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

By Michinori Ōki, Hiizu Iwamura and Naohiro Hayakawa

(Received July 9, 1964)

Since the success in the optical resolution of 6, 6'-dinitrodiphenic acid achieved by Christie and Kenner,[2] there have been accumulated many examples of the enantiomers of biphenyls in which the rotation around the pivot bond in the biphenyl skeleton is restricted either by the bulky groups on the ortho-positions or by bridging the two ortho-positions on either ring with a suitable ring number. As early as 1927[3] the kinetic examination of the restricted rotation was performed by measuring the rate of the racemization of the optically labile biphenyls with a polarimeter. The collected data were analyzed by Adams and Yan[4] in order to correlate the optical stability with the steric bulkiness of the ortho-substituents; that study contributed much to modern structural organic chemistry inasmuch as it introduced a measure of steric effects.

Although it is convenient, however, the polarimetric method expects inevitably the prior optical resolution of the samples, and so it can not be applied to those with a short life-time (with a $t_{1/2}$ less than a few minutes at room temperature). Lately the demand for

---

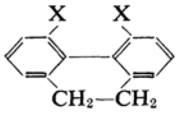
[1] Preliminary communication; M. Ōki, H. Iwamura and N. Hayakawa, This Bulletin, **36**, 1542 (1963).

[2] G. H. Christie and J. Kenner, *J. Chem. Soc.*, **1922**, 614.

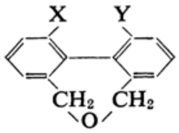
[3] R. Kuhn and O. Albrecht, *Ann*, **455**. 272 (1927).

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

means of measuring the faster rate of rotation and inversion has been met, by the NMR technique[1,5,6] which, when properly applied,[7,8] should explore the rate processes with the first order rate constant of 1 to 10^3 sec^{-1}. The present paper constitutes a full description of a study of the rates of inversion of 9, 10-dihydrophenanthrenes (I, III, V) and 5, 7-dihydrodibenz [c, e] oxepins (II, IV, VI, VII, VIII).[1]



I: $X=H$
III: $X=CH_3$
V: $X+X=CH_2CH_2$



II: $X=Y=H$
IV: $X=Y=CH_3$
VI: $X+Y=CH_2OCH_2$
VII: $X+Y=CH_2CH_2$
VIII: $X=H$, $Y=NO_2$

When these biphenyls are fixed as nonplanar or when the half-lives of their inversion are relatively long, the spectra of the bridging methylene groups will be composed of the A_2B_2 multiplets in I, III and V and AB quartets in II, IV, VI, VII and VIII. On the occasion of the other extreme, e. g., when the rate of the inversion is large relative to the chemical shift, δ_{AB}, in c. p. s. units, the spectra of the bridging methylene groups are expected to be composed of a singlet (A_4 and A_2 respectively). In the intermediate rate of the inversion, the spectra will change with the temperature, and the shape can be related to the life-time of the inversion. Therefore, the measurement of the NMR spectra was performed over a wide range of temperature.

Experimental

Spectral Measurements.—The NMR spectra were preliminarily obtained on a Varian V-4300 spectrometer operating at 56.4 Mc./sec., with a variable temperature probe accessory and a Dewar probe insert attached. The temperature was read from the microvoltage in the copper-constantan thermocouple mounted on the inside wall of the probe insert according to the calibration curve; the temperature can be regarded as accurate to ±1.0°C. Later all the measurements above −60°C were reexamined on a Varian A-60 spectrometer equipped with a variable temperature accessory at 60 Mc./sec.; the spectral data to be reported are based on the latter measurement unless otherwise stated.

The samples for the low- and high-temperature measurement were dissolved in carbon disulfide and in tetrachloroethylene respectively, to make ca. 10% solutions.

Within the measurement of a given sample, the strength of H_1 was held constant at around 0.04 mG. of the dial setting of the r. f. field, and the spectra were established as being far below the saturation condition by observing no lowering in the peak intensity on a slight raising of the r. f. field. The apparent amplitude of the normal signals decreases as the temperature ascends, mainly because of the thermal expansion of the solvent and the consequent apparent dilution. Accordingly, only the recorder level was changed, if necessary, from temperature to temperature, to determine the desired amplitude of the signals. Frequencies were read with respect to tetramethylsilane as an internal standard, and the usual sweep rate was 1 c.p.s./sec.

