

**ARRHENIUS PARAMETERS AND TRANSITION STATE THEORY FUNCTIONS FOR  
RACEMISATION OF 8, 8'-BIS-(ETHOXYMETHYL) AND 8, 8'-BIS-  
(METHOXYMETHYL)-1, 1'-BINAPHTHYL**

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**Abstract.** Optically active 8, 8'-bis(ethoxymethyl)-1, 1'-binaphthyl and 8, 8'-bis(methoxymethyl)-1, 1'-binaphthyl have been synthesised and their rates of racemisation studied. From the experimental results the Arrhenius parameters  $E$  and  $\log_{10} A$  and the Transition State Theory Functions  $\Delta \neq H$ ,  $\Delta \neq F$ ,  $\Delta \neq S$  for racemisation have been determined. A comparison is made with other optically active 8, 8'- and 2, 2'-disubstituted-1, 1'-binaphthyls investigated previously.<sup>1, 2, 5, 6</sup>

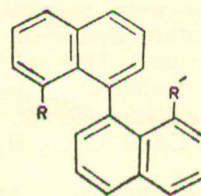
Optically inactive 8,8'-bis(ethoxymethyl)- and 8,8'-bis(methoxymethyl)-1, 1'-binaphthyl have been previously prepared by Badar and Harris.<sup>2</sup> In the present communication optically active 8,8'-bis(ethoxymethyl)-1, 1'-binaphthyl and 8,8'-bis(methoxymethyl)-1, 1'-binaphthyl have been obtained and their rate coefficients for racemisation have been determined and the Arrhenius parameters and Transition Theory Functions calculated. The optical activity of these compounds is compared with those of 1,1'-binaphthyl itself and its 8,8'- and 2,2'-disubstituted derivatives previously investigated.<sup>1-3</sup>

The rates of racemisation have been determined in *N,N*-dimethyl formamide. The rate coefficients for the racemisation have been determined at various temperatures between 95–135°C. The energy of activation for racemisation  $E_{rac}$  was obtained from the measured racemisation velocity constants both by the graphical method and the least square calculations.  $\Delta \neq F$ , the change in the standard free energy, was calculated from the absolute rate equation,<sup>4</sup>  $K_{rac} = k(KT/h)\exp(-\Delta \neq F/RT)$ .  $\Delta \neq H$ , the enthalpy of activation for racemisation, was calculated from the relationship  $\Delta \neq H = E - RT$ .  $\Delta \neq S$ , the entropy of activation, was calculated from the equation  $K_{rac} = k(KT/h)\exp(-\Delta \neq H/RT)\exp(\Delta \neq S/R)$ . The transmission coefficient  $k$  was taken to be unity and a comparison made with other already measured 8,8'-substituted binaphthyls as shown in the Table 1.

The synthesis of the optically active 8,8'-bis(ethoxymethyl)-1,1'-binaphthyl and 8,8'-bis(methoxymethyl)-1,1'-binaphthyl compounds is based upon the optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid.<sup>1</sup> The treatment of the acid with diazomethane gave optically active dimethyl ester which, on reduction with lithium aluminium hydride yielded optically active 8,8'-diol. The diol on treatment with hydrobromic acid produced optically active 8,8'-bis(bromomethyl)-1,1'-binaphthyl. This dibromo compound, dissolved in ethanol or methanol on treatment with aqueous silver nitrate solution, gave bis(ethoxy) or bis(methoxy) compound as illustrated in the chart.

The values of  $\log_{10} A$ ,  $\Delta \neq S$ ,  $\Delta \neq H$  and  $\Delta \neq F$  given in the table 1 are the averages taken over the whole range of temperature. The Arrhenius parameters  $E$  and  $\log_{10} A$  and the 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 energies of activation of 8,8'-bis(ethoxymethyl)-1,1'-binaphthyl ( $E$ , 29.44 or 29.4 kcal/mole) and 8,8'-bis(methoxymethyl)-1,1'-binaphthyl ( $E$ , 29.39 or 29.4 kcal/mole) respectively can be compared with those of 8,8'-disubstituted-1,1'-binaphthyls (Table 1) which include 8,8'-acid (4), dimethyl ester (5), the diol (7), dimethyl compound (8) and dibromo (9). The  $E$  value for the racemisation of 8,8'-acid and its ester were found to be 22.0 kcal/mole the  $E$  values for diol, dimethyl and dibromo compounds were 29.2, 27.6 and 29.6 kcal/mole respectively.



