenstein and S. Meiboom, J. Chem. Phys. **27**, 1067 (1957).

³ H.S. Gutowsky and C.H. Holm, *ibid.* **25**, 1228 (1956); L.H. Piette and W.A. Anderson, *ibid.* **30**, 899 (1959); P. Gray and L. Reeves, *ibid.* **32**, 1878 (1960); B. Sunners, L.H. Piette and W.G. Schneider, Can. J. Chem. **38**, 681 (1960).

(Contribution from The Kedzie Chemical Laboratory,
Michigan State University, East Lansing, Michigan)

-2-

Fig. 1 shows that the barrier height for DMP decreases from 9.2 ± 0.8 kcal./mole for the pure amide to 6.3 ± 0.5 kcal./mole for 11.0% mole percent amide in carbon tetrachloride solution. This large decrease in E_a on dilution with carbon tetrachloride may be due to a decrease in contribution of the highly polar resonance form I with decrease in the dielectric constant of the medium ($\epsilon \approx 2.2$ for CCl_4 , $\epsilon \approx 38$ for DMP). The high barriers for internal rotation about the C-N bond of most amides are attributed to the contribution of the structure analogous to I to the resonance hybrid. The barrier height should, therefore, be sensitive to any changes in the importance of this form.



The value of E_a for DMP is similarly found to be lower in dilute dibromomethane solutions. It drops to 7.1 ± 0.8 kcal./mole for 10.1% mole percent amide. The dielectric constant of dibromomethane is about 7.2. However, for solutions of intermediate concentration of DMP in dibromomethane the barrier height appears to rise, reaching a maximum of about 10.3 kcal./mole at about 66 mole percent amide. This suggests that hydrogen bonds of the type $\text{HBr}_2\text{C}-\text{H} \cdots \text{O}=\text{C}-\text{N}(\text{CH}_3)_2$ may stabilize the polar form I and increase the barrier height on initial dilution. That the maximum in E_a appears to occur at about 66 mole percent amide may mean that only one hydrogen atom of the solvent interacts with each oxygen atom of the amide.

The observed effects of solvents on the barrier height for DMP are supported by the data shown in Fig. 2. These results show somewhat similar effects of dilution on the barrier height for DMCC.

To learn more about the nature of these solution effects, one of us (MTR) is studying solutions of other substituted amides and solvents.

Sincerely,

James C. Woodbrey
James C. Woodbrey*

Max T. Rogers

Max T. Rogers

* Present Address: W.R. Grace & Company
Research Division
Analytical & Physical Research Department
Clarksville, Maryland

(Contribution from The Kedzie Chemical Laboratory,
Michigan State University, East Lansing, Michigan)

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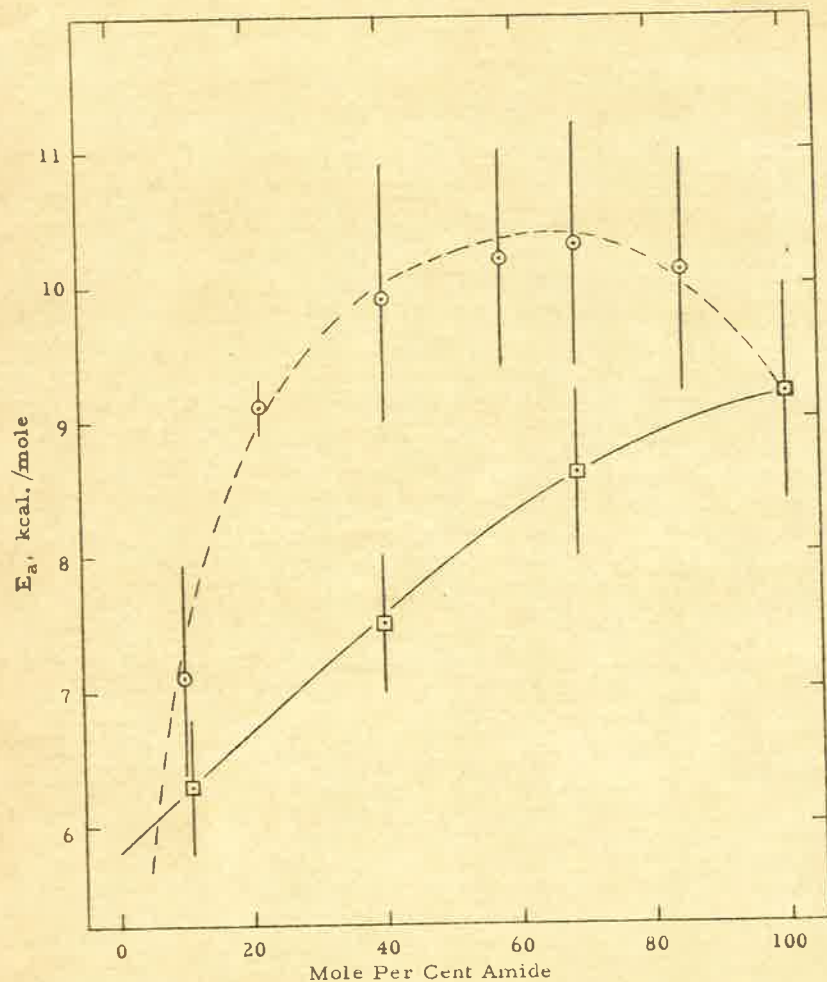


