Tetrahedron Letters No.45, pp. 3339-3343, 1964. Pergamon Press Ltd.
Printed in Great Britain.

ANALYSIS OF THE N.M.R SPECTRUM OF DIOXANE-1,3

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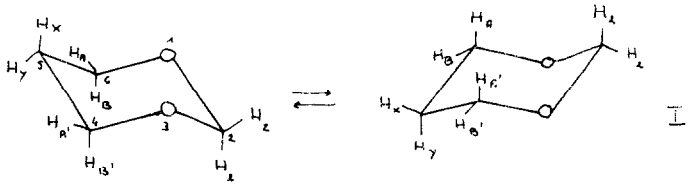
(Received 22 September 1964)

The Analysis of the AA'BB'XY spectrum of Dioxane-1,3 gives coupling constants between geminal and vicinal protons which are near to the corresponding couplings in other recently investigated dioxanic compounds.

Dioxane-1,3 exists in a dynamical equilibrium between the two equally probable conformations



I

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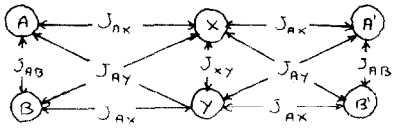
The chemical shifts of the two protons on each C atom become equal by the fast exchange between the two conformations. The chemical shifts of the protons at C_4 and C_6 and the coupling constants J_{AB} and $J_{A'B'}$ are equal because of the symmetry of the molecule. We expect two different vicinal couplings :

$$J_{AX} = J_{BY} = J_{A'X} = J_{B'Y} = 1/2\ (J_{ae} + J_{ea})$$

$$J_{AY} = J_{BX} = J_{A'Y} = J_{B'X} = 1/2\ (J_{aa} + J_{ee})$$

In figure 1* we give the experimental and theoretical spectrum of the AA'BB' and XY protons. The protons on C_2 give one single line.

The theoretical spectrum was determined according to the system



The calculation was done using the computer programs NMREN and NMRIT from Swalen and Reilly (1).

From the spectrum it was not possible to determine the relative signs of the geminal and vicinal couplings, but we assumed the vicinal couplings to be positive and the geminal couplings to be negative (2)

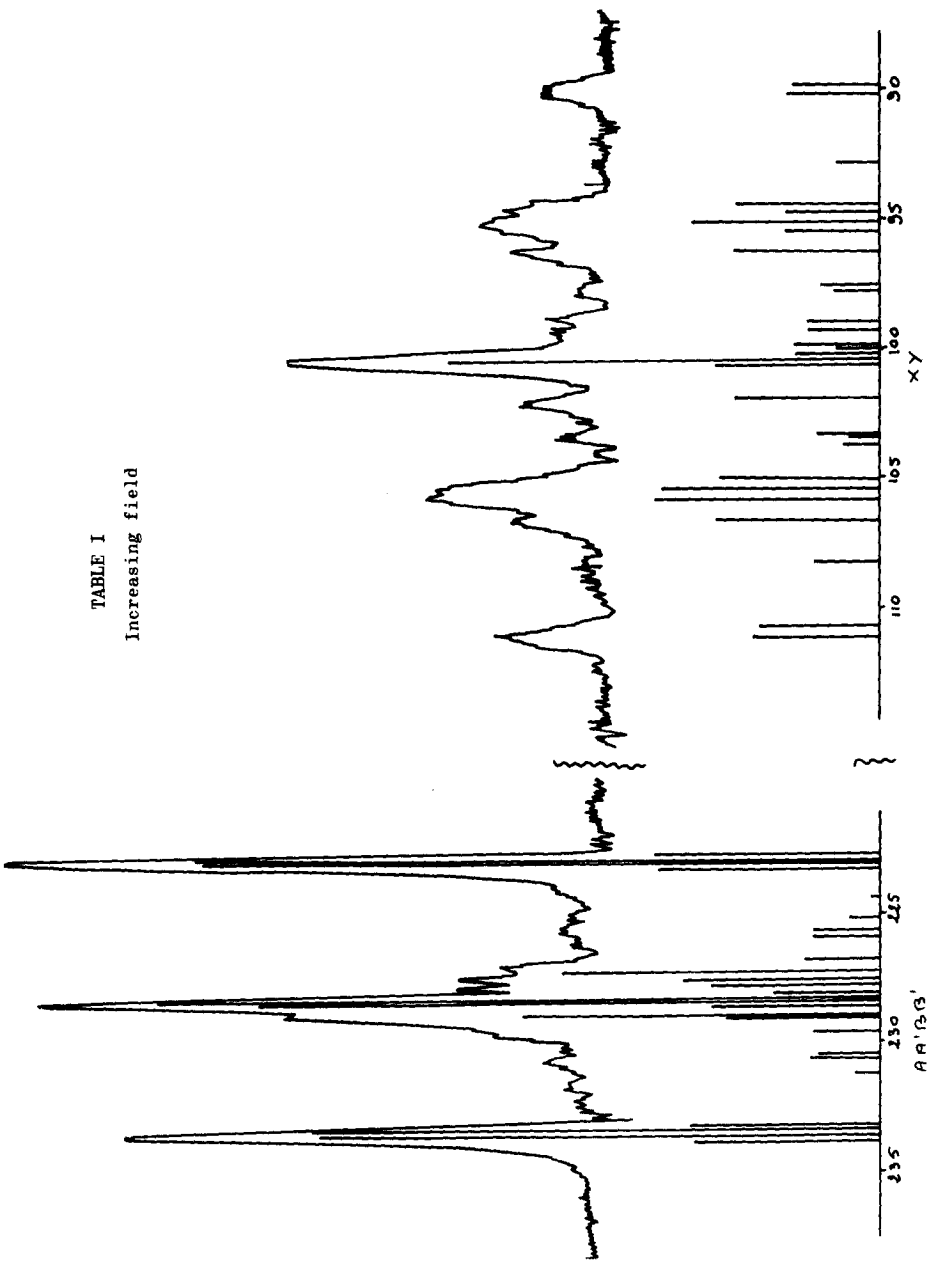
*Fig.1 Experimental and calculated NMR spectra of the AA'BB' and XY parts of dioxane-1,3 at 60Mcps. The two parts of the spectrum are recorded with different signal amplitudes. The compound was dissolved in CCl_4 (10 %).

