Pakistan J. Sci. Ind. Res., Vol. 14, No. 6, December 1971

THE ENERGY BARRIER FOR THE RACEMISATION OF OPTICALLY ACTIVE 8,8′-BISBROMOMETHYL-1,1′-BINAPHTHYL

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(Received November 19, 1970; revised April 20, 1971)

Optically active 8,8′-(bisbromomethyl)-1,1′-binaphthyl has been synthesised[1] and its rates of racemisation studied. From experimental results the Arrhenius parameters E and $\log_{10}A$ and transition state theory functions $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ for the racemisation have been determined and a comparison has been made with other optically active 8,8′- and 2,2′-disubstituted-1,1′-binaphthyls investigated previously.[1,2]

8,8′-Bisbromomethyl-1,1′-binaphthyl as an optically active entity has already been prepared[1] but its rates of racemisation were not measured. In the present communication the rate coefficients for the racemisation of optically active 8,8′-bisbromomethyl-1,1′-binapthyl have been determined and Arrhenius parameters and transition state theory functions have been calculated. The synthesis of the optically active 8,8′-bisbromomethyl-1,1′-binaphthyl is based on optically active 1,1′-binaphthyl-8,8′-dicarboxylic acid. The treatment of 8,8′-dicarboxylic acid with diazomethane gave optically active dimethyl ester[2] which on reduction with lithium aluminium hydride gave active 8,8′-bishydroxymethyl-1,1′-binaphthyl,[1] which on treatment with warm hydrobromic acid gave the optically active 8,8′-bisbromomethyl-1,1′-binaphthyl. Its rates of racemisation have been determined in *o*-xylene and the rate coefficients for the racemisation have been determined at various temperatures between 95° and 135°C. The energy of activation for racemisation E_{rac}, of Arrhenius equation $k_{rac}=Ae\,(-E_{rac}/RT)$ was obtained from the measured racemisation velocity constants both by graphical method and by least square calculation. $\Delta F^{\ddagger}$, the change in standard free energy, was calculated from the absolute rate equation,[4] $k_{rac}=(kT/h)e(-\Delta F^{\ddagger}/RT)$, $\Delta H^{\ddagger}$, the enthalpy of activation for racemisation, was calculated from the relationship $\Delta H^{\ddagger}=E-RT$ and $\Delta S^{\ddagger}$, the entropy of activation, from $k_{rac}=k\,(kT/h)\,e\,(-\Delta H^{\ddagger}/RT)e\,(-\Delta S^{\ddagger}/R)$, and a comparison made with other already measured (Chart 1) 8,8′-disubstituted-1,1′-binaphthyls as shown in Table 1.

The values of $\log_{10}A$, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ given in the Table are the averages taken over the whole range of temperature. The Arrhenius parameters E and $\log_{10}A$ and transition state theory functions have been used to describe the optical stability of each compound, and also the half-life period which is a direct measure of optical stability of any compound at a given temperature.

The optical stability of 8,8′-bisbromomethyl-1,1′-binaphthyl ($E=29.6$ kcal/mole) can be compared with those of 8,8′-disubstituted-1,1′-binaphthyls which include 8,8′-acid (4) dimethyl ester (5), hydroxy ester (6), diol (7) and dimethyl compound (8). The value of E for the racemisation of 8,8′-acid[2] and ester were found to be 22 kcal/mole the value of E for the racemisation of diol[1] and dimethyl compound[1] were 29.2 and 27.6 kcal/mole and E value for the racemisation of hydroxyester[1] was 25.8 kcal/mole.

The much higher values for diol, dibromo and dimethyl compounds are accounted for by the presence of three dimensional groups $-CH_2Br$, $-CH_2OH$, and $-CH_3$ which present a higher angular blocking area to passing than the $-COOH$ and $-COOCH_3$ groups which are flat and hence present smaller blocking area to passing.

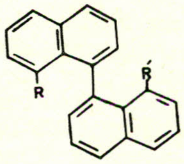
When the optical stability of 8,8′-bisbromomethyl-1,1′-binaphthyl, 8,8′-bishydroxymethyl-1,1′-binaphthyl and 8,8′-dimethyl-1,1-′binaphthyl is compared, the order of stability would be dibromo > diol > dimethyl.