Since T_2 is practically determined by the inhomogeneity of the magnetic field, T_2 was regarded as independent of the kind of proton and so was measured directly from the width of the signal of tetramethylsilane by the wiggle-decay measurement.[7,9,10]

Materials.—The samples used for the measurement were known compounds, unless otherwise stated, and their physical constants agreed well with those in the literature.

1, 11-Ethano-5, 7-dihydrodibenz[c, e]oxepin (VII).—Ozone was passed from the generator into a solution of 5 g. of 4, 5-dihydropyrene in 100 ml. of chloroform for five hours at the nominal rate of 2 g./hr. at 0°C. Chloroform was distilled under diminished pressure, and the residue was dissolved in 50 ml. of ether. The solution was then added, drop by drop, into a solution of 5 g. of lithium aluminum hydride in 100 ml. of ether. This mixture was heated under reflux for an hour. The excess lithium aluminum hydride was destroyed by the addition of ethyl acetate, and then 100 ml. of 5% sulfuric acid was added to decompose the alkoxides. The organic layer was separated, and the aqueous layer was extracted with three 50 ml. portions of ether. The combined ether solution was washed with a 5% sodium bicarbonate solution and dried over potassium carbonate. The residue, obtained after the removal of the ether, was freed from the unoxidized starting material by chromatography on an alumina column; 4, 5-dihydropyrene was eluted with petroleum ether, and 4, 5-bishydroxymethyl-9, 10-dihydrophenanthrene, with ether.

The bishydroxymethyl compound was, without identification, dissolved in 100 ml. of toluene and heated under reflux with 0.5 g. of *p*-toluenesulfonic acid for eight hours. The solution was washed twice with 5% sodium bicarbonate, and the toluene was distilled off. The residue was recrystallized from petroleum ether to give 2 g. of 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%.

1-Nitro-5, 7-dihydrodibenz[c, e]oxepin (VIII). — To

---

[5] W. L. Meyer and R. B. Meyer, *J. Am. Chem. Soc.*, **85**, 2170 (1963).

[6] R. J. Kurland, M. B. Rubin and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964).

[7] H. Strehlow, in A. Weissberger, "Technique of Organic Chemistry," Vol. VIII, Interscience, New York, N. Y. (1963), Chap. 17, p. 865.

[8] H. Iwamura, *Kagaku no Ryoiki*, **17**, 266 (1963).

[9] B. A. Jacobsohn and R. K. Wangsness, *Phys. Rev.*, **73**, 942 (1948).

[10] G. V. D. Tiers, *J. Phys. Chem.*, **65**, 1916 (1961).

a stirred mixture of 300 ml. of a sodium borohydride solution (1 M in diethylene glycol diethyl ether) and 50 ml. of an anhydrous aluminum chloride solution (2 M in the same solvent),11) 20 g. of dimethyl 6-nitrodiphenate12) was added; the resulting solution was warmed on a water bath to 75°C. After five hours' heating, the mixture was cooled to room temperature and poured onto ice-water containing 1 N hydrochloric acid to decompose the remaining reagent; the solution was then evaporated on a water bath, and the higher boiling solvent was distilled under reduced pressure by the application of a water pump. The remaining solid was recrystallized from benzene to afford 13 g. of 2,2'-bishydroxymethyl-6-nitrobiphenyl, m. p. 93°C.

Found: C, 64.95; H, 5.37; N, 5.46. Calcd. for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05; N, 5.40%.

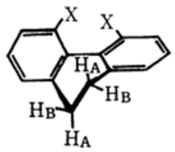
The bishydroxymethyl compound (7.8 g.) was heated with 200 ml. of 50% sulfuric acid at 100°C for an hour.13) On cooling, the oily mass solidified and was recrystallized from ethanol to give 5.0 g. of the desired oxepin, m. p. 115°C.

Found: C, 69.84; H, 4.68; N, 5.79. Calcd. for $C_{14}H_{11}O_3N$: C, 69.90; H, 4.59; N, 5.80%.

