

ARRHENIUS PARAMETERS AND TRANSITION STATE THEORY FUNCTIONS FOR THE RECEMISATION OF 8, 8'-BIS (PROPOXYMETHYL)-1,1'-BINAPHTHYL

Fatima Bi and Yasmeen Badar

PCSIR Laboratories, Karachi, Pakistan

(Received November 11, 1980)

Optically active 8,8'-bis(Propoxymethyl)1,1'-binaphthyl has been synthesised and Arrhenius Parameters and Transition State Theory functions for racemisation have been calculated from measurement of velocity constants for racemisation; a comparison is made with other optically active 8,8'- and 2,2'-di-substituted 1,1'-binaphthyls investigated previously [1-6].

INTRODUCTION

In pursuing our study of optically labile molecules which are distorted in the ground state [1-7] we have synthesised optically active 8,8'-bis(propoxymethyl)-1,1'-binaphthyl and determined its velocity constants for racemisation in solution and calculated the Arrhenius parameters and transition state theory functions. The optical stability of the compound is compared with those of 1,1'-binaphthyl itself and its 8,8'- and 2,2'-disubstituted derivatives (Table 1).

The synthesis of the new optically active compound is also based on optically active 1,1'-binaphthyl 8,8'-dicarboxylic acid; treatment of this with diazomethane gives the optically active dimethyl ester. Lithium aluminium

hydride reduction of this diester yielded 8,8'-bis (hydroxymethyl)-1,1'-binaphthyl; warm hydrobromic acid converted the optically active diol into optically active bisbromomethyl-1,1'-binaphthyl [4], which on treatment with n-propyl alcohol and silver nitrate gave the bis(propoxymethyl)-1,1'-binaphthyl.

The rates of racemisation have been determined in N,N-dimethylformamide. The rate coefficients for the racemisation have been determined at various temperatures between 95-120°.

The energy of activation was obtained from the measured racemisation velocity constants both by graphical and by least squares calculation. ΔF^\ddagger , the change in the standard free energy, was calculated from the absolute rate equation [3]. $K_{rac} = k (KT/h \exp (-\Delta F^\ddagger/RT))$, the enthalpy

Table 1. Arrhenius Parameters and Transition State Theory Functions for Racemisation of 8,8'-Disubstituted 1,1'-Binaphthyls

S.No.	8,8'-Substituents in 1,1'-binaphthyls.		Solvents	Temp. range °	No. of rates	$t_{1/2}$ in minutes		E Kcal. mole ⁻¹	Log ₁₀ A	H [‡] kcal mole ⁻¹	S [‡] eu	F [‡] kcal mole ⁻¹	Reference
						50°	100						
	8	8'	N,N-DMF										
1.	H	H	"	31-59	7	14.5	-	22.5	12.1	21.9	-5.2	23.5	2
2.	-COOH	H	"	19-69	11	15.4	-	22.4	12.0	21.8	-5.5	23.5	2
3.	-COOH	-COOC ₂ H ₅	"	30-75	10	18.3	-	21.2	11.4	20.9	-8.5	23.7	2
4.	-COOH	-COOH	"	14-90	14	51.5	-	22.1	11.3	21.5	-9.1	24.4	2
5.	-COOCH ₃	-COOCH ₃	"	30-75	17	23.0	-	22.0	11.6	21.4	-7.5	23.8	2
6.	-CH ₂ OH	-COOCH ₃	"	55-95	9	-	14.1	25.8	12.0	25.1	-6.2	27.2	1
7.	-CH ₂ OH	-CH ₂ OH	"	95-130	6	-	395.5	29.2	12.6	28.4	-3.4	29.8	1
8.	-CH ₃	-CH ₃	"	100-130	7	-	678.8	27.6	11.0	26.8	-9.4	30.4	1
9.	-CH ₂ Br	-CH ₂ Br	o-xylene	95-135	8	-	728.6	29.6	12.0	28.8	-3.5	30.5	5
10.	-CH ₂ OCH ₃	-CH ₂ OCH ₃	N,N-DMF	96-130	6	-	336	29.4	12.7	28.7	-2.9	29.8	6
11.	-CH ₂ OC ₂ H ₅	-CH ₂ OC ₂ H ₅	"	96-130	6	-	519.3	29.4	12.5	28.7	-3.7	30.1	6
12.	-CH ₂ OC ₃ H ₇	-CH ₂ OC ₃ H ₇	"	95-120	5	-	528.0	29.4	12.7	28.7	-2.16	29.5	-