Figure 1 Concentration dependencies of the energy barrier E_a for internal rotation about the central C-N bond of N,N-dimethylpropionamide in: (a) dibromomethane solutions - -○- -○- -, and (b) carbon tetrachloride solutions —□—□—.

(Contribution from The Kedzie Chemical Laboratory,
Michigan State University, East Lansing, Michigan)

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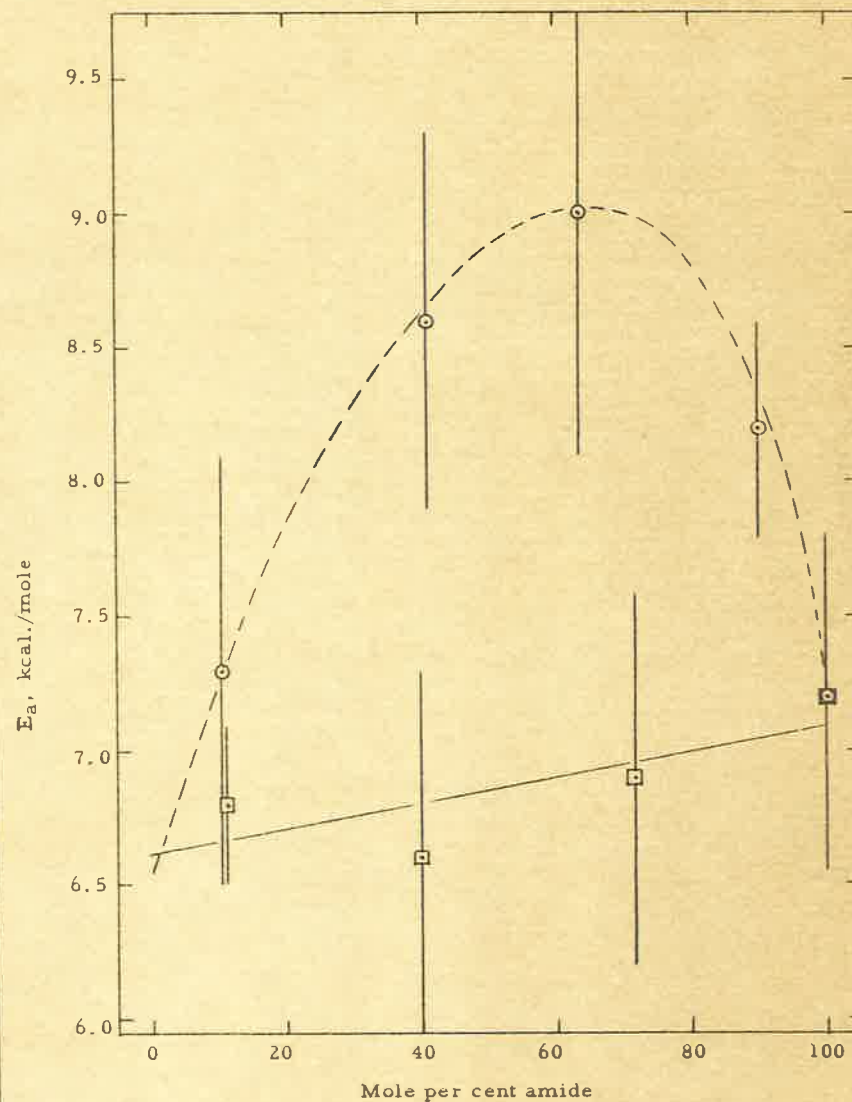


figure 2 Concentration dependencies of the energy barrier E_a for internal rotation about the central C-N bond of N,N-dimethylcarbamyl chloride in: (a) dibromomethane solutions - -○- -○- -, and (b) carbon tetrachloride solutions —□—□—.

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE.
TELEPHONE 56491.

26th September, 1960.