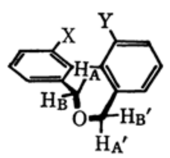
Results and Discussion

The *o,o'*-bridged biphenyls can be classified into three groups according to the characteristic dependence of their NMR spectra on the change in temperature.

i) Rigid Biphenyls and Biphenyls of a Slow Inversion Rate.—III,13) IV14) and VI15) have been separated into optical antipodes and shown not to racemize easily at room temperature. In these rigid structures, two protons on a methylene group are situated in different magnetic environments and, consequently, are not equivalent (IX and X). As expected, the signals assigned to the methylene protons are of a multiplet structure, although, in the spectrum of III, the separation is not clear and the broadness of the signal relative to those of methyl and TMS is the sole indication at 60 Mc./sec.16) Table I shows the observed chemical shifts and coupling constants of the methylene protons, together with the half-life of racemization at room temperature.



IX



X

TABLE I. RIGID BIPHENYLS AND BIPHENYLS OF A SLOW INVERSION RATE

Compound	Spectrum pattern	τ-value (center)	δ_{AB} c.p.s.	J_{AB} c.p.s.	$t_{1/2}^{23°}$ min.
III	(A_2B_2)	7.38	(6)	—	162$^{14)}$
IV	AB	6.00	19.6	11.0	
VI	AB	5.65	22.8	11.5	11

TABLE II. LONG-RANGE SHIELDING OF METHYLENE PROTONS BY THE BENZENE RINGS

		ρ_1*	z_1	ρ_2	z_2	$\Delta\sigma$ p.p.m.	δ_{AB} p.p.m.
III	H_A	2.27	0.65	2.14	1.50	−0.62	0.22
	H_B	2.47	0.25	3.27	0.91	−0.84	
IV	H_A	2.28	0.40	1.43	1.63	+0.05	0.74
	H_B	2.35	0.19	2.60	2.10	−0.69	

* ρ and z are cylindrical coordinates expressed in units of the radius of the benzene ring (1.39Å) with the z axis normal to the plane of the ring at its center and with the origin at the center. 1 and 2 refer to the contiguous and the remote benzene rings respectively.

In order to see the origin of the difference in the chemical shift between the two methylene protons, δ_{AB}, molecular models were set up using conventional structural dimensions,17) and the difference in the effect of the long-range shielding of the two benzene rings on the two protons in a methylene group was calculated according to the numerical table of Johnson and Bovey.18) As regards the length of the pivot bond, *R*, and the interplanar angle, θ, made by the two benzene rings, of III and IV, it is not proper to adopt those of I and II19) respectively, because the conjugation bands in the ultraviolet spectra of III and IV have been shown20) to exhibit a hypsochromic shift of 4∼5 mμ from those of I and II respectively. Therefore, these parameters were calculated according to the method of Suzuki19,21) from the absorption maxima of the conjugation band; $R=1.49$Å and $\theta=29°$

---

11) H. C. Brown and B. C. S. Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

12) J. W. Brooks, M. M. Harris and K. E. Howlett, *J. Chem. Soc.*, **1957**, 1934.

13) G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953).

14) K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, **84**, 3018 (1962).

15) K. Mislow and M. A. W. Glass, ibid., **83**, 2780 (1961).

16) In the "High Resolution NMR Spectra Catalog," Vol. II, issued by Varian Associates, Palo Alto, California, U. S. A., the methylene proton signal measured at 100 Mc./sec. is listed as spectrum No. 654, δ_{AB} being 0.1 p. p. m.

17) Ar-C_{sp^3} distance, 1.51 Å; C-H distance, 1.09 Å; C-O distance, 1.42 Å; CH_2-CH_2 distance, 1.54 Å.

18) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

19) H. Suzuki, This Bulletin, **32**, 1340, 1350, 1357 (1959).

20) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, **1955**, 3776.

21) ν_A's are 38314 cm^{-1} (261.0 mμ) and 41152 cm^{-1} (243 mμ) for III and IV respectively. As the longer-wavelength-side reference, ν_L=37735 cm^{-1} (265 mμ) of 9,10-dihydrophenanthrene was adopted, for which θ=20° (G. H. Beavan, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1952**, 854).

for III, and $R=1.51$Å and $\theta=57°$ for IV.[22]

Table II summarizes the results of the calculation. Agreement in δ_{AB} is fairly good in III, considering the approximation used in the calculation. In IV, however, the calculation leads to a δ_{AB} value higher by 0.4 p. p. m.; this discrepancy should be ascribed to the anisotropy of the neighboring oxygen atom.

