248. *Optical Activity in the* 1,1′*-Binaphthyl Series. Optically Active* 8,8′*-Dimethyl-*1,1′*-binaphthyl.*

By YASMEEN BADAR, ANN S. COOKE, and MARGARET M. HARRIS.

Several new compounds in the 8,8′-disubstituted 1,1′-binaphthyl series have been prepared, five of them in the optically active state. Arrhenius parameters and transition-state theory functions for racemisation have been determined for four of them; the optical lability of the new compounds is discussed in comparison with that of 1,1′-binaphthyl itself and of its 8,8′- and 2,2′-disubstituted derivatives previously investigated.

THE Arrhenius parameters and transition-state theory functions for the racemisation of 1,1′-binaphthyl-8,8′-dicarboxylic acid (Ia) and of its methyl ester are remarkably close to those for 1,1′-binaphthyl (Ib) itself.[1] In contrast, 2,2′-disubstituted 1,1′-binaphthyls show high optical stability.[2] The ease with which restriction of rotation can be overcome in the 8,8′-disubstituted compounds may be attributed in part to the deformation of the molecule consequent upon steric repulsion of substituents in naphthalene *peri*-positions; this raises the ground-state energy and also leads to the possible adoption of a mesoid conformation (II) which allows the passing of the pairs of obstacles (by the *trans* route) one at a time rather than simultaneously; simultaneous passing would be required if the transition state were planar or if a racemoid conformation were adopted.

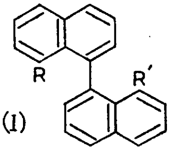
It is a facilitating factor in the configurational inversion of the mesoid distorted model (II) that the 1,1′-bond is able to bend laterally to enable one pair to pass, whereas in the racemoid distorted model, or in a planar model where both pairs pass simultaneously, no

---

[1] Cooke and Harris, *J.*, 1963, 2365, and references cited therein.

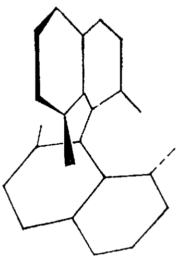
[2] Hall and Turner, *J.*, 1955, 1242.

such bending can be energetically advantageous because the relief from compression gained on one side of the bond would be annulled by an equal added pressure on the other.



(I)

	R	R'		R	R'
(Ia)	CO_2H	CO_2H	(Ig)	$CH_2{\cdot}OEt$	$CH_2{\cdot}OEt$
(Ib)	H	H	(Ih)	$CH_2{\cdot}OMe$	$CH_2{\cdot}OMe$
(Ic)	CO_2Me	CO_2Me	(Ii)	CH_2Br	CO_2Me
(Id)	$CH_2{\cdot}OH$	CO_2Me	(Ij)	Me	Me
(Ie)	$CH_2{\cdot}OH$	$CH_2{\cdot}OH$	(Ik)	$CH_2\overset{+}{N}C_9H_8Br^-$	$CH_2\overset{+}{N}C_9H_8Br^-$
(If)	CH_2Br	CH_2Br			



(II)

When the 8,8'-groups are identical, and not too large, passing on one side can give a mesoid intermediate which has a centre of symmetry and has thus lost its optical activity at this stage; the energetically important step is passing on one side. This is not the case when the 8- and 8'-substituents are different; no centre of symmetry exists in the intermediate.

The optical lability of the 8,8'-dicarboxylic acid and its esters is so striking that it seemed desirable to investigate the possibility that it depends upon some property peculiar to these groups rather than upon the overall distorted geometry of the molecule. The groups CO_2H, CO_2Me, and CO_2Et all have a similar " planar " structure as obstacles; we have now made four new optically active compounds with " tetrahedral " obstacles in the 8,8'-positions: CO_2Me, $CH_2{\cdot}OH$ (Id); $CH_2{\cdot}OH$, $CH_2{\cdot}OH$ (Ie); CH_2Br, CH_2Br (If); Me, Me(Ij). Velocity constants for racemisation of (Id), (Ie), and (Ij) were measured in *NN*-dimethylformamide solution; the results, with relevant figures for comparison, are presented in Table 1.