The E value of dibromo compound (29.6) is slightly greater than the E value of diol (29.2); the E value of diol (29.2) is greater than that of dimethyl compound (27.6) but the rate of racemisation of the diol in *N,N*-dimethyl formamide is much quicker and the E value does not fall in the order with the stability by half-life period (Table 1). This must be due to the $\Delta S^{\ddagger}$ values which are -9.3 for 8, 8′-dimethyl-1,1′-binaphthyl and -3.66 for the diol. Presumably the diol is more associated with the solvent in the ground state than the dimethyl compound. Since there is a little difference between E values of dibromo, diol and dimethyl compounds, it may be conculded

TABLE 1.—ARRHENIUS PARAMETERS AND TRANSITION STATE THEORY FUNCTIONS FOR RACEMISATION OF 8,8′-SUBSTITUTED 1, 1′-BINAPHTHYLS.

8,8′-Substituents in 1,1′-binaphthyls		Solvents	Temp range (°C)	No. of rates	$t_{\frac{1}{2}}$ (min)		E (kcal mole^{-1})	$\log_{10}A$	$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ *eu*	$\Delta F^{\ddagger}$ (kcal mole^{-1})	Ref
8	8′				50°C	100°C						
H	H	N,N-DMF	31–59	7	14.5	—	22.5	12.1	21.9	—5.2	23.5	2
—COOH	H	,,	19–69	11	15.4	—	22.4	12.0	21.8	—5.5	23.5	2
—COOH	—$COOC_2H_5$	,,	30–75	10	18.3	—	21.6	11.4	20.95	—8.5	23.7	2
—COOH	—COOH	,,	14–90	14	51.5	—	22.1	11.3	21.5	—9.1	24.4	2
—$COOCH_3$	—$COOCH_3$	,,	30–75	17	23.0	—	22.0	11.6	21.4	—7.5	23.8	2
—CH_2OH	—$COOCH_3$	,,	55–95	9	—	14.1	25.8	12.0	25.1	—6.2	27.2	1
—CH_2OH	—$COOCH_3$	,,	95–130	6	—	395.5	29.2	12.6	28.4	—3.4	29.8	1
—CH_3	—CH_3	,,	100–130	7	—	678.8	27.6	11.0	26.8	—9.4	30.4	1
—CH_2Br	—CH_2Br	*o*-xylene	95–135	8	—	728.6	29.6	12.58	28.83	—3.5	30.132	

Values of $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, are the average for the temperature range over which measurements were made.



	R	R′		R	R′
1.	H	H	6.	CH_2OH	$COOCH_3$
2.	COOH	H	7.	CH_2OH	CH_2OH
3.	COOH	$COOC_2H_5$	8.	CH_3	CH_3
4.	COOH	COOH	9.	CH_2Br	CH_2Br
5.	$COOCH_3$	$COOCH_3$			

Chart 1

that this is mainly >CH_2 group which accounts for the opposition to inversion. Although the optical stability of these compounds is very high and the methyl, hydroxymethyl and bromomethyl groups present a distinctly higher barrier to inversion than those of acid and ester, yet the optical stability does not approach that of 2,2′-disubstituted-1,1′-binaphthyls.

As a result of these studies it may be concluded that all these compounds are strained in their ground state as these are much less stable than the 2,2′-disubstituted-1,1′-binaphthyls. The strain is obvious also from the models. As the strain energy required in bending the group out of plane makes it easy for the molecule to racemise, the energy barrier will be reduced by the strain energy. This is a reason that the observed E value is very small in all 8,8′-disubstituted compounds.

Experimental

Optical rotations were measured with a simple visual polarimeter and refer to λ5890 A°. For measuring the rate of racemisation *o*-xylene was used as a solvent, for determining rotations of the brucine salts chloroform was used and *N,N*-dimethyl formamide was employed for rotations of all other compounds.