The spectra of this class of biphenyls can thus be characterized by the split methylene signals and by no temperature dependence of the spectra in the conventional temperature range of the commercial NMR spectrometer. The rate of inversion can be estimated to be not more than δ_{AB} sec^{-1} at the highest temperature attained by the measurement. Thus, the upper limit of the rate and the lower limit of the energy of activation for racemization can be drawn.

ii) Biphenyls of a Fast Inversion Rate.—I, V and XI show a singlet methylene signal at room temperature and retain the singlet as low as −90°C. Table III shows the chemical shifts of the methylene protons at room temperature. They are quite independent of the temperature, and only the displacement within 10 c. p. s. towards the higher applied magnetic field is usually observed as the temperature is lowered to −60°C.

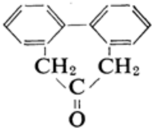

XI

TABLE III. THE CHEMICAL SHIFTS OF THE METHYLENE PROTONS
(in carbon disulfide at room temperature)

	I	V	XI
τ-value	7.18	7.15	6.68

There are three possibilities for the temperature-independent singlet methylene signals: 1) The inherent identity of the chemical shifts of the two methylene protons by the genuine or virtual coplanarity of the skeleton. Fluorene, which has a singlet methylene signal at τ, 6.19, is a typical example. 2) The coincidence of the chemical shifts, which in this case are determined by the anisotropy of the neighboring groups, mainly of the two benzene rings, and by the solvent effect, as exemplified by the methylene protons in 1, 11-dimethyl-5, 7-dihydrodibenz [c, e] thiepin in deuteriochloroform.[23,24] 3) rapid inversion and consequent averaging of the magnetic environment.

Case 2 can possibly be explored by the study of the solvent effect.[24] Cases 1 and 3 can be discriminated by the inspection of the ultraviolet spectra, since the ultraviolet spectroscopy conforms to the Franck-Condon principle and, even in case 3, information on the structure at the ground state can be obtained and the non-coplanarity is accompanied by a hypsochromic shift of the conjugation band at ca. 250 mμ.

As far as I, V and XI are concerned, it is likely[20] that they belong to case 3. In these circumstances, the rates of inversion can be estimated to be not less than δ_{AB} sec^{-1} at the lowest temperature measured, and so the higher limit of the energy of activation can be deduced. Since log A of the inversion in *o, o'*-bridged biphenyls is, on the average, 12,[25] the activation energy of the inversion is obtained as less than 9 kcal./mol. in I, V and XI.

iii) Biphenyls of an Intermediate Inversion Rate. — Although VII shows, at room temperature, two singlet signals at τ 7.20 and τ 5.75 due to the protons on the CH_2CH_2 and CH_2OCH_2 groups respectively, the latter signal begins to decrease and gradually broaden as the temperature goes down to −50°C. At −58°C, the separation into a vague multiplet sets in. At −60°C, a resonance pattern of a characteristic AB-quartet can be clearly recognized, as is shown in Fig. 1. Below −80°C, the signal is rigorously determined as $\delta_{AB}=$ 25.9 c. p. s. and $J_{AB}=11.4$ c. p. s. at 56.4 Mc./sec. Even at this temperature, the signal at the higher applied magnetic field does 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. Since the exchange broadening of the two interacting nuclear spin resonance signals has been treated theoretically by Alexander,[26] the analysis of the variation in this behavior of spectra with the temperature can be performed. The height of the coalesced singlet relative to that at zero life-time, $(v/v_0)_{max}$, can be related to the

---

[22] In order to accomodate the molecular models with these structural parameters, a slight distortion of the bond angles in the cyclohexadiene and the dihydrooxepin rings in III and IV respectively is necessary. They are within 2° and do not affect the result materially.

[23] "High Resolution NMR spectra Catalog," Vol. II, No. 657, Varian Associates, Palo Alto, California, U. S. A.

[24] While this manuscript was being prepared, K. Mislow and his coworkers published a lengthy NMR study of the bridged biphenyls and showed a remarkable solvent effect (*J. Am. Chem. Soc.*, **86**, 1710 (1964)).

[25] D. M. Hall and M. M. Harris, *J. Chem. Soc.*, **1960**, 490.