Drs. A.A. Bothner-By and B. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.,
U. S. A.

Dear Aksel and Barry..

I apologise for the fact that you found it necessary once again to prod me into contributing to your excellent Newsletter. I've actually had 'Newsletter' chalked on the blackboard in my room for three months, but 'The pathway to hell

(1) First of all I should like to make a slight correction to my previous letter in No.15. There I stated, correctly, that we had found that analysis of an ABC X spectrum can in principle give the relative signs of all the coupling constants: this is possible because strong coupling between the A, B and C nuclei gives rise often to an asymmetrical X spectrum and the orientation of this asymmetrical pattern as a whole with respect to the ABC spectrum determines the relative signs of the AB and AX types of coupling constant. We have (see below) applied this method to the determination of the relative signs of the HH and HF coupling constants in vinyl fluoride: but the example that I quoted (the vinyl, ABC, and allylic, X, hydrogens of 3 methyl butene-1) in fact does not (as I erroneously stated) give this information because of the complexity of the X spectrum caused by coupling with the methyl protons. Thus the long-range coupling constants maintain their sign ambiguity and should read:

$J_{12} = \pm 6.5$, $J_{13} = \mp 1.2$, $J_{14} = \mp 1.7$ Of course, on earlier precedent we prefer the top signs as originally quoted, but these are not in fact experimentally determined after all. Sorry!

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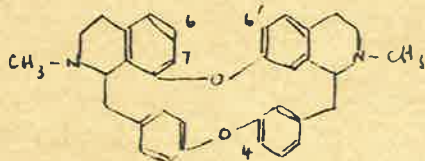
(2) Mr. Banwell's results for the coupling constants of vinyl fluoride are J_{HH} (trans) = 12.8 (assumed +ve), and it then follows that J_{HH} (cis) = +4.9, J_{HH} (geminal) = - 3.2, J_{HF} (trans) = +52.4, J_{HF} (cis) = +20.1 and J_{HF} (geminal) = +84.7 in units of c/s. Bak, Shoolery and Williams have previously shown that in fluorobenzene ortho and meta J_{HF} coupling constants are positive with respect to J_{HH} (ortho). As the latter has almost certainly the same sign as J_{HH} (cis) in vinyl compounds it follows that all J_{HF} coupling constants so far determined are of the same sign and positive in this sense.

(3) Our work on the NMR spectrum of vinyl compounds, $CH_2 = CH X$, has now been completed and will appear before long in 'Molecular Physics' (Banwell and Sheppard). The main conclusions are that the cis, trans and geminal coupling constants vary roughly in unison and approximately linearly with the electronegativity of the adjacent atom X. The points for X = C, N, O, and F fall on an excellent straight line, whereas those for Cl and Br are not far off: it seems that these coupling constants are mostly determined by inductive effects probably transmitted through the σ bonds; on the other hand the difference between the chemical shift of the proton nearest to X and the mean of those of the $-CH_2$ groups varies roughly linearly with Taft's, σ_R , resonance parameter i.e. the chemical shifts are largely dependent on π -electron effects.

(4) Mr. Turner has a paper in press (also in 'Molecular Physics') describing the application of the 'wobble-beat' method to analysing the spacings within an unsymmetrical four-line pattern such as that obtained from a 3:1 mixture of SiH_3D (giving a 1:1:1 triplet) and SiH_4 (giving a singlet of intensity equal to the others, separated from the centre one by the isotope effect in the hydrogen chemical shifts).

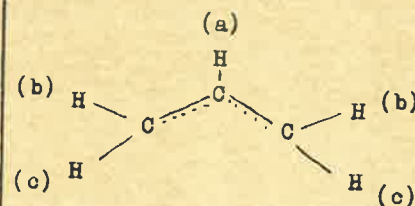
By this means he and Dr. Ebsworth obtained the value of 0.411 ± 0.003 c/s for the HD coupling constant and 0.0080 ± 0.0005 ppm. for the chemical shift. This method relies on the use of a computer but is of considerable accuracy and is capable of generalisation to other fairly simple systems.

