The NMR Spectra of the Acetal of 2,4-Pentanediol

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(Received December 27, 1963)

2,4-Pentanediol is a model compound of polyvinylalcohol (PVA), with the lowest molecular weight among this series and with optical isomers corresponding to the stereoregularity of the polymer. It has been shown, through a comparison of the reaction rate of the meso type of 2,4-pentanediol (which corresponds to isotactic PVA) with that of the racemic type (which corresponds to syndiotactic PVA), that the rate of acetal formation from PVA and acetaldehyde depends upon the stereospecificity. The rate of the formation of the racemic acetal is about 20 times that of the meso type.[1] The reaction rate of PVA is of the same order as that of pentanediol, according to its tacticity. In determining the difference in reaction rates, two kinds of acetal were separated by gas chromatography and identified by NMR. The identification of these compounds was straightforward. A process for calculating the energy levels and transition probabilities of the $ABKLX_3Y_3$ system has been developed.[2] This process made it possible to accomplish the complete analysis of the NMR spectra of the compounds. Through this analysis, spin-spin coupling constants and chemical shifts are obtained, as well as information concerning the structures and conformations of the acetals.

Experimental

Acetal was formed by adding *p*-toluene sulfonic acid to a solution of 2,4-pentanediol and acetaldehyde at 60°C. After the water had been eliminated, the product was distilled. The acetal was allowed to pass through a gas chromatographic column 4 mm. in diameter and 2 m. long which was maintained at 100°C, using hydrogen as a carrier gas. This column was filled with Shimadzu DOP-A. The two species of acetal were completely separated. The first fraction was designated f_1, and the second one, f_2. The NMR spectra were measured at 60 Mc./sec. and 40 Mc./sec. at room temperature. The positions of spectral lines and coupling constants were determined by the usual side-band method.

1) K. Fujiiwara, S. Matsumoto and Y. Fujiwara, Abstracts of the 12th Symposium on Polymer Chemistry, Tokyo (1963) p. 114.
2) Y. Fujiwara and S. Fujiwara, This Bulletin, 37, 1005 (1964).

Results and Discussion

The NMR spectra of f_1 and f_2 are shown in Fig. 1, and all lines have been assigned as shown, with consideration given to the position and the shape. f_1 has two doublets of methyl protons, one being about twice the size of the other, while f_2 has three doublets with almost equal intensity. Two different structures of acetal are formed in accordance with the structures of pentanediol (Fig. 2). Structure I comes from the meso type, and structure II, from the racemic type. Structure I has two methyl groups in equatorial positions at 4 and 6 carbons and one at 2 carbon. Structure II has one equatorial methyl group at 6, one axial methyl group at 4 and one at 2; i.e., the three methyl groups are not equivalent. This suggests that f_1 has structure I and f_2 has structure II. This identification is confirmed through the analysis of protons other than methyl groups.

The spectra of methine and methylene protons were analyzed by the method previously described;[2] the results are shown in Table I.

TABLE I. COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR $ABKLX_3Y_3$ SYSTEM

	(A=B X=Y)		(A≒B X≒Y)	
	60 Mc.	40 Mc.	60 Mc.	40 Mc.
$\lvert J_{AK} \rvert$	10.73	10.73	11.26	11.26
$\lvert J_{AL} \rvert$	2.62	2.62	3.06	3.06
$\lvert J_{AX} \rvert$	6.20	6.20	6.14	6.14
$\lvert J_{KL} \rvert$	13.06	13.06	12.70	12.70
ν_{LK}	21.32	14.21	−25.94	−17.29
ν_{BA}	0	0	16.22	10.81
$\lvert J_{BK} \rvert$	10.73	10.73	7.02	7.02
$\lvert J_{BL} \rvert$	2.62	2.62	0.58	0.58
$\lvert J_{BX} \rvert$	6.20	6.20	6.80	6.80

in c.p.s.