Values of ΔF^\ddagger , ΔH^\ddagger , are the averages for the temperature range over which measurements were made.

of activation for racemisation was calculated from the relationship $\Delta H^\ddagger = E - RT$. The entropy of activation from the equation $K_{\text{rac}} = k(hT/h) \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)$. The transmission coefficient was taken to be unity.

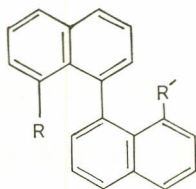


FIG. 1

	R	R'	R	R'
1.	H	H	10CH ₂ OCH ₃	-CH ₂ OCH ₃
2.	COOH	-H	11-CH ₂ OC ₂ H ₅	-CH ₂ OC ₂ H ₅
3.	-COOH	-COOC ₂ H ₅	12-CH ₂ OC ₃ H ₇	-CH ₂ OC ₃ H ₇
4.	-COOH	-COOH		
5.	-COOH ₃	-COOH ₃		
6.	-CH ₂ OH	-COOCH ₃		
7.	-CH ₂ OH	-CH ₂ OH		
8.	-CH ₃	-CH ₃		
9.	-CH ₂ Br	-CH ₂ Br		

The optical stability of the new compound can be compared with those of 1,1'-binaphthyl-8,8'-dicarboxylic acid its ester, the derived diol, dibromo compound, methoxymethyl and ethoxymethyl 1,1'-binaphthyls. The values of E_{rac} which express the difference between the energy of the transition state and of the ground state are very closely similar in the cases of 1,1'-binaphthyl-8,8'-di-carboxylic acid its ester and 1,1'-binaphthyl itself, lying within 1.5 Kcal mole⁻¹ of each other (Table 1). The E value for the racemisation of diol, dimethyl, dibromo-methyl, methoxymethyl and ethoxymethyl compounds were 29.2, 27.6, 29.6, 29.4 and 29.4, respectively. The higher E values for these compounds are accounted for by the presence of three dimensional groups, CH₂Br, CH₃, CH₂OH, CH₂OCH₃ and CH₂OC₂H₅ groups, presenting higher angular blocking areas to passing than those of COOCH₃ and COOH groups which are flat and present smaller blocking areas to passing.

The E value of 8,8'-bis(propoxymethyl)-1,1'-binaphthyl (29.5 K_{cal}) is slightly greater than the E value of the diol and the dimethyl compound and very slightly smaller than the di-bromocompound (29.6). As in the case of the diol, ethoxy and methoxy compounds the rate of racemisation of the propoxy compound in N,N-dimethyl-formamide is also quicker and the E values do not fall in the order of the half life periods; this must again be due to ΔS^\ddagger which are -9.4 e.u. for dimethyl compound and 3.4, 2.9, 3.7 and -2.16 for the diol, methoxy, ethoxy and propoxy compounds probably because they are more associated with the solvent in the ground state than is the dimethyl compound.

When the optical stabilities of the 8,8'-bis-(propoxymethyl)-1,1'-binaphthyl and the methoxymethyl and ethoxymethyl are compared the E value of the propoxy compound may be regarded as the same within the experimental error, the significance of the near equality of the E values may be due to the fact that in the transition state the group attached to oxygen are all turned right out of the way.