(5) In the field of the NMR spectra of large molecules, we (Dr. Bick, Mr. Harley-Mason, Mr. Vernengo and myself) have studied the spectra of a considerable family of bisbenzylisoquinoline alkaloids and have found that the locations of methoxy groups can often be readily determined by the chemical shifts of the sharp OCH_3 resonances. Thus in alkaloids of the repandine and oxyacanthine types of structure



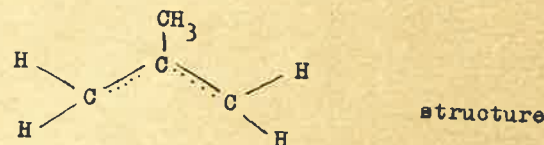
methoxys at positions 4, 6, 6' and 7 have characteristic chemical shifts and can hence be identified as such. The 6' methoxyl resonance also has consistently different values dependent on whether the two asymmetrical carbon atoms (adjacent to N) are of the (++) or (+-) types, and the NCH_3 resonances differ depending on whether the ether linkage between the two lower benzene rings is as drawn or goes in diagonally the opposite sense as in berbamine and tetrandrine types of alkaloid. This work will appear in J. Chem. Soc. in several months time. A study of another large molecule, gibberellic acid, has recently been published (J. Chem. Soc. 1960, 3040). It seems to us that OCH_3 and NCH_3 resonances are going to play an important part in evaluating subtle structural features of alkaloids as C-CH_3 resonances have with steroids.

(6) I should now like to make some points in relation to recent contributions to the Newsletter. With respect to the ring-inversion work described by Reeves and Strømme (No.23) and Claeson, Androes and Calvin (No.22), Mr. Harris is making similar measurements on perfluorocyclohexane which has a 'broad' spectrum at room temperature. Also, with Dr. Chatt and Dr. Shaw, I have been studying the NMR spectra of the Pd coordination complexes $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$, $[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)]$ and $[\text{Pd I}(\text{C}_3\text{H}_5)]_2$ with allyl (C_3H_5) ligands from which we deduce the essentially planar structure of the ligand and the following patterns of coupling constants that are similar to those reported by Moore, Jonassen and Joyner (No.23) for C_4H_7 .



$J_{ab} = 6 \text{ to } 7 \text{ c/s}$
 $J_{ac} = 10 \text{ to } 14 \text{ c/s}$
 $J_{bc} = 0 \text{ (within experimental error)}$

The chemical shifts vary somewhat from complex to complex. We have also studied a complex $[\text{PdCl}(\text{C}_4\text{H}_7)]_2$ which is considered to have the



and (consistent with the above results and a zero $J_{\text{CH}_3\text{-H}}$ coupling) we find no fine structure on the 3 peaks due to the CH_3 and the two H_2 groups.

(7) I should like to sound the reactions (if any) of Newsletter readers to a proposal that coupling constant data be presented in such a form as to correct for the differing magnetic properties of the nuclei involved. Thus, in theoretical terms, the coupling constant J_{AB} in cycles per second (c/s) between two nuclei A and B can be expressed as $J_{AB} = f(E) \gamma_A \gamma_B$ where $f(E)$ is some function of the electronic structure of the molecule concerned and γ_A and γ_B are the magnetogyric ratios of the two nuclei. As a chemist, or as a theoretical chemist, one is interested in the extent to which this type of experimental data can be correlated - if at all - with other electronic properties of the molecule (e.g. bond orders, the electronic wave functions etc.); for this purpose it is $f(E)$, or some quantity proportional to this, which is relevant and not the experimental parameter J_{AB} . In various studies that we have made during the last few years we have been concerned on different occasions with the relative magnitudes of coupling constants involving the pairs of nuclei HH and ^{13}CH , HH and PH, HH and ^{29}SiH , HH and HF, HPT and HP and we have spent quite a little time looking up the magnetogyric ratios of ^{13}C , Pt, P etc. to convert our data tabulated in c/s to 'nuclear-free' units. I should like to propose tentatively that NMR spectroscopists aim at quoting as before 'raw' experimental data of coupling constants in c/s, but that we quote our derived values in coupling units, (c.u.?!) given by $J_{AB} \gamma_H \gamma_H / \gamma_A \gamma_B = f(E) \gamma_H \gamma_H$ where γ_H is the magnetogyric ratio of the hydrogen nucleus. On this choice of units the coupling data for a pair of hydrogen nuclei remain numerically as measured in c/s, those for ^{13}CH , HF etc. pairs of nuclei have to be multiplied by $\gamma_H / \gamma^{13}\text{CH}$, γ_H / γ_F etc., and those between FF, PP nuclei etc. by γ^2_H / γ^2_F , γ^2_H / γ^2_P etc. For example in such units the coupling data for the

^{11}BH , ^{13}CH , ^{15}NH nuclei in BH_4^- , CH_4 and NH_4^+ would have more direct significance in relation to the electronic structures of these isoelectronic species. Some may feel that at the moment this is a piece of pedantry, but a number of us already habitually do this conversion between DH and HH and I suspect that as NMR spreads more and more to other nuclei than hydrogen such a scheme will become of importance. If so, we might as well start out on a defined line at an early stage to avoid subsequent confusion.