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

Fig. 1. Temperature dependence of the methylene proton signals of VII (at 56.4 Mc./sec.).

mean life-time, τ, through the observed parameters, δ_{AB}, J_{AB}, and T_2, according to Eq. 1.

$$(v/v_0)_{max}=1-\frac{2T_2\delta_{AB}^2\tau+(T_2^2\delta_{AB}^4+\delta_{AB}^2)\tau^2}{4+4\left(\frac{1}{T_2}+T_2\delta_{AB}^2\right)\tau+\left\{\left(\frac{1}{T_2}+T_2\delta_{AB}^2\right)^2+J_{AB}^2\right\}\tau^2} \qquad (1)^{27)}$$

Furthermore, at the very time of coalescence, Eq. 2 is obtained, provided $1/T_2$ is zero:

$$\tau_c=\frac{\sqrt{2}}{\pi(\delta_{AB}^2+6J_{AB}^2)^{1/2}} \qquad (2)^{28)}$$

Figure 2 corresponds to Eq. 1 applied to VII, and τ at a given temperature can now be obtained graphically from the $(v/v_0)_{max}$ observed in Table IV. $\log(1/\tau)$'s make a straight line against $1/T$, and from the slope, the energy of activation of the inversion can be determined (Table VI).

Since the two methylene groups in VIII are no longer equivalent, VIII exhibits double AB-quartets at room temperature: CH_2 attached to the benzene ring without a nitro-group, τ, 5.77 (center), $\delta_{AB}=28.7$, $J_{AB}=11.80$ c. p. s.; and attached to the benzene ring with a nitro-group, τ, 5.61 (center), $\delta_{AB}=16.05$, $J_{AB}=11.4$ c. p. s.

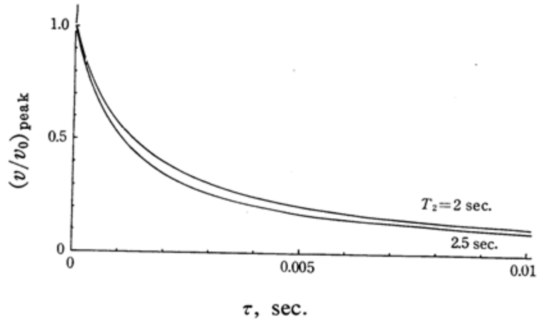


Fig. 2. Relation between the relative peak heights and the mean life-time for VII; $\delta_{AB}=27.5$, $J_{AB}=11.4$ c. p. s., in Eq. 1.[29]

TABLE IV. VARIATION IN THE PEAK HEIGHTS OF THE METHYLENE SIGNALS IN VII WITH THE TEMPERATURE

t, °C	$(v/v_0)_{max}$**	$\log(1/\tau)$
40	0.999	—
22	0.986	4.80
0	0.965	4.37
−10	0.909	3.92
−20	0.804	3.50
−30	0.678	3.18
−40	0.538	2.95
−50	0.241	2.38
−58	—	1.94*

* $\log(1/\tau_c)$

** The v at each temperature is relative to the height of the TMS signal on the same chart.

Contrary to the optically rather stable biphenyls (group i), the quartet signals deform easily as the temperature rises. The quartet at the lower applied magnetic field begins to broaden earlier and coalesces at 56°C, while that at the higher field has the coalescence temperature of 65°C. In the preliminary communication,[1] the kinetic parameters of the rate process were determined from the two coalescence temperatures of the resonance signals with different chemical shifts. Since it is difficult to determine the temperature of coalescence as accurately as ±2°C, however, there is a danger that the data will contain undesirable errors. Therefore, VIII was subjected to the same analysis as was VII.

Figure 3 shows the dependence of the apparent spectra on the temperature. In Table V are recorded the data on the peak heights.

$\log(1/\tau)$'s from two pairs of CH_2 protons lie on the same line against $1/T$ (Fig. 4);

---

[27] Obtained from the imaginary part of Eq. 57 in reference 26 by putting $\Delta=0$. v_0 can be obtained by extrapolating the peak height, v, vs. the $1/T$ curve to an infinite temperature.

[28] Equation 2 is derived by putting the second derivative at $\Delta=0$ of the imaginary part of Eq. 57[26] equal to zero. τ_c stands for the life-time just when the quartet signal coalesces to a singlet signal.