R	R	R	R
1. H	H	6. CH <sub>2</sub> OH	COOCH <sub>3</sub>
2. COOH	H	7. CH <sub>2</sub> OH	CH <sub>2</sub> OH
3. COOH	COOC <sub>2</sub> H <sub>5</sub>	8. CH <sub>3</sub>	CH <sub>3</sub>
4. COOH	COOH	9. CH <sub>2</sub> Br	CH <sub>2</sub> Br
5. COOCH <sub>3</sub>	COOCH <sub>3</sub>	10. CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>
		11. CH <sub>2</sub> OCH <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>

TABLE 1. ARRHENIUS PARAMETERS AND TRANSITION STATE THEORY FUNCTION FOR RACEMISATION OF 8,8'-SUBSTITUTED 1,1'-BINAPHTHLYLS.

S. No.	8, 8'-Substituents in 1,1'-binaphthyls	Solvents	Temp. range (°C)	No. of rates	t <sub>1/2</sub> (min)		log <sub>10</sub> A	Δ≠H kcal/mole	Δ≠S eu	Δ≠F kcal/mole	Ref
					50	100					
1	H	N,N.D.M.F.	31-59	7	14.5	—	12.1	21.9	-5.2	23.5	2
2	-COOH	"	19-69	11	15.4	—	12.0	21.8	-5.5	23.5	2
3	-COOH	"	30-75	10	18.3	—	11.4	21.0	-8.4	23.7	2
4	-COOH	"	14-90	14	51.5	—	11.3	21.5	-9.1	24.4	2
5	-COOCH <sub>3</sub>	"	30-75	17	23.0	—	11.6	21.4	-7.5	23.8	2
6	-CH <sub>2</sub> OH	"	55-95	9	—	14.1	12.0	25.1	-6.2	27.2	1
7	-CH <sub>2</sub> OH	"	95-130	6	—	395.5	12.6	28.4	-3.4	29.8	1
8	-CH <sub>3</sub>	"	100-130	7	—	678.8	11.0	26.8	-9.4	30.4	1
9	-CH <sub>2</sub> Br	o-xylene	95-135	8	—	728.6	12.6	28.8	-3.5	30.1	6
10	-CH <sub>2</sub> OCH <sub>3</sub>	N,N.D.M.F.	96-130	6	—	336.0	12.7	28.6	-2.9	29.8	
11	-CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	"	96-130	6	—	519.3	12.5	28.7	-3.7	30.1	

Values of Δ≠F, Δ≠H, and Δ≠S, are the average for the temperature range over which measurements were made.

The evidently higher values for the diol, dibromo and dimethyl compounds could be accounted for on the basis of the presence of three dimensional groups —CH<sub>2</sub>Br, —CH<sub>2</sub>OH, and —CH<sub>3</sub> which present a higher angular blocking area to passing than the —COOH and —COOCH<sub>3</sub> groups which are flat and hence present smaller angular blocking area to passing.

When the optical stability of 8,8'-bis(bromomethyl)-1,1'-binaphthyl, 8,8'-bis(hydroxymethyl)-1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyl is compared the order of stability would be dibromo > diol > dimethyl.

The *E* values of the ethoxy compound, 29.3 kcal/mole and the methoxy compound, 29.4 kcal/mole are very slightly greater than the *E* value of the diol, 29.2 kcal/mole and slightly smaller than the dibromo compound, 29.6 kcal/mole. As in the case of diol the rate of racemisation of ethoxy and methoxy compounds in N,N-dimethyl formamide is quicker and the *E* value does not fall in the order of stability of half-life period (Table 1). This must be due to the Δ≠*S* values, which are -9.4 e.u. for 8,8'-dimethyl-1,1'-binaphthyl and -3.5, -2.9 and -3.7 kcal/mole for the diol, methoxy and ethoxy compounds respectively. Presumably they are more associated with the solvent in the ground state than is the dimethyl compound.