The methyl and hydroxymethyl groups present a distinctly higher barrier to inversion than the carboxylic acid or ester groups, yet the optical stability does not approach that of the 2,2'-disubstituted compounds; we take the latter point as evidence that the observed activation energy, E_{rac}, in all the 8,8'-disubstituted compounds is substantially lowered by the ground-state energy.[1] The obstacle effect of the methyl and hydroxymethyl groups is enhanced by the fact that they are forced by their nature to subtend a larger angle at the 1,1'-pivot bond than are carboxylic acid or ester groups, thus introducing an element of higher compression into the mesoid transition state. The hydroxymethyl group shows a larger blocking effect (Table 1) than the methyl group but this is compensated for by a smaller negative entropy term, possibly attributable to a small degree

TABLE 1.

Arrhenius parameters and transition-state theory functions for racemisation in the 1,1'-binaphthyl series; solvent, *NN*-dimethylformamide.

	Substituents		10^5k (sec.$^{-1}$)		$t_{\frac{1}{2}}$ (min.)		E (kcal. mole^{-1})	$\log_{10} A$ (sec.$^{-1}$)	$\Delta F^{\ddagger}$ * (kcal. mole^{-1})	$\Delta H^{\ddagger}$ * (kcal. mole^{-1})	$\Delta S^{\ddagger}$ * (e.u.)
	8	8'	100°	50°	100°	50°					
1	Me	Me	1·50	—	679	—	27·6	11·0	30·4	26·8	−9·4
2	$CH_2{\cdot}OH$	$CH_2{\cdot}OH$	3·3	—	395	—	29·2	12·6	29·8	28·4	−3·4
3	$CH_2{\cdot}OH$	CO_2Me	72	0·347	14·1	2226	25·8	12·0	27·2	25·1	−6·2
4[1]	CO_2H	CO_2H	—	22·4	—	51·5	22·1	11·3	24·4	21·5	−9·1
5[1]	CO_2Me	CO_2Me	—	49·4	—	23·0	22·0	11·6	23·8	21·4	−7·5
6[1]	CO_2H	CO_2Me	—	61·4	—	18·3	21·6	11·4	23·7	20·95	−8·4
7[1]	CO_2H	H	—	75·0	—	15·4	22·4	12·0	23·5	21·8	−5·5
8[1]	H	H	—	79·4	—	14·5	22·5	12·1	23·5	21·9	−5·2

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

of solvation (comparable with, but less dramatic than, that of the dicarboxylic acid in aqueous alkaline solution [1]), so that the overall free-energy of racemisation is reduced. A factor which may lower E_{rac} in the acids and esters, apparent from the study of putative models, is that in the transition state one of the carboxylic acid or ester groups may be able to adopt a conformation more nearly planar with its attached naphthalene ring than it can in the ground state, thus giving a resonance energy increment over that of the ground state.

Comparison between 1,1′-*Binaphthyl and* 8,8′-*Dimethyl*-1,1′-*binaphthyl.*—E_{rac} for 8,8′-dimethyl-1,1′-binaphthyl (27·6 kcal. mole^{-1}) can be compared with that of 1,1′-binaphthyl itself (22·5 kcal. mole^{-1}) [1] on the basis of steric blocking and ground-state energy factors alone, since it is unlikely that the methyl groups can make any appreciably different resonance-energy contribution to the ground state and to the transition state. Unfortunately, no satisfactory experimental value exists for the blocking effect of unbuttressed methyl groups in a biphenyl. Methyl buttressed by another methyl group provides the steric block in 2,2′,3,3′-tetramethylbenzidine,[3] which has E_{rac} 17·7 ± 0·3 kcal. mole^{-1} in ethyl acetate solution; the amino-groups probably decrease E_{rac} by 1 kcal.[4,5] so the rotational barrier due to the 2,2′-methyl groups passing 6,6′-hydrogen atoms is approximately 19 kcal. mole^{-1}; of this only a small part can be due to buttressing since it is known [6] that the buttressing effect of iodine by ortho-iodine in a sterically similar situation adds only 6·4 kcal. mole^{-1} to the energy of activation for racemisation. If 4 kcal. mole^{-1} is the energy barrier in biphenyl itself,[7] then 15 kcal. mole^{-1},* less a figure smaller than 6, is the energy *increment* on exchanging two methyl groups for two hydrogen atoms in sterically effective positions. The closest comparable unbuttressed activation energy, experimentally determined, is for bromine [the van der Waals radius of Me (2·0 Å) is considered to be very close to that of bromine (1·95 Å) [8]]; E_{rac} for 2,2′-dibromobiphenyl-4,4′-dicarboxylic acid is 19 kcal. mole^{-1}.[9]† The increment in E_{rac} in substituting Br for H in the 2- and 2′-positions in biphenyl can be estimated as (19 − 4 − 1·5) = 13·5 * kcal. mole^{-1}, allowing 1·5 kcal. mole^{-1} for the stabilising effect of the carboxyl groups.[4,5] We now find that the increment in substituting Me for H in the 8- and 8′-positions in 1,1′-binaphthyl is only about 5 kcal. mole^{-1}; the smallness of this figure we attribute to the ground-state distortion in the 8,8′-dimethyl-1,1′-binaphthyl molecule in comparison with 1,1′-binaphthyl itself, and to the availability of the mesoid racemisation path. On the increment basis we should predict that the value of E_{rac} for 2,2′-dimethyl-1,1′-binaphthyl would be of the order of 37—40 kcal. mole^{-1}; this value is not yet known.