[29] T_2 values ranged between 2.0 and 2.5 sec. in the present measurements. The Arrhenius parameters are rather insensitive to T_2, and the error of ± 0.5 sec. in T_2 corresponds to the 5% inaccuracy of the results.

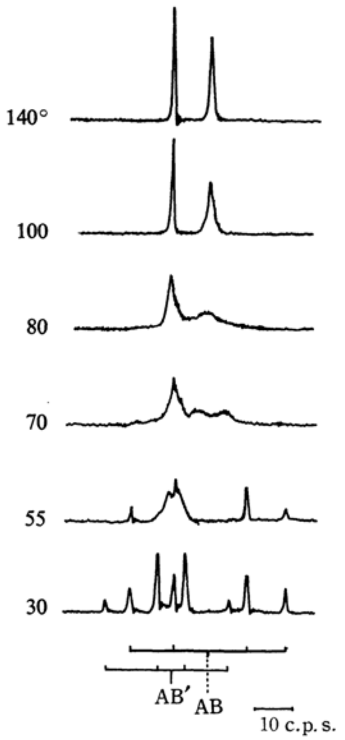
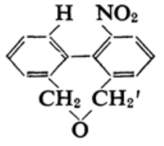


Fig. 3. Temperature dependence of the methylene proton signals of VIII.

TABLE V. VARIATION IN THE PEAK HEIGHTS OF THE METHYLENE SIGNALS IN VIII WITH THE TEMPERATURE



t, °C	$(v/v_0)_{max}$	τ, sec.	$(v/v_0)'_{max}$	τ', sec.
60	—	—	0.303	0.0089
70	0.171	0.0057	0.459	0.0046
80	0.267	0.0034	0.642	0.0022
90	0.476	0.0014	0.798	0.0010
100	0.648	0.00066	0.908	0.00039
110	0.824	0.00026	0.936	0.00028
120	0.835	0.00024	0.963	0.00016
140	0.905	0.00013	0.982	0.000075

from the slope, the energy of activation was determined (Table VI).

Although the authors could not find the broadening of the singlet signal in II in a preliminary study, later measurements revealed a coalescence temperature of as low as ca. −85°C, as has been pointed out by Kurland.[6] II, therefore, belongs to this class of biphenyls and will be dealt with in relation to the effect of the internal interaction of the substituents on the rate of inversion, together with 5, 7-dihydrodibenz [c, e] thiepin and 1-methyl-3,4 : 5,6-dibenzocyclohepta-3, 5-dien-1-ol.

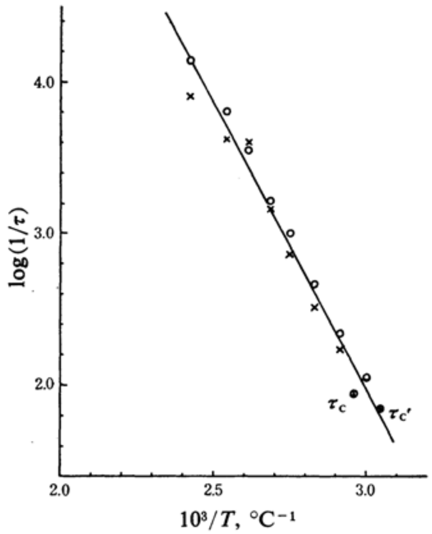


Fig. 4. Temperature dependence of the inversion rate for VIII.

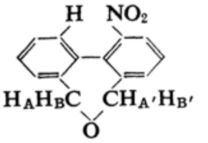


TABLE VI. ARRHENIUS PARAMETERS OF THE INVERSION OF o, o'-BRIDGED BIPHENYLS

	E, kcal./mol.	$\log A$
I	<9	12*
II	9.6±0.7[6]	
III	23.1[14]	12.8
IV	20	
V	<9	12*
VI	20.2[15]	11.7
VII**	10.5±0.5	12.6±0.4
VIII**	16.5±0.7	12.8±0.4

* Assumed value

** Present work

In conclusion, the NMR technique is unique in determining the rate of inversion of those biphenyl derivatives which can not be submitted to the conventional polarimetric method because of their too great optical lability. The technique will undoubtedly find more applications in related fields.

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

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