When the optical stability of 8,8'-bis(ethoxymethyl)-1,1'-binaphthyl and 8,8'-bis(methoxymethyl)-1,1'-binaphthyl is taken into consideration the *E* value for the ethoxy compound is slightly greater than the *E* value of the methoxy compound as would be expected. It would be concluded from the results obtained that the capacity of the substituents to restrict rotation would be in the order —CH<sub>2</sub>Br > —CH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub> > —CH<sub>2</sub>OCH<sub>3</sub> > —CH<sub>2</sub>OH > —CH<sub>3</sub> > —COOH > —COOCH<sub>3</sub>.

Since there is a little difference between the *E* values of diol, ethoxy compound, methoxy compound and dibromo compound it may be inferred that this is mainly the >CH<sub>2</sub> group which accounts for the opposition to inversion. Although the optical stability of these compounds is very high and the methyl, hydroxymethyl, bromomethyl, ethoxymethyl and methoxymethyl groups present distinctly higher barriers to inversion than those of the acid and ester yet the optical stability does not approach that of 2,2'-disubstituted -1,1'-binaphthyls.

In the light of these studies it may be concluded that all the compounds are strained in their ground state since they are much less stable than the 2,2'-disubstituted-1,1'-binaphthyls. The strain is apparent also from the models. As the strain energy required in bending the group out of plane makes it easy for the molecules to racemise, the energy barrier will be reduced by the strain energy. This is a reason that the observed *E* value is small in all the 8,8'-disubstituted compounds when compared with the *E* values in 2,2'-disubstituted compounds.<sup>1-3</sup>

### Experimental

Optical rotations were measured with a simple visual polarimeter (5890Å). N,N-dimethyl formamide was used as a solvent for measuring the rate

of racemisation and for determining rotations of all the compounds. Chloroform was used as a solvent for determining rotations of the brucine salts.

The readings for all rate determinations were recorded 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  $\alpha=0$  and the identity of the recovered material was established by m.p., mixed m.p. and IR spectra.

*Preparation of (+) 8,8'-Bis(methoxymethyl)-1,1'-binaphthyl.* (+) 8,8'-Bis(bromomethyl)-1,1'-binaphthyl<sup>2</sup> (1.0 g) was dissolved in boiling methanol and aqueous silver nitrate solution was added in excess. The precipitate of silver bromide thus obtained was filtered off and washed a few times with ether and benzene. Evaporation of the solvent and later crystallisation from ethanol gave (+) 8,8'-bis(methoxymethyl)-1,1'-binaphthyl 0.60 g; m.p. 66–67°C,

$[\alpha]_D^{30} = +124$ . Found : C, 84.5; H, 6.2; O, 9.3%. requires : C, 84.2; H, 6.5; O, 9.3%

*Racemisation in N,N-Dimethyl Formamide.*

Temp (°C)	96.2	100.2	105.2	110.2	122.00	130.40
$\log_{10} K$ (sec <sup>-1</sup> )	2.17	3.438	5.825	8.21	1.758	5.35
$t_{\frac{1}{2}}$ (min)	531.8	336.1	198.4	140.7	41.8	22.09

whence  $E_{rac}$  29.3 kcal/mole graphical; 29.4 kcal/mole least square calculation.

*Preparation of (+) 8,8'-Bis(ethoxymethyl)-1,1'-binaphthyl.* (+) 8,8'-Bis(bromomethyl)-1,1'-bi-

naphthyl (0.5 g) was dissolved in hot ethanol. Aqueous silver nitrate solution was added in excess. The precipitate of silver bromide was filtered, washed with ether and the combined filtrate was evaporated to dryness. The residue obtained was extracted with ether which gave a sticky substance on removing the solvent. This substance was crystallised from ethanol (0.41 g, m.p. 75–77 °C,  $[\alpha]_D^{30} = +123$ ).

(Found : C, 84.4; H, 7.2; O, 8.4%.

requires : C, 84.3; H, 7.1; O, 8.6%)

*Racemisation in N,N-Dimethyl Formamide.*

Temp (°C)	96.2	100.2	105.01	10.2	120.2	130.4
$\log_{10} K$ (sec <sup>-1</sup> )	1.324	2.224	3.532	5.773	1.377	3.077
$t_{\frac{1}{2}}$ (min)	872.6	519.3	326.6	200.3	83.87	37.52

whence  $E_{rac}$  29.4 kcal/mole graphical; 29.6 kcal/mole least square calculations.

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