Readings for all rate determinations were taken by using a 1-dm micropolarimeter tube. Portions of solutions were sealed in glass ampoules kept in thermostatic oil bath and withdrawn at suitable intervals of time to record the readings. All racemisations were followed to $[\alpha]_D = 0°$ and the identity of the recovered material was established by m.p. mixed m.p. and IR spectrum.

(+) *and* (—)—*1,1′-binaphthyl-8,8′-dicarboxylic acid.*—The (+) and (—)-1, 1′-binaphthyl-8,8′-dicarboxylic acids were obtained as brucine salts by the method of Meisenheimer and Beiswenger.[3]

brucine+acid $[\alpha]_D = +386°$, m.p.=220–235°C

brucine—acid $[\alpha]_D = +424°$, m.p.=265–270°C

The (+) and (—) acids were precipitated by shaking the chloroform solution of brucine salts with aqueous sodium hydroxide followed by neutralisation with dilute hydrochloric acid.

(—) acid $[\alpha]_D = —502°$, m.p.=316–320°C

(+) acid $[\alpha]_D = +455°$, m.p.=315–320°C

(±)-*Dimethyl-1, 1′-binaphthyl-8, 8′-dicarboxylate*[2].—Finely ground 1, 1′-binaphthyl-8, 8′-dicarboxylic acid (2.50 g) was added to the cold ethereal solution of diazomethane. The acid dissolved with effervescence and a solid mass was obtained after completion of the reaction. It was filtered, shaken with aqueous sodium carbonate followed by two washings with water and dried; m.p. 156–158°C. Recrystallisation from ethanol yielded a pure compound, m.p. 158–159°C.

(+) *and* (—)-*Dimethyl-1,1′-binaphthyl-8, 8′-dicarboxylate.*[2]—(+) and (—)-1′1′-binaphthyl-8, 8′-dicarboxylic acids were separately added to the cold ethereal solution of dizomethane. A crystalline solid mass was obtained in each case which was washed with aqueous sodium hydroxide followed by washings with water and dried.

(+) dimethyl ester $[\alpha]_D = +144°$, m.p. = 124–128°C
(—) dimethyl ester $[\alpha]_D = -159°$, m.p. = 122–127°C

(±)-8,8′-*Bishydroxymethyl-1,1′-binaphthyl.*[1]— (±)-Dimethyl-1,1-′binaphthyl-8,8′-dicarboxylate (5.00 g) in 500 ml absolute ether was treated with lithium aluminium hydride (1.50 g). The mixture was refluxed for 3 hr. The excess of metal hydride, left unreacted after completion of the reaction, was decomposed with water and hydrochloric acid. The ethereal layer was washed with water and dried (Na_2SO_4). The solvent was removed and the residual mass was crystallised from benzene, m.p. 150–151°C.

(—)-8,8′-*Hydroxymethyl-1,1′-binaphthyl.*[1]—(—)8,8′-Bishydroxymethyl-1, 1,1′-binaphthyl was obtained on treating the (+) dimethyl ester with lithium aluminium hydride in the same way as in (±) diol, $[\alpha]_D$—21, m.p. 141–144°C.

(±) - 8,8′ - *Bisbromomethyl - 1,1′ - binaphthyl.*—8,8′ - Bishydroxymethyl-1,1′-binaphthyl (2.50g) was dissolved in 25 ml hot glacial acetic acid and to this solution were added 50 ml hot hydrobromic acid. A yellow crystalline solid separated which was filtered, washed thoroughly with water and dried, m.p. 178–179°C. Recrystallisation from chloroform yielded light-yellow crystals, m.p. 190–191°C.

(—) - 8,8′ - *Bisbromomethyl - 1,1′ - binaphthyl.*—The (—)-8,8′-bishydroxymethyl-1,1′-binaphthyl (0.50g) was dissolved in 10 ml hot glacial acetic acid to which 5 ml hot hydrobromic acid (d=1.5) were added. An impure crystalline compound was obtained which yielded a pure compound on recrystallisation from chloroform, m.p. 182°–184°C; $[\alpha]_D = 117°$.