(8) and finally, could I put in a plea for more standardisation of initials as used in nuclear magnetic resonance? I prefer N.M.R. (or N-M-R) as in the title of your Newsletter, but one now has NSR (nuclear spin resonance- could be nitrogen spin resonance!) PMR (paramagnetic resonance, proton magnetic resonance, - could be phosphorus magnetic resonance!). Someone will invent PSR before long if they haven't already done so! Our organic and inorganic colleagues get awfully confused. May I suggest as a standard phrase 'NMR spectra of X nuclei' or just 'X NMR spectra' where X reads 'hydrogen (or proton), phosphorus etc., with, if necessary, the isotope indicated.

I hope this brings my subscription up-to-date. With my best wishes to you both and to Paul Lauterbur.

Yours sincerely,

homan
N. Sheppard.

(Received)

When fluorine is attached to a carbon atom bearing a heavy isotope such as D(1) or ^{13}C (2) or when it is joined directly to ^{13}C (3), an

- (1) G. V.D. Tiers, J. Am. Chem. Soc., 79, 5585 (1957).
- (2) G. V.D. Tiers, J. Phys. Soc. Japan, 15, 354 (1960).
- (3) P. O. Lauterbur, private communication; to be published.

"isotope effect" is observed which consists of a shift of the fluorine¹⁹ nuclear spin resonance (NSR) peak center in the direction of greater shielding, relative to the corresponding peak due to the "normal", (light) compound. Smaller effects in the same direction have been observed in proton NSR spectroscopy. (4) (5) (6).

- (4) G. V. D. Tiers, J. Chem. Phys., 29, 963 (1958).
- (5) G. V.D. Tiers, J. Phys. Chem., 64, 373 (1960).
- (6) H. S. Gutowsky, J. Chem. Phys., 31, 1683 (1959).

Recently, a start has been made toward the theoretical explanation of such isotope shifts (6). It is therefore, of particular interest to examine more diverse examples of these effects to provide experimental evidence concerning the relative importance of various parameters. In the present work the pair of isotopes compared, ^{28}Si and ^{29}Si , represent by far the most convenient choice from the second row of the periodic table. The hexacoordinate fluosilicate anion was studied in aqueous solution.

Experimental

Ammonium fluosilicate (Harshaw Chem. Co.), 0.200 g., was dissolved in 0.80 ml. of H_2O .

The solution was rather acidic, pH 3.0 ± 0.3 ; in the preparation of the second sample a small amount of solid ammonium carbonate was added to

- 2 -

adjust the pH to about 5.5, in order to ^{inhibit the} ^{29}Si fluoride exchange (7).

- (7) E. L. Muettterties & W. D. Phillips, J. Am. Chem. Soc., 81, 1084 (1959).

The solution was filtered to remove any insoluble matter, and was placed in a standard 5 mm. O.D. NSR sample tube.

A detailed description has been given of the NSR spectrometer and of the measurement techniques (5), the latter having been developed for the detection of the similarly small ^{13}C -H isotope effect. All NSR work was done at 25.0°C . The doublet due to $^{29}\text{SiF}_6^-$ was found to be centered at slightly higher field (more shielded) than the single very strong peak due to $^{28}\text{SiF}_6^-$. Line widths, W (in c/s) measured at half-maximal intensity, were quite reproducible but were pH-dependent; the $^{29}\text{SiF}_6^-$ peaks being relatively more broadened at low pH than the "image" peaks (5) derived from $^{28}\text{SiF}_6^-$. The experimental results are presented in Table I; all errors are expressed as the standard deviation of the averaged value.

Table I

The Excess Fluorine NSR Shielding, Δ , Produced by ^{29}Si in Aqueous Ammonium Fluosilicate Solutions

pH	Δ , p.p.m.	J, c/s ($^{29}\text{SiF}_6^-$)	No. of meas.	W, c/s $^{29}\text{SiF}_6^-$ peaks	No. of meas.	W, c/s $^{28}\text{SiF}_6^-$ image	No. of meas.
3.0	$+ 0.004$ ± 0.003	108.37 $\pm .25$	12	1.57 $\pm .03$	22	0.97 $\pm .02$	44
5.5	$+ 0.0042$ ± 0.0012	108.00 $\pm .10$	10	0.87 $\pm .04$	16	0.90 $\pm .04$	32

Discussion

It is seen from the results in Table I that the ^{29}Si -F isotope effect is so small as to be barely detectable. The ^{13}C -F effect is about thirty times as large (2,3), indicative of a strong, inverse dependence upon bond length.