The coupling constants and chemical shifts obtained were confirmed by comparison with the observed and calculated spectra at 60 and 40 Mc./sec. as shown in Figs. 3 to 6. Though some combination lines are missing because of their low intensity, the agreement is quite satisfactory. It is shown that, as expected, A is equivalent to B and X to Y for

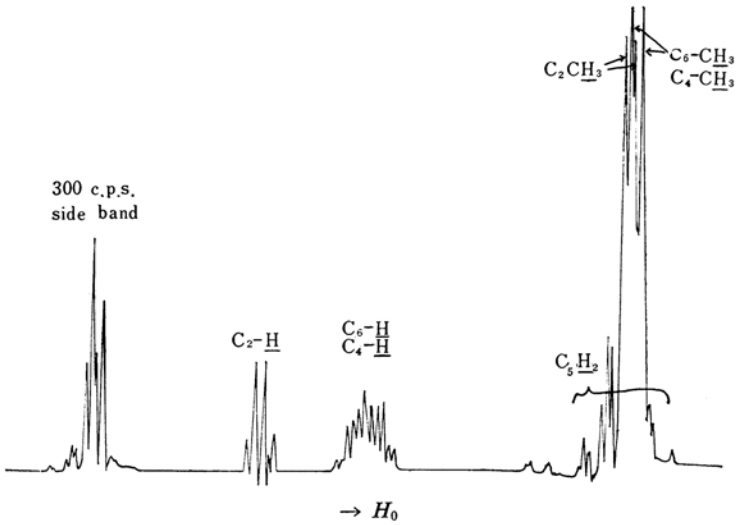

Fig. 1. a) NMR spectra of f_1 at 60 Mc./sec.

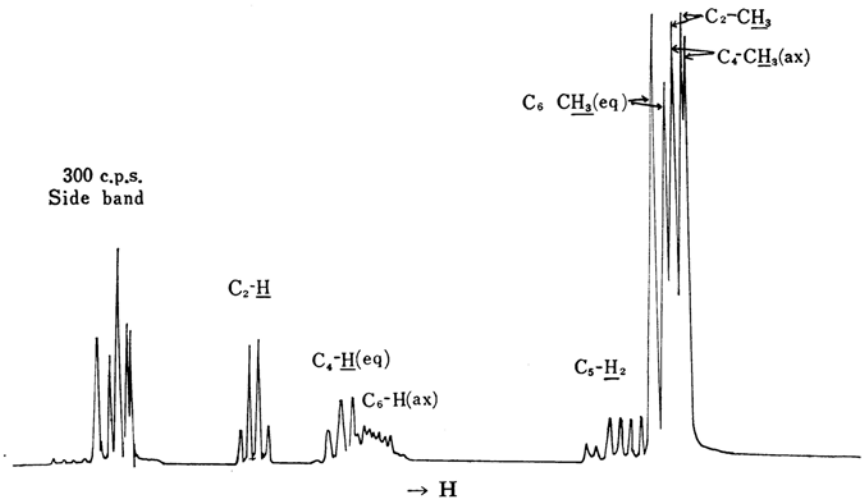

Fig. 1. b) NMR spectrum of f_2 at 60 Mc./sec.

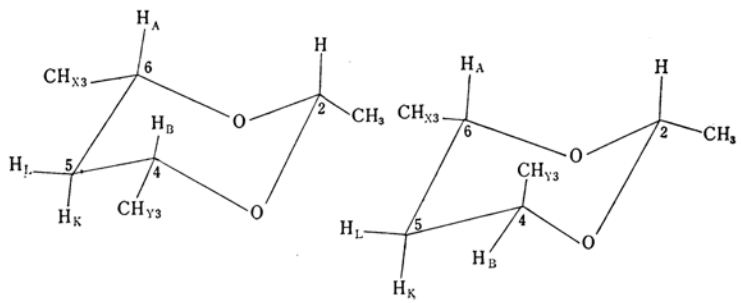

Fig. 2. Structures of acetals of 2,4-pentanediol.