(1) J.D.Swalen, C.A.Reilly, J.Chem.Phys. 37, 21 (1962)

(2) F.A.L.Anet, J.Am.Chem.Soc. 84, 3767 (1962)
P.C.Lauterbur, R.J.Kurland, J.Am.Chem.Soc. 84, 3405 (1962)

TABLE I

Increasing field



The determined parameters are :

$\tau_X = \tau_Y = 1,68$ ppm

$\tau_A = \tau_{A'} = \tau_B = \tau_{B'} = 3,80$ ppm

$\tau_2 = 4,70$ ppm

$J_{AX} = J_{BY} = J_{A'X} = J_{B'Y} = 3,8$ cps

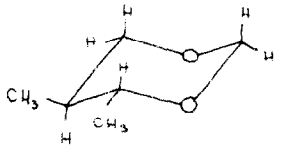
$J_{AY} = J_{BX} = J_{A'Y} = J_{B'X} = 6,7$ cps

$J_{AB} = J_{A'B'} = (-)\ 11,0$ cps

$J_{XY} = (-)\ 12,6$ cps

These coupling constants can be compared with the values recently found in substituted dioxanes (3,4,5).

Some of these compounds like Dimethyl-4,5-dioxane-1,3 (trans)



II

exist in one fixed conformation. One observes coupling constants :

$|J_{gem}|_4 \simeq J_{gem\ 6} \simeq 11,0 \ldots 11,5$ cps

$|J_{gem}|_2 \simeq 6,0$ cps

$|J_{4a-5a}| \simeq |J_{5a-6a}| \simeq 9,0 \ldots 11,0$ cps

$|J_{4e-5a}| \simeq |J_{5a-6e}| \simeq 4,2 \ldots 4,5$ cps

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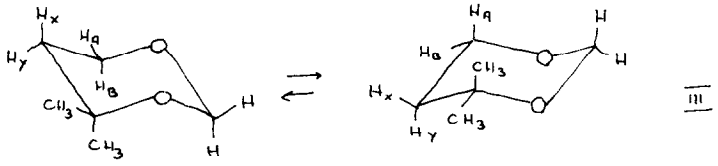
(3) J.Delmau, M.Davidson, G.Parc, M.Hellin, Bull.Soc.Chim. p.241, (1964)

(4) C.Barbier, M.Davidson, J.Delmau, Bull.Soc.Chim. p.1046 (1964)

(5) J.Delmau, C.Barbier, J.Chem.Phys., 41, 1106 (1964)

In Dimethyl-4,4-dioxane-1,3 where two equally probable conformations exist :



III

one observes the couplings

1) J_{AB} = (-) 11,0 cps or 2) J_{XY} = (-) 11,0 cps

J_{XY} = (-) 12,6 cps J_{AB} = (-) 12,6 cps

$1/2\ (J_{ae} + J_{ea})$ = 3,9 cps

$1/2\ (J_{aa} + J_{ee})$ = 6,9 cps

The vicinal couplings in I, II and III are very similar. The results for the geminal couplings in I and II confirm the first assignment of the coupling constants in III.

We thank Dr A. Melera from the "Research Institute of the Varian AG" in Zürich for the running of the spectrum with the A60 NMR spectrometer, Dr J.D. Swalen for the computer program, the "European Organisation for Nuclear Research" (CERN) for the possibility to use the IBM 7090 computer, the "Fond national suisse pour la recherche scientifique" for financial support and the "Laboratoire du Centre d'études supérieures de raffinage et de génie chimique de l'Institut Français du Pétrole" which synthetised the dioxanic compounds.