This point will be discussed more fully in a subsequent paper dealing with NH_4^- and BF_4^- isotope effects (8).

(8) J. W. Currier and G. V. D. Tiers, to be submitted for publication.

Puettterties and Phillips (7) noted the acid-catalyzed broadening (at very low pH) of the SiF_6^- peak, which they attributed to "fluorine exchange between SiF_6^- species", e.g. HSiF_6^- ; exchange between SiF_6^- anions would not cause any broadening. However, this hypothesis cannot account for the substantially greater broadening of $^{29}\text{SiF}_6^-$ relative to $^{28}\text{SiF}_6^-$ at low pH, shown in Table I. From the stability constant for SiF_6^- at pH 3.0(9) it is calculated that less than 0.1% of the fluorine in the solution is present as fluoride ion,

(9) I. G. Ryss, Z. Obshch. Khim, 16, 331 (1946); Chem. Abst. 41, 639 (1947).

from which it follows that negligible broadening and no differential broadening, would result from exchange with fluoride ion itself.

On the other hand, exchange of fluorine (perhaps via fluoride ion) between the isotopic fluosilicate anions would produce exactly the observed differential broadening of the $^{29}\text{SiF}_6^-$ peaks. Since there is only a 2.3% chance that a fluorine, once lost, will return to a $^{29}\text{SiF}_6^-$ anion having similar spin, the predominant process results in broadening; while for $^{28}\text{SiF}_6^-$ the chance of such return is 95.4%, hence broadening is slight. Stated otherwise, the rate constant, k ($\approx 1/\tau_{\text{ex}}$), calculated from the broadening of lines for "slow exchange" (10) must be corrected for the

(10) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Inc., New York, 1959, p. 221. The apparent line width due to instrumental factors is corrected for as in ref. (5).

inherent probability of the process in question, if the true pseudo-first-order rate constant, k_1 , is desired. Here $k_1 = k(^{29}\text{SiF}_6^-)/.977 = k(^{28}\text{SiF}_6^-)/.046$ from which one would expect the broadening of the $^{28}\text{SiF}_6^-$ peak to be only 4.7% as great as that for $^{29}\text{SiF}_6^-$. While the data of Table I strongly confirm the expected differential broadening, the sample-to-sample reproducibility of line width measurements is insufficient for a critical test of the predicted ratio. The relatively precise differential broadening (Table I) leads (10) to $k_1 = 3.3 \pm 0.1 \text{ sec}^{-1}$ (per fluorine atom) for loss of fluorine from fluosilicate ion at 25° and pH 3.0 ± 0.3 . If, however, only the first fluorine is removed, giving species such as $\text{SiF}_5\text{OH}^{(7)}$ or SiF_5^- , the rate constant listed above must be multiplied by six.

Acknowledgement. - I am greatly indebted to Mr. Donald Hotchkies for the careful NSR spectral work exemplified by Table I.

Contribution No. from
the Central Research Dept. of the
Minnesota Mining and Mfg. Co.
St. Paul 19, Minnesota

George Van Dyke Tiers.

Syn-anti Isomerism in Some Ketoximes

Ernest Lustig

Chemistry Division, National Bureau of Standards, Wash. 25, D. C.

Syn-anti isomerism has been detected in several aliphatic ketoximes and some ketoxime ethers from the appearance of two resonance lines for the protons on carbon atoms next to the $>C=NOH$ or $>C=NOR$ group. The separation of these lines depends on concentration and on the presence of aromatic compounds, acids, or bases.

Acetone oxime shows a methyl doublet having a separation of about 0.08 p.p.m. for a 10 percent solution in benzene. The doublet collapses into a singlet on dilution with CCl_4 . In non-aromatic solvents, only a single methyl peak is found.

This solvent effect may be rationalized in the following way: the oxime molecules form some kind of a complex with benzene (or aromatic) molecules (see e.g. Reeves and Schneider, Can. J. Chem. 35, 251 (1957)). The two (non-equivalent) methyl groups of acetone oxime very rarely come to lie in equivalent regions of the anisotropic field of benzene (see e.g. Johnson and Bovey, J.Chem. Phys. 29, 1012 (1958) and references therein), because acetone oxime does not possess any symmetry; thus a "shift" is produced. The $>C=NOH$ or $>C=NOR$ group seems to be closer to the benzene ring than other parts of the oxime molecule, since the anisotropy of the benzene field is experienced only by protons on carbon atoms adjacent to these groups. The relevant part of the diethyl ketoxime spectrum consists of a pair of methylene quadruplets, but only a single methyl triplet. Another distance effect may be that the "splitting" for $(CH_3)_2C=NOCH_3$ is only about one-third of that for $(CH_3)_2C=NOH$, other things being equal.

In the case of unsymmetrical ketoximes, syn and anti forms may exist simultaneously. In a mixture of the two phenylacetone oximes, as obtained by standard methods for the preparation of oximes, two methyl singlets and two methylene singlets are observed; similarly, the butanone oxime spectrum shows two CH_3-CNOH peaks, two $-CNOH-CH_2-CH_3$ quadruplets and one $-CH_2-CH_3$ triplet.

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The intensity of the two methyl peaks in acetone oxime is the same, as one would expect (e.g. under the assumption of equal relaxation times). But in all isomeric mixtures studied, the intensity ratios of proton resonances corresponding to analogous groups (e.g. the methylenes in butanone oxime) are different from unity. This suggests that there is an equilibrium between syn and anti forms which interconvert slowly, if at all. At any rate, it appears possible to demonstrate directly syn-anti isomerism in ketoximes and to use NMR to monitor the separation of syn and anti isomers.

In strongly acidic or basic solutions of acetone oxime, the two methyl resonances are separated by 0.05 to 0.07 p.p.m. The respective oxime ions formed seem to be responsible for the appearance of two peaks caused by asymmetry and/or exchange effects.

[Contribution from Mellon Institute]

The Proton Magnetic Resonance Spectra of Olefins. I.

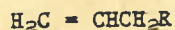
Propene, Butene-1, and Hexene-1.

Aksel A. Bothner-By and C. Naar-Colin

Abstract

The high-resolution proton magnetic resonance spectra of propene, butene-1, and hexene-1 have been obtained on "neat" samples and on samples in dilute carbon tetrachloride solution. The spectra have been analyzed in terms of chemical shifts and spin-spin coupling constants. Some possible explanations of the chemical shifts are discussed. The spin-spin coupling constants observed in butene-1 may indicate that the three rotational conformers are equally abundant in the liquid.

TABLE I

Chemical Shifts and Coupling Constants for 1-Alkenes^a

Chemical Shift	R = H		R = CH ₃		R = C ₃ H ₇	
	Neat	Standard	Neat	Standard	Neat	Standard
W(1)	255.97	255.97	252.36	253.18	255.89	256.55
W(2)	307.46	307.00	307.98	308.08	307.61	307.30
W(3)	302.20	302.20	302.99	303.64	303.55	303.55
W(4)	500.3	497.2	481.2	480.0	478.3	477.9
Terminal Methyl	---	---	541.2	540.3	548.3	545.7
Coupling Constant						
A _{1,2}	10.02		10.32		10.23	
A _{1,3}	16.81		17.23		17.03	
A _{1,4}	6.40		6.22		6.55	
A _{2,3}	2.08		1.96		2.23	
A _{2,4}	-1.33		-1.26		-1.18	
A _{3,4}	-1.75		-1.66		-1.51	

^a On a frequency scale with W(SiMe₄) = +600.00

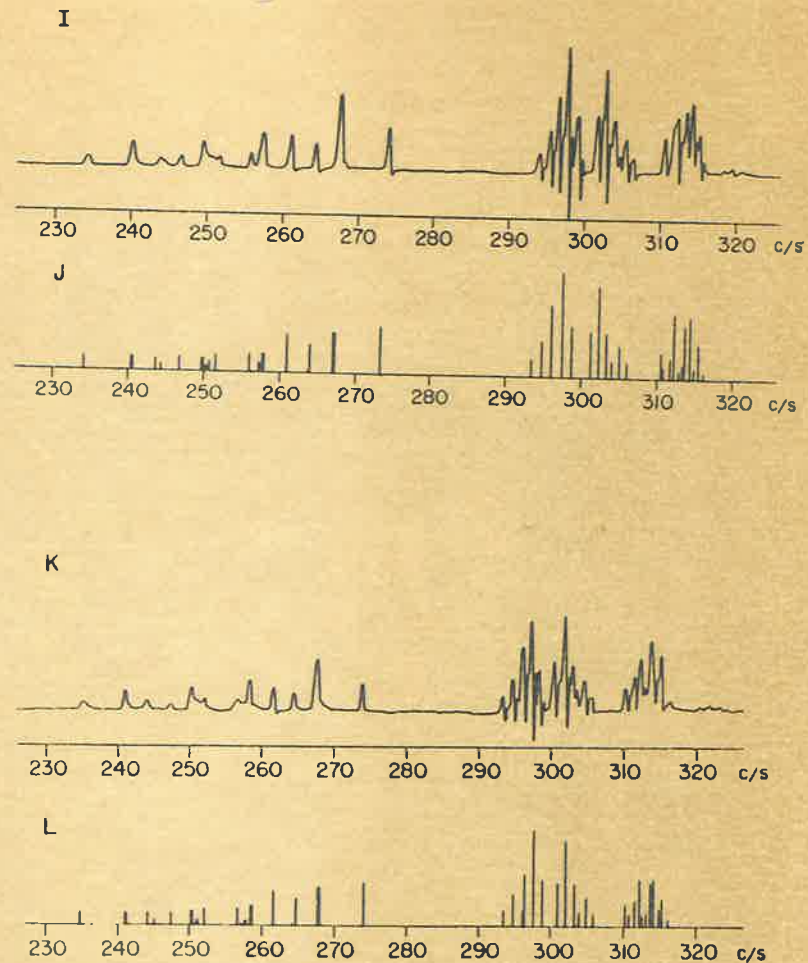
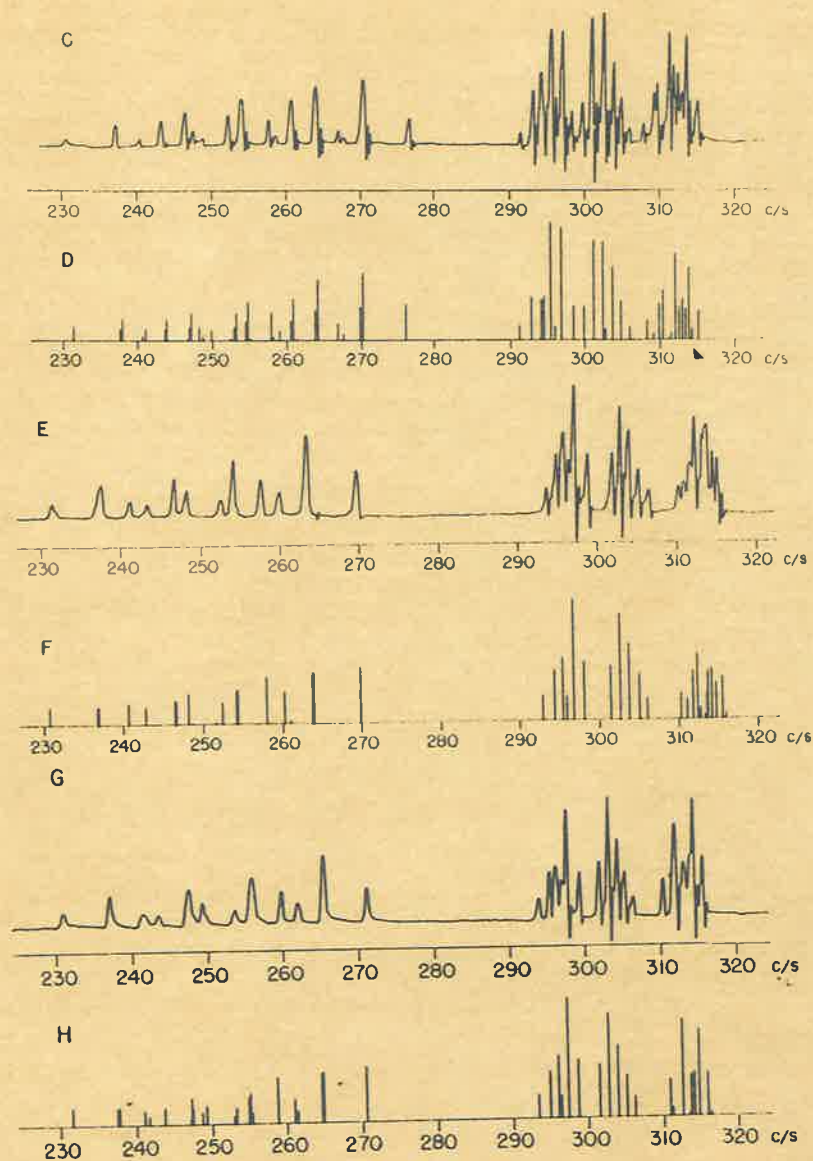


Fig. 1.

C OBSERVED } PROPENE STANDARD
 D CALCULATED }
 E OBSERVED } BUTENE-1 HEAT
 F CALCULATED }
 G OBSERVED } BUTENE-1 STANDARD
 H CALCULATED }
 I OBSERVED } HEXENE-1 HEAT
 J CALCULATED }
 K OBSERVED } HEXENE-1 STANDARD
 L CALCULATED }

Fig. 1.