f_1, but that A is not equivalent to B and X not to Y for f_2. It is noted that $J_{BK} \neq J_{BL}$ for f_2. Contrary to this finding, the structure suggests that $J_{BK} = J_{BL}$, because both couplings are vicinal ones in the gauche position. The discrepancy may result from strain in the structure caused by an outward slanting of the axial methyl. ν_{LK} is expected to be smaller for structure II than for structure I. However, experimental results show that the ν_{LK} for f_2 has a larger absolute value than f_1 and that the sign is negative. J_{AK} is quite large compared with J_{AL}, and it is not unlikely that both A and K are axial protons. Therefore the negative value of ν_{LK} means that the axial proton at 5 carbon appears at a lower field

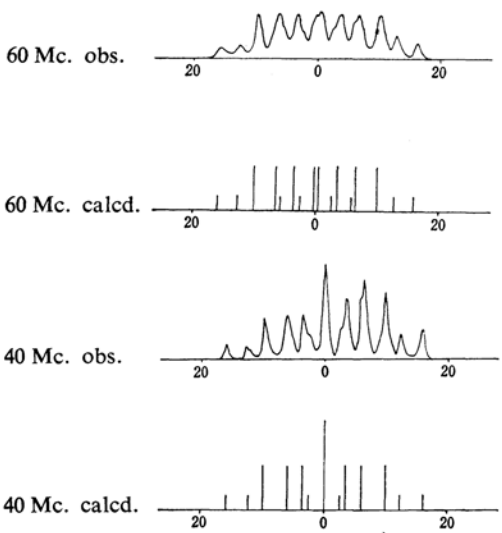

Fig. 3. NMR spectra of A in $AKLX_3$.

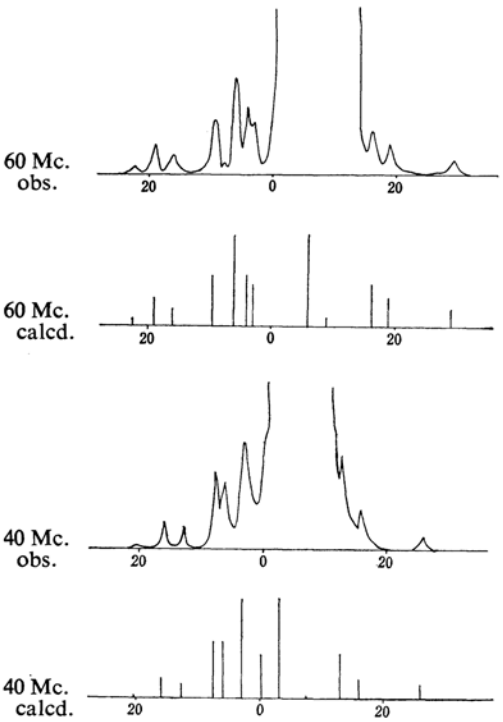

Fig. 4. NMR spectra of KL in A_2KL system.

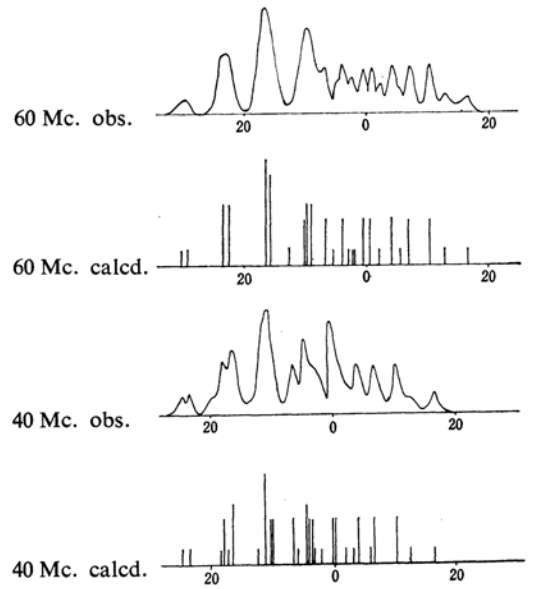

Fig. 5. NMR spectra of AB in $ABKLX_3Y_3$.