Recently, Newman and his co-workers,[10] using heats of combustion, have estimated strain energies in the ground state of certain overcrowded molecules containing methyl

---

* Professor Mislow has pointed out (personal communication, October 1964) that had we used an alternative value for the energy barrier for biphenyl itself, 0·5 kcal. mole^{-1} (F. J. Adrian, *J. Chem. Phys.*, 1958, **28**, 608), these figures would have been 18·5 and 17 kcal. mole^{-1}, and the contrast between the binaphthyl and the biphenyl increments have been still more striking. Professor Mislow and his co-workers (K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 1733) compute 19 kcal. mole^{-1} as the energy increment when two methyl groups replace two hydrogen atoms in blocking positions in 9,10-dihydrophenanthrene; this case is not strictly comparable with the present one in which methyl is passing hydrogen (as we suppose) on two sides of the molecule.

† A recent publication (L. Melander and R. E. Carter, *Acta Chem. Scand.*, 1964, **13**, 1138) gives E_{rac} as 17·91 kcal. mole^{-1} for this racemisation. The reason for the discrepancy between this and the value 19 (18·8 by least-squares calculation, approximated to the nearest integer in consideration of the low optical rotations and the experimental difficulties involved [9]) is not obvious; the difference does not invalidate the present discussion.

[3] Theilacker and Hopp, *Chem. Ber.*, 1959, **92**, 2293.
[4] Cheung King Ling and Harris, *Chem. and Ind.*, 1962, 1378.
[5] Chua Cheung King Ling and Harris, *J.*, 1964, 1825.
[6] Reiger and Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19.
[7] Howlett, *J.*, 1960, 1055.
[8] Maccoll, *Progr. Stereochem.*, 1954, **1**, 365.
[9] Harris and Mitchell, *J.*, 1960, 1905.
[10] Frisch, Barker, Margrave, and Newman, *J. Amer. Chem. Soc.*, 1963, **85**, 2356.

groups attached to aromatic systems; comparison was made between molecules in which the methyl groups were so placed that they contribute to the strain and others in which they do not. The size of their figures seems consistent, on a liberal interpretation, acknowledging that the aromatic frameworks are different, with the estimate previously made [11,1] for the strain imposed by two *peri*-methyl groups on naphthalene, and with our present results.

Attempts are in progress to remedy our ignorance of the direct blocking effect of methyl groups in biphenyl systems and to provide comparison with CO_2H, CO_2Me, and $CH_2{\cdot}OH$ groups in circumstances in which the ground-state strain must be very small.

The synthesis of the new optically active compounds was based upon optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid; treatment of this with diazomethane gives the optically active dimethyl ester.[1] Lithium aluminium hydride reduction of the diester, with control of the time of reaction so as to retain optical activity, yielded mainly 8,8'-bishydroxymethyl-1,1'-binaphthyl (its sign of rotation the reverse of that of the parent ester) together with some 8-hydroxymethyl-8'-methoxycarbonyl-1,1'-binaphthyl, separable by chromatography. Warm hydrobromic acid converted the optically active diol into the optically active bisbromomethylcompound.