The mother liquor from the optically active (—)-diol was concentrated to a sticky mass. It was dissolved in benzene and eluted over a column of alumina with a mixture of benzene and petro-

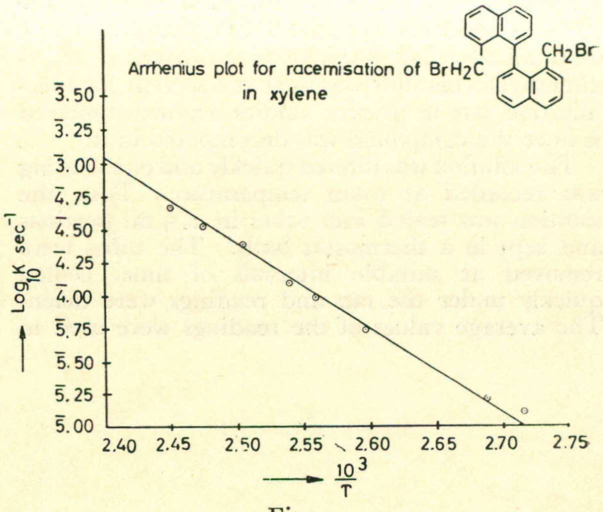


Fig. 1.

TABLE 2.—DETERMINATION OF RATE COEFFICIENT FOR THE RACEMISATION OF 8,8′-BISBROMOMETHYL 1,1′-BINAPHTHYL, SOLVENT *o*-XYLENE.

Temp. °C	First reading	No. of readings	Time during which readings were taken (min)	$\log_{10}$ k(sec^{-1})	$t\frac{1}{2}$ (min)
95.4	(—)0.747	6	300	$\bar{5}$.1430	830.50
100.0	(—)0.820	6	250	$\bar{5}$.2220	728.60
112.0	(—)1.900	7	180	$\bar{5}$.7359	121.57
117.6	(—)1.160	7	180	$\bar{5}$.9869	22.43
120.6	(—)2.114	7	120	$\bar{4}$.0828	94.00
126.2	(—)0.990	8	105	$\bar{4}$.4200	51.00
130.9	(—)1.128	8	70	$\bar{4}$.5315	35.10
134.9	(—)1.019	7	30	$\bar{4}$.6689	24.80

whence E_{rac} = 29.6 kcal $mole^{-1}$ (graph)
= 29.42 kcal $mole^{-1}$ (least sq. calculations)
$\log_{10}A$ = 12.58
$\Delta H^{\ddagger}$ = 28.83 kcal $mole^{-1}$
$\Delta S^{\ddagger}$ = 3.5 e.u.
$\Delta F^{\ddagger}$ = 30.132 kcal $mole^{-1}$

leum ether (1:9). All fractions except a first few were collected together and concentrated resulting in again a sticky substance. It was dissolved in hot glacial acetic acid to which hot hydrobromic acid was added. A yellow bromo compound separated which was filtered, washed twice with water and dried. It was then crystallised from chloroform, m.p. 182–184°C, $[\alpha]_D = -268°$

Racemisation of (—)-8,8′-*bisbromomethyl*-1,1′-*binaphthyl*.—The rates of racemisation of the (—)-8,8′-bisbromomethyl-1,1′-binaphthyl were determined using *o*-xylene as a solvent. *N*,*N*-dimethyl formamide was used as a solvent for racemisation but in present studies *o*-xylene replaced it since the compound was decomposed in it.

The solution was filtered quickly and one reading was recorded at room temperature. Then the solution was sealed into tubes in 2.5 ml portions and kept in a thermostat bath. The tubes were removed at suitable intervals of time, cooled quickly under the tap and readings were taken. The average values of the readings were used to plot the graph of $\log_{10}(\alpha_{t} - \alpha_{\infty})$ against time, and straight lines were obtained. The log of the rate constant k was plotted against the reciprocal of absolute temperature (0°C was taken as 273.2°C) and slope of straight line (Fig. 1) obtained was used to calculate the Arrhenius parameters E, $\log_{10}A$ and the transition state theory functions $\triangle H,^{\ddagger}$ $\triangle F^{\ddagger}$ and $\triangle S^{\ddagger}$ (Table 2).

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