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No. 27

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
THE UNIVERSITY OF TOKYO
BUNKYO-KU, TOKYO

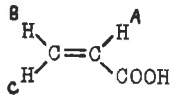
December 9, 1960

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

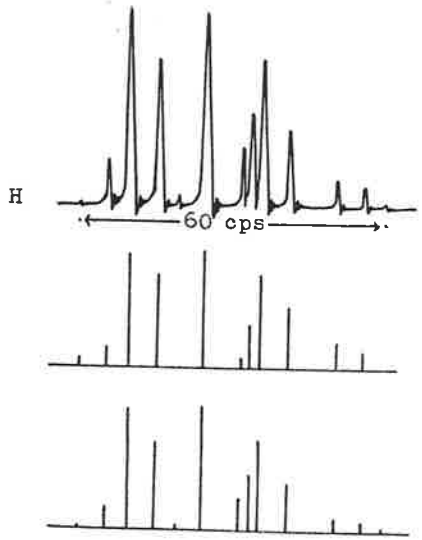
Dear Dr. Bothner-By

We hope this communication will be of some interest to you. The NMR spectra of acrylic acid and its derivatives were studied, which were analyzed by the use of parametron digital computer with 512 words at the physics department of this university. In our program, the postulated values of the chemical shifts and the spin-spin coupling constants can be refined by using the least squares method and, finally, the frequency of the calculated spectrum is fitted with the observed one.

We found that the two sets of the spin-spin coupling constants of the same sign were able to result in frequency which is fitted to the observed one of acrylic acid as shown in the figure.



at 56.44 Mc.



$\nu_C - \nu_B$ =32.5 cps
$\nu_A - \nu_B$ =12.6
J_{AC} =+15.4
J_{AB} =+ 9.5
J_{BC} =+ 4.2

$\nu_C - \nu_B$ =31.1
$\nu_A - \nu_B$ =11.6
J_{AC} =+17.2
J_{AB} =+10.2
J_{BC} =+ 1.7

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This fact may be suggest that some times a number of possible sets of the parameters which result in the frequency of the observed spectrum can exist in the complex NMR spectrum. Since all sets of such possible parameters can not be known a priori, the determination of relative sign of the spin-spin coupling constants is, therefore, not an easy problem, unless the observed spectrum is highly accurate. One of the possible methods to avoid this difficulty is to take the relative intensity of the spectrum as well as the frequency in the least squares method.

A set of equations which gives the corrections Δq to the postulated parameters q^0 was derived as

$$\sum_{i=1}^{m}\left\{W_i\left(\omega_i^t-\omega_i^0(q^0)\right)\left(\frac{\partial\omega_i}{\partial q_k}\right)_0+W_i'\left(I_i^t-I_i^0(q^0)\right)\left(\frac{\partial I_i}{\partial q_k}\right)_0\right\}$$
$$=\sum_{i}^{m}\sum_{j}^{m}\left\{W_i\left(\frac{\partial\omega_i}{\partial q_k}\right)_0\left(\frac{\partial\omega_i}{\partial q_j}\right)_0+W_i'\left(\frac{\partial I_i}{\partial q_k}\right)_0\left(\frac{\partial I_i}{\partial q_j}\right)_0\right\}\Delta q_j$$

$$k=1,2,\cdots\cdots,n$$

In these equations, the notations ω_i^t and ω_i^0 (I_i^t and I_i^0) refer to the frequency (the relative intensity) of the ith component line of the observed and calculated spectrum, respectively, and Wi and Wi′ are the weights of the observed quantity. When a spectrum of n component lines is observed N times, the weights are given by

$$W_i = N(N-1)\Big/\sum_{k=1}^{N}(\xi_{ik}-\bar{\xi}_i)^2, \qquad W_i' = N(N-1)\Big/\sum_{k=1}^{N}(|\zeta_{ik}-\bar{\zeta}_k|+\alpha)^2$$

$$\xi_{ik} = \omega_{ik} - \sum_{j=1}^{m}\omega_{jk}/n \quad . \qquad \zeta_{ik} = n\,I_{ik}\Big/\sum_{j=1}^{m} I_{jk}$$

$$\bar{\xi}_i = \sum_{k=1}^{N}\xi_{ik}/N \, . \qquad \bar{\zeta}_i = \sum_{k=1}^{N}\zeta_{ik}/N$$

A small quantity α in Wi′ is used for the reason that the observed intensity is less accurate than the frequency. If the ith component line corresponds to the transition, $n \to m$, the derivatives in the equations can be expressed as