Attempts to study the optical stability of the 8,8'-bisbromomethyl-1,1'-binaphthyl (If) were thwarted by the ease with which it decomposed at the temperatures required for racemisation. From it optically active 1,1'-binaphthyl-8,8'-bis(methylenequinolinium) dibromide, (Ik) was made. This compound could not be racemised without decomposition.

It has been reported [12] that replacement of chlorine by the hydroxyl group in 1-(chloromethyl)naphthalene is difficult but that replacement to form ethers is easy. We find that 8,8'-bisbromomethyl-1,1'-binaphthyl is converted immediately and quantitatively into the corresponding diol in aqueous acetone in the presence of silver nitrate. Methanol or ethanol, with silver nitrate, gave the bismethoxymethyl and bisethoxymethyl compounds (Ih) and (Ig).

Treatment of the bisbromomethyl compound with lithium aluminium hydride, a method previously used [13] to prepare methyl naphthalenes, gave 8,8'-dimethyl-1,1'-binaphthyl; racemic and optically active specimens were prepared in this way.

In several of the compounds studied the infrared spectra (in Nujol mull) showed minor but distinct differences between the racemic and optically active forms. For example, the spectrum of (+)- or (—)-1,1'-binaphthyl-8,8'-dicarboxylic acid shows a sharp peak at 5·84 μ which is missing in that of the (±)-compound, where the first peak in the carbonyl region is at 5·98 μ; this may indicate intramolecular hydrogen bonding in the latter and not in the former isomer. The racemic dimethyl ester crystallises in two forms, plates and elongated prisms; these show characteristic differences in the 12—14 μ region; both the (+)-form and the (—)-form show the same spectrum as the (±)-plates in this region. The (±)-bisbromomethyl compound has a band at 13·97 μ which is replaced by one at 14·16 μ in the optically active forms.

(±)-8,8'-Dimethyl-1,1'-binaphthyl shows peaks in the same positions as its (+)- or (—)-modification; nevertheless, (±) mixed with (+) show a substantial melting point depression on admixture.

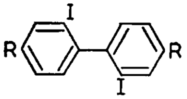
Influence of Remote Substituents on Racemisation Rates.—Some experimental data are available [4,5] for the effect of identical pairs of 4,4'-substituents on the racemisation parameters of 2,2'-di-iodobiphenyl. We have now determined the racemisation parameters for 4,4'-diamino-1,1'-binaphthyl in *NN*-dimethylformamide solution and can compare them with those for other suitably substituted 1,1'-binaphthyls previously determined (Table 2). The trend of influence of polar factors is the same in each series, although the magnitude of the effect varies; electron-donors reduce E_{rac}, electron-attractors increase it.

---

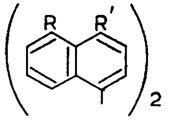
[11] Packer, Vaughan, and Wong, *J. Amer. Chem. Soc.*, 1958, **80**, 905.
[12] Wolthuis and Van der Jagt, *J. Org. Chem.*, 1964, **29**, 963.
[13] Mitchell, Topsom, and Vaughan, *J.*, 1962, 2526.

TABLE 2.

Racemisation in *NN*-dimethylformamide.



R =	NH_2	NH·COMe	H	CO_2H	CO_2Me
$t_{½}^{25°}$ (min.)	5·3	14·5	95	104	104
E_{rac}	19·9	20·6	21·0	21·6	22·3



R =	H	H	CO_2Me	CO_2H
R' =	NH_2	H	H	H
$t_{½}^{50°}$ (min.)	5·8	14·5	101	271·5
E_{rac}	21·9	22·5	23·8	24·1

In each case the change from NH_2 to CO_2Me is accompanied by a rise in E_{rac} amounting to approximately 10% of its total value; this is large enough to warrant consideration when responsibility for experimental racemisation barriers is allocated to various sources; although suggestions have been put forward,[5] * the mode of operation of these remote effects is not fully understood.