As has already been noted by Badar, Cooke and Harris^[4] and by Badar and her co-workers^[5,6] the methyl, hydroxymethyl, methoxymethyl ethoxymethyl groups present distinctly higher barrier to inversion than the carboxylic acid or ester groups yet the optical stabilities do not approach that of the 2,2'-disubstituted compounds. The observed activation energy E_{rac} in all the 8,8'-disubstituted compounds is substantially lowered by the ground state energy. The obstacle effect of the methyl, hydroxymethyl and ethoxymethyl groups is enhanced by the fact that they are forced by their nature to subtend a larger angles at the 1,1'-bond than the carboxylic acid or ester groups thus introducing a higher compression into mesoid transition states. Clearly the steric effect of the propoxymethyl group is very similar.

EXPERIMENTAL

Polarimetric Works; Optical rotation were measured with a simple polarimeter (Schnzdt Haensch 13199 $\lambda=5890 \text{ \AA}$). A 2 dm, centre filling polarimeter tube was used for the specific rotation of brucine salts and a micro-polarimeter tube (1 dm) for other optically active compounds.

Table 2. Racemisation of (-) 8,8'-Bis(Propoxymethyl)-1,1'-Binaphthyl in N,N'-Dimethylformamide.

Temp (°C)	95.2	100.0	105.4	110.5	120.0
10 k (Sec ⁻¹)	2.021	4.45	7.537	1.398	2.598

Whence $E = 29.5$ (graphical) and $30.2 \text{ K}_{\text{cal}} \text{ mole}^{-1}$ (by least squares calculation).

N,N-Dimethylformamide was normally used as a solvent for measuring the rates of racemisation, but chloroform was used when measuring the rotation of the alkaloidal salts.

Determination of K_{rac} were made over a range of 96–120° and were recorded using a 1 dm micropolarimeter tube. 1.5 ml portions of solutions were sealed in glass ampules, kept in thermostatic oil bath and withdrawn within suitable intervals of time to record the readings; all racemisations were followed to $\alpha=0$ and the identity of the recovered compounds was established by m.p., mixed m.p. and IR Spectra.

Preparation of (+) 8,8'-Bis(propoxymethyl)-1,1'-Binaphthyl. (+) 8,8'-Bis(bromomethyl)-1,1'-binaphthyl (1.5 g) was dissolved in boiling n-propanol, and freshly prepared 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(propoxymethyl)-1,1'-binaphthyl (0.95 g) m.p. 68–70°. Found C, 84.7; H, 7.5; O, 7.8 Calculated for $C_{28}H_{30}O_2$; C, 84.4; H, 7.6; O, 8.0%.

Preparation of (-) 8,8'-Bis(propoxymethyl)-1,1'-binaphthyl. (-) 8,8'-Bis(bromomethyl)-1,1'-binaphthyl

(1.00 g) was dissolved in boiling n-propanol, and freshly prepared 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-(propoxymethyl)-1,1'-binaphthyl (0.7 g). m.p. = 60–61°. $[\alpha]_D^{20} = -78^\circ$.

REFERENCES

1. Ann. S. Cooke and M.M. Harris, J. Chem. Soc., 2365 (1963).
2. D.M. Hall and E.E. Turner, J. Chem. Soc., 1242 (1955).
3. Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (Mc Graw-Hills, New York, 1941).
4. Yasmeen Badar, Ann. S. Cooke and M.M. Harris, J. Chem. Soc., 1412 (1965).
5. Yasmeen Badar, K. Fatima, M.S.H. Siddiqui and M.E. Hamdard, Pakistan J. Sci. Ind. Res. 14, 463 (1971)
6. Yasmeen Badar, K. Fatima A. Dareshani and M.E. Hamdard, Pakistan J. Sci. Ind. Res., 18, 250 (1975).
7. D.M. Hall and M.M. Harris, J. Chem. Soc. (1960), 490 and references therein.