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$$\left(\frac{\partial \omega_i}{\partial q_k}\right)_0 = (\psi_m^\circ - \psi_n^\circ | K_k | \psi_m^\circ + \psi_n^\circ)$$

$$\left(\frac{\partial I_i}{\partial q_k}\right)_0 = 2\left[(\psi_m^\circ | I_x | \psi_n^\circ)\{\sum_i'(E_m^\circ - E_i^\circ)^{-1}(\psi_i^\circ | K_k | \psi_m^\circ)(\psi_i^\circ | I_x | \psi_n^\circ) + \sum_i'(E_n^\circ - E_i^\circ)^{-1}(\psi_i^\circ | K_k | \psi_n^\circ)(\psi_m^\circ | I_x | \psi_i^\circ)\}\right]$$

, where K_k is a spin operator such as

$$K_k = I_{zA} \quad \text{if} \quad q_k = \nu_A \ ,$$
$$K_k = I_A \cdot I_B \quad \text{if} \quad q_k = J_{AB} \ .$$

The shape of the multiplet lines in the complex spectrum was also investigated by quantum statistics, from which interest informations on the intensity of the multiplet lines were obtained. The saturation of the multiplet lines of acrylic acid was analyzed by the theory.

yours sincerely

Hiroshi Shimizu

Hiroshi Shimizu

Yoji Arata

Yoji Arata

Shizuo Fujiwara

Shizuo Fujiwara

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

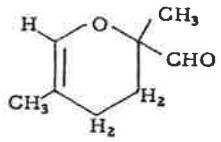
November 15, 1960

Dr. Aksel Bothner-by
Department of Chemistry
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel,

It seems to be assumed usually that spin-spin couplings, except those involving fluorine-fluorine interactions, are negligibly small over more than three bonds in saturated systems. At this time, we should like to report four examples of H-H and H-F spin-spin couplings that involve more than three consecutive single bonds, which were discovered here by Donald R. Davis and Raymond P. Lutz. Each of these systems is characterized by having either fixed or at least reasonably favored geometrical conformations.

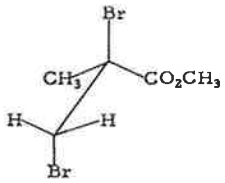
Our first example of long-range proton-proton couplings in saturated systems is the 1.3 cps splitting of the aldehyde proton in methacrolein dimer (I). The resonance involved is a doublet, the spacing of which is field-invariant.



I

The coupling probably involves one of the ring protons located at the β position relative to the aldehyde group. The vinyl hydrogen is definitely not implicated because the appearance of its resonance does not change when deuterium is substituted for the aldehyde hydrogen.

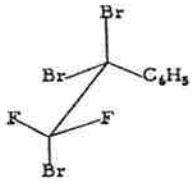
Another example involving proton-proton interactions is afforded by methyl α,β-dibromoisobutyrate (II), which exists in a preferred conformation, probably IIa, with the bromines <u>trans</u>. One of the nonequivalent methylene



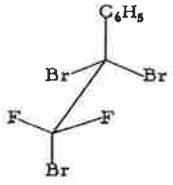
IIa

protons of II is coupled to the protons of the C-methyl group with J = 0.75 cps (cf. Fig. 1A). It is not known whether the coupled proton is that which is trans or gauche to the methyl group. We hope to check this point with appropriate stereospecifically deuterium-labeled compounds.

Our third example is 1,1-difluoro-1,2,2-tribromo-2-phenylethane (III), which below -60° displays the n.m.r. spectrum expected for the "locked-in" rotational conformers, with the "D, L" configurations (IIIa) being particularly



IIIa

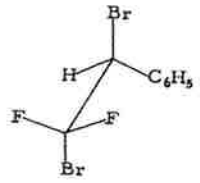


IIIb

favored. At -85°, the fluorine spectrum shows unmistakable evidence of H-F coupling across at least five bonds, three of them in a row saturated. This coupling is stereospecific. As can be seen from Fig. 1B, only one of the fluorines of IIIa is involved, and this is coupled to two phenyl protons (presumably those at the 2,6 positions) with J = 1.6 cps.

At 25°, the fluorine resonance of III is several cycles broad; but, at 85°, it becomes a clean triplet with J = 1.1 cps. The fact that J does not drop to half of its low-temperature value for one fluorine may indicate that some contribution to the long-range H-F couplings arises from the conformation IIIb with both the fluorines gauche to the phenyl group. In agreement with this idea, the fluorine resonance of IIIb is seen in Fig. 1B to be broader than that of the apparently uncoupled fluorine of IIIa.

Long-range H-F couplings have also been seen with 1,1-difluoro-1,2-dibromo-2,2-phenylethane (IV), which is expected by analogy with III to exist principally as IVa. The n.m.r. spectrum of IV (Fig. 1C) at 25° shows the



IVa

expected nonequivalent fluorines each split by three-bond coupling to the proton at the two position. The fluorine most strongly coupled to the proton is also coupled to two of the phenyl protons with J = 1.0 cps. This result is most interesting because if the strong H-F three-bond coupling involves trans groups, then the five-bond couplings are gauche and possibly exerted through space instead of through the bonds.

With all good wishes.

Very truly yours,

Jack

John D. Roberts

JDR:jmm

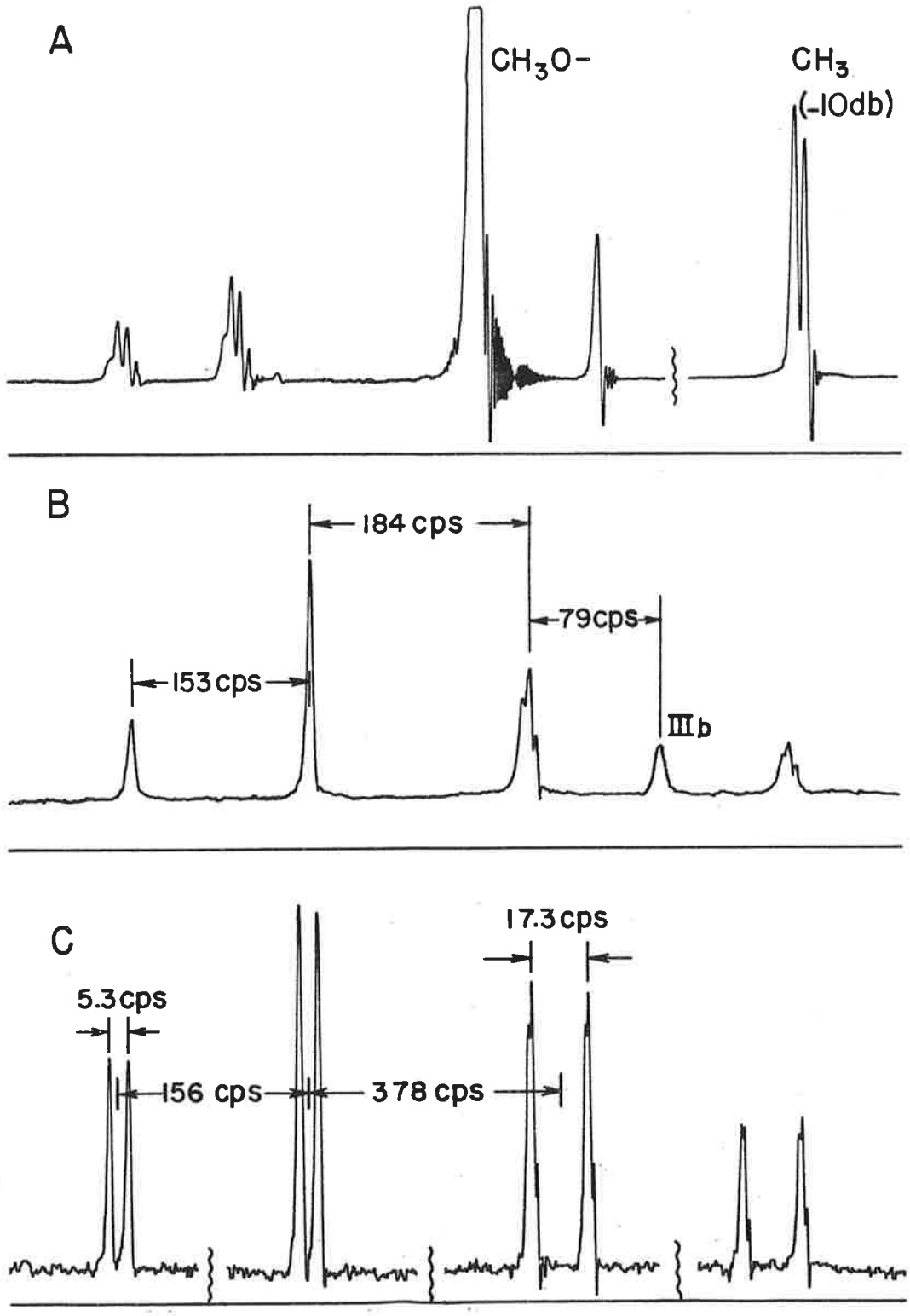


Fig. 1. – Nuclear magnetic resonance spectra: A, protons of methyl α,β-dibromoisobutyrate (II) at 60 Mc. and 25° with discontinuous sweep, one of the resonances of the CH_2 quartet being hidden under the CH_3O resonance; B, fluorines of 1,1-difluoro-1,2,2-tribromo-2-phenylethane (IIIa) at 56.4 Mc. and −84°; C, fluorines of 1,1-difluoro-1,2-dibromo-2-phenylethane (IV) at 56.4 Mc. and 25° with discontinuous sweep. Increasing magnetic field from left to right.