EXPERIMENTAL

Optical rotations were measured with a spectropolarimeter (Bellingham and Stanley) and refer to $\lambda = 5461$; the solvent was *NN*-dimethylformamide. Readings for all rate determinations at the lower temperatures were made using a jacketed 2 dcm. tube, with fused end-plates, round which a fast stream of water was passed from a thermostat (Circotherm); for the higher temperatures, portions of a single solution were sealed in glass ampoules, kept in an oil thermostat, and withdrawn at suitable intervals for reading at room temperature. All racemisations were followed to $\alpha = 0°$, and the identity of the recovered (±)-material established by m. p., mixed m. p., and infrared spectra. Values of [α] reported refer to material obtained by synthesis which is chemically purified but not necessarily optically pure.

(±)-8,8'-*Bishydroxymethyl*-1,1'-*binaphthyl* (Ie).—(±)-8,8'-Dimethoxycarbonyl-1,1'-binaphthyl [1] (5 g.; 1M) suspended in sodium-dried ether (1 l.) was added to lithium aluminium hydride (1·5 g.; 3M) and heated under reflux for 4 hr. After decomposition of excess of reagent with wet ether, water, and then dilute sulphuric acid, the ether layer was separated, washed, dried, and the ether removed. Crystallisation from benzene gave the diol in the form of two molecular proportions with one of benzene, m. p. 151—152°; vacuum-drying for 2 hr. at 100° removed the benzene (0·9890 g. lost 0·1063 g. Calc. for $2C_{22}H_{18}O_2,C_6H_6$: 0·1092 g.) leaving the (±)-*diol* (3·9 g.), m. p. 151—152° (Found: C, 83·9; H, 5·7; O, 10·4. $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·8; O, 10·2%). This compound was also prepared by reduction of (±)-8-hydroxymethyl-8'-methoxycarbonyl-1,1'-binaphthyl (Id) (see below).

(−)-8,8'-*Bishydroxymethyl*-1,1'-*binaphthyl*.—This was prepared as above from (+)-8,8'-dimethoxycarbonyl-1,1'-binaphthyl (Ic) (7·5 g., [α] +200°, prepared from dicarboxylic acid, [α] +405°) but heated for only 1½ hr. The (−)-*diol*. (1·4 g.), [α] −32°, had m. p. 147°.

Racemisation in NN-*dimethylformamide solution*.—

Temp. (°c)	95	100	110	120	125	130
10^5k (sec.$^{-1}$)..................	1·57	3·15	7·78	18·5	33·8	44·2
$t_{½}$ (min.)	734	374	148·5	62·6	34·1	26·1

whence E_{rac} = 29·2 kcal. mole^{-1} (graphical), 29·1 (least-squares calculation). The diol recovered after racemisation had m. p., mixed m. p., and infrared spectrum identical with that of the (±) diol. After filtering off the crystalline lævorotatory diol the filtrate was run on to an alumina column and eluted with a benzene–ether mixture. A small amount of 8-hydroxymethyl-8-methoxycarbonyl-1,1'-binaphthyl was collected first, while the remainder, which could not be crystallised (but nevertheless appeared from its infrared spectrum to contain the

---

* Formula (III) on p. 1830 (ref. 5), which refers to this subject, has three errors in printing; the right-hand nitrogen atom should carry a positive charge, the 2-position of the left-hand benzene ring should carry an iodine atom, and the axis of the right-hand benzene ring should not be collinear with the 1,1'-bond.

major part of the diol) was used to prepare (−)-8,8′-bisbromomethyl-1,1′-binaphthyl (see below).

(+)-8,8′-*Bishydroxymethyl*-1,1′-*binaphthyl* (Ie).—This was prepared similarly to the (−)-diol, from the (−)-dimethyl ester (5·0 g.), and gave the (+)-*diol* (0·9 g.), m. p. 142·5—145°, [α] +45°. On racemisation it gave the (±)-diol. (+)-Bisbromomethyl compound was prepared from the residue after crystallising the (+)-diol, as described below.