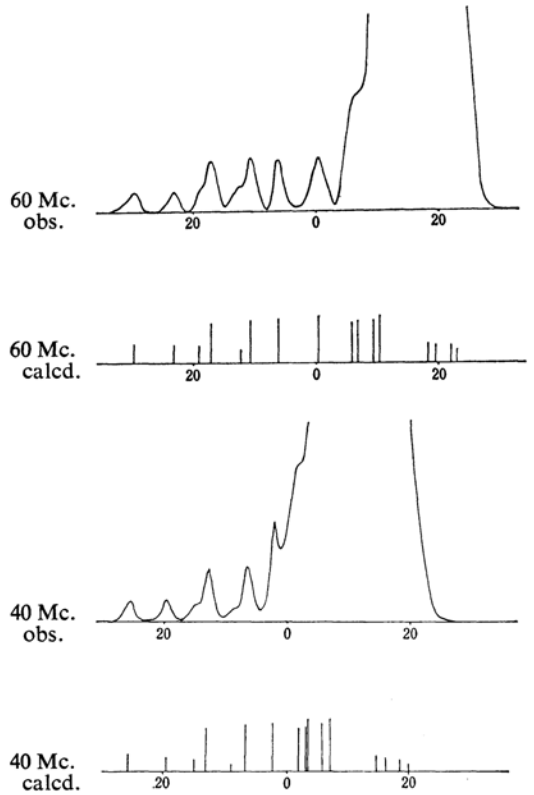

Fig. 6. NMR spectra of KL in $ABKLX_3Y_3$.

than the equatorial one. This may be attributed partly to the structural strain mentioned above, and partly to the difference in magnetic anisotropy between oxygen and carbon. There is a slight possibility of missassignment of the spectrum due to one spectrum of this system being partly hidden by the large methyl signal, leading to such an apparent anomaly.

The methyl group at 2 is supposed to be equatorial, since if two kinds of methyl groups are positioned at 2 carbon, the methine proton at 2 must give two quartets; this is contradictory to the experimental findings.

A possible exchange between two chair forms is excluded by the fact of a large difference in the chemical shifts and coupling contants of the methylene protons, K and L; any such exchange would make the two protons nearly equivalent. This has been confirmed also by the temperature effects on the spectra. 1, 3-Dioxane undergoes ring inversion at temperatures higher than $-80°C$.[4] For 4, 4-dimethyl-1, 3-dioxane the incipient temperature is about $-50°C$.[4] 2, 4-Pentanediol-acetal (2, 4, 6-trimethyl-1, 3-dioxane) is supposed to have a higher incipient temperature because of high structural hindrance. The temperature change from $-77°C$ to $+150°C$ does not effect any change in the spectra of 2, 4, 6-trimethyl-1, 3-dioxane except for slight changes in the chemical shift. The same reasons may be given to explain the exclusion of the boat form of f_2.

As f_1, it can be said that only one stable form exists; this seems to be a chair form with all methyl groups in quatorial positions. This conclusion is consistent with energy considerations and with the structure of para-acetaldehyde.[3]

The authors wish to thank Messrs. Osamu Yamamoto of the Government Chemical Industrial Research Istitute, Shoichi Hayashi of The Institute of Physical and Chemical Research, and Naohiro Hayakawa of the Japan Atomic Energy Research Institute for their aid in obtaining the NMR spectra. They also wish to thanks Dr. Kiyoshi Fujii of the Kurashiki Rayon Co., Ltd., for preparing the samples.

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4) H. Frieblin, S. Kabuss, W. Maier and A. Lüttringhaus, *Tetrahedron Letters* (1962), 683.