NMR Studies of Rates of the Inversion of o, o′-Bridged Biphenyls[1]

By Michinori Ōki, Hiizu Iwamura and Naohiro Hayakawa

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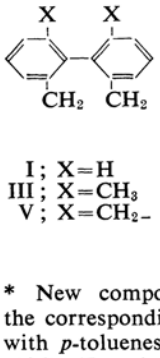
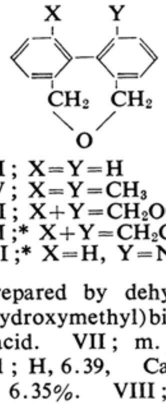


I ; X=H
III ; X=CH_3
V ; X=CH_2-



II ; X=Y=H
IV ; X=Y=CH_3
VI ; X+Y=CH_2OCH_2
VII ;* X+Y=CH_2CH_2
VIII ;* X=H, Y=NO_2

* New compounds prepared by dehydrating the corresponding bis(hydroxymethyl)biphenyls with *p*-toluenesulfonic acid. VII ; m. p. 92∼93°C, Found : C, 86.51 ; H, 6.39, Calcd. for $C_{16}H_{14}O$: C, 86.45 ; H, 6.35%. VIII ; m. p., 115°C, Found : C, 69.84 ; H, 4.68 ; N, 5.78, Calcd. for $C_{14}H_{11}O_3N$: C, 69.90 ; H, 4.59 ; N, 5.80%.

In the course of infrared spectral study, it became necessary to know the rates of the inversion of 9, 10-dihydrophenanthrene (I), 2, 7-dihydro-3, 4 : 5, 6-dibenzoxepin (II), and their derivatives. Since the half-lives of the inversion of these samples are expected to be too short to allow the conventional optical resolution which is inevitable for the polarimetric method,[2,3] the authors adopted the NMR technique,[4] which has lately been successfully applied to the analyses of the rate processes.[5,6]

If I and II are fixed as non-planar or if the half-lives of their inversion are relatively long, the spectra of the bridging methylene groups will be composed of the A_2B_2- and AB-spin patterns respectively, since the two protons on a methylene group are situated in a different magnetic environment. This is the case in III, IV and VI.[7] III shows a broad signal at τ, 7.38, δ_{AB} being less than 5 c. p. s., while IV shows an exact AB-quartet at τ, 6.00 (center), with $\delta_{AB}=19.6$ c. p. s. and $J_{AB}=11.0$ c. p. s.

On the contrary, I, II and V show a singlet

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[1] Presented in part at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[2] R. Kuhn and O. Albrecht, *Ann.*, **455**, 272 (1927).

[3] R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 261 (1932).

[4] The NMR spectra were measused on a Varian V-4300 spectrometer operating at 56.4 Mc./sec., and variable with a temperature probe accessory and a Dewar probe insert attached. The samples were dissolved in carbon disulfide containing 1% tetramethyl silane to make a 5% solution.

[5] A typical example can be seen in the study of the chair-chair interconversion of cyclohexane (F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, *J. Am. Chem. Soc.*, **84**, 386 (1962)).

[6] Lately, Meyer and Meyer (ibid., **85**, 2170 (1963)) have shown the applicability of the NMR method to the study of the rates of rotation of 2, 2′-bis(hydroxymethyl)biphenyls; their report prompted the present authors to report these preliminary findings.

[7] K. Mislow and M. A. W. Glass (ibid., **83**, 2780 (1961)) were the first in observing the non-equivalent methylene-bridge protons in VI.

methylene signal at room temperature and retain the singlet at temperatures as low as −90°C. The rates of the inversion are estimated to be not less than $10^2\ \mathrm{sec}^{-1}$ at −90°C, and by assuming $\log A=12$,[8] the activation energy of the inversion is obtained as less than 9 kcal./mol.

VII, at room temperature, also gives two singlet signals at τ, 7.20 and τ, 5.75; these signals are due to the protons on the $-CH_2CH_2-$ and $-CH_2OCH_2-$ groups respectively. Interestingly, the latter signal begins to lower and broaden gradually as the temperature goes down to −50°C, and at −55°C, separation into vague multiplet sets in. At −60°C, a resonance pattern of a characteristic AB-quartet is clearly recognized. At −80°C or lower, the signal is rigorously determined as $\delta_{AB}=25.9$ c. p. s. and $J_{AB}=11.4$ c. p. s. Even at this temperature, the signal at the higher applied magnetic field will not separate into an apparent multiplet but is only broadened a little. Since the δ_{AB} of the methylene protons on the $-CH_2CH_2-$ group is smaller, the averaging of the resonance signals is still occurring in the rate process through which the signal due to $-CH_2OCH_2-$ with a larger δ_{AB} does not coalesce. Assuming that the relation, $\tau=\sqrt{2}/2\pi\delta_{AB}=1/2k$, holds when the quartet signal coalesces to a broad singlet, k is found to be $58\ \mathrm{sec}^{-1}$ at −55°C. The exchange broadening of two interacting nuclear spin resonance signals has been treated theoretically by Alexander.[9] For the fast exchange limit, the height of the coalesced singlet relative to that at $\tau\rightarrow 0$, can be related to the mean life-time. From the limiting slope, $\tau\rightarrow 0$, together with the velocity obtained above at the very temperature of coalescence, the energy of activation and the Arrhenius factor of inversion are determined:

$E=11.2\pm 2$ kcal./mol., and $\log A=12.9\pm 1.5$.

Since the two methylene groups in VIII are no longer equivalent, VIII exhibits double AB-quartets at room temperature; CH_2 substituting the benzene ring without a nitro group, τ, 5.77 (center), $\delta_{AB}=27.0$, and $J_{AB}=11.80$ c. p. s.; and CH_2 substituting the benzene nucleus with a nitro group τ, 5.61 (center), $\delta_{AB}=15.1$, and $J_{AB}=11.4$ c. p. s. Thus the rate of inversion may be estimated to be less than $50\ \mathrm{sec}^{-1}$ at room temperature. As the temperature rises, the quartet singnal at a lower applied magnetic field begins to broaden and coalesce (at 48°C) earlier than that at a higher magnetic field (at 56°C). From the two coalescence temperatures of the resonance signals with a different chemical shift, the kinetic parameters of the rate process are determined as follows: $E=15.5\pm 2$ kal./mol. and $\log A=12.0\pm 1.5$.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo (M. Ō. & H. I.)

Japan Atomic Energy Research Institute
Tokai-mura, Ibaragi (N. H.)

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[8] On an average, log *A* of the inversion in *o, o'*-bridged biphenyls is 12 (D. M. Hall and M. M. Harris, *J. Chem. Soc.*, **1960**, 490).

[9] S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962).