(±)-8,8′-*Bisbromomethyl*-1,1′-*binaphthyl* (If).—The above (±)-diol (5 g.), dissolved in hot glacial acetic acid, was treated with hot hydrobromic acid (*d* 1·5; 85 c.c.). The (±)-*bisbromomethyl compound* separated quickly as a light yellow crystalline powder and was recrystallised from chloroform, giving 5·7 g. (82%), m. p. 191—192° (taken quickly using an apparatus preheated to 172°; slow heating from room temperatures gives a lower melting point) (Found: C, 60·2; H, 3·6; Br, 36·5. $C_{22}H_{16}Br_2$ requires C, 60·0; H, 3·7; Br, 36·3%). Treatment with silver nitrate of the bromo-compound in aqueous acetone solution regenerated the (±)-diol, m. p. and mixed m. p. 151—152°.

(+)- *and* (−)-8,8′-*Bisbromomethyl*-1,1′-*binaphthyl.*—Treatment of the (−)-diol, [α] −58·6°, with hydrobromic acid as described above gave the (−)-*bisbromomethyl compound*, m. p. 179—182°, [α] −358° (Found: C, 59·3; H, 3·5; Br, 37·1%). The (+)-*compound*, similarly prepared from (+)-diol (0·5 g.), [α] +45°, melted at 179—181° and had [α] +185° (0·45 g.). Attempts to racemise either of these compounds led to their decomposition.

Further quantities of these bromo-compounds, with higher specific rotations, were obtained by treatment of the non-crystalline residues from the crystallisation of the (+)- and the (−)-diols with hydrobromic acid. In this way were obtained the (−)-bisbromomethyl compound (4·5 g.), $[\alpha]^{19}$ −466·6°, m. p. 189—190° (preheated bath), and a similar quantity of the (+)-bisbromomethyl compound, $[\alpha]^{19}$ +470°, m. p. 186° (preheated bath) (Found: Br, 36·3. $C_{22}H_{16}Br_2$ requires Br, 36·3%). It seems that the crystalline optically active diol is less optically pure than the portions which have, so far, resisted crystallisation. In one experiment, the specific rotation of the semi-liquid residue before treatment with hydrobromic acid, was *ca.* −167°.

(±)-8-*Hydroxymethyl*-8′-*methoxycarbonyl*-1,1′-*binaphthyl* (Id).—(±)-8,8′-Bismethoxycarbonyl-1,1′-binaphthyl (5 g.) suspended in dry ether (750 c.c.) was added, with stirring, to lithium aluminium hydride (1 g. suspended in 750 c.c. of ether) and stirred at room temperature for 1 hr. After decomposition in the usual way, the ethereal layer was separated, washed, dried, and the ether removed; the residue was dissolved in benzene, run on to an alumina column, and eluted with 10% ether in benzene; this gave unchanged dimethyl ester (0·2 g.). Elution with ether then gave (±)-8-*hydroxymethyl*-8′-*methoxycarbonyl*-1,1′-*binaphthyl* (2·3 g.), m. p. 122—125° (Found: C, 80·6; H, 5·5; O, 14·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3; O, 14·0%). Further elution of the column with methanol gave (±)-8,8′-bishydroxymethyl-1,1′-binaphthyl, m. p. 151°. Further reduction of (Id) with lithium aluminium hydride gave the (±)-diol, m. p. 151°.

(−)-8-*Hydroxymethyl*-8′-*methoxycarbonyl*-1,1′-*binaphthyl.*—This was prepared as above from (−)-dimethyl ester; the (−)-*ester-alcohol* had $[\alpha]^{17\cdot5}$ −145°, m. p. 128—130°, shrinking at 122°.

Racemisation in NN-*dimethylformamide solution.*

Temp. (°c) ...	55	60	65	69·5	74·5	80	85	89	95
10^5k (sec.$^{-1}$)...	0·59	1·14	2·14	3·40	5·40	11·1	15·6	25·6	46·6
$t_{\frac{1}{2}}$ (min.)	1949	1014	540	339	215	104	74·2	45·2	24·8

whence $E = 25{\cdot}8$ kcal. mole^{-1} (graphical), 25·85 (least-squares calculation).

(±)-8,8′-*Bisethoxymethyl*-1,1′-*binaphthyl* (Ig).—(±)-8,8′-Bisbromomethyl-1,1′-binaphthyl (2·28 g.) was dissolved in boiling ethanol (98%), and aqueous silver nitrate added; the silver bromide precipitate weighed 1·90 g. (calc. for 2 equiv.: 1·94 g.). Evaporation of the solvent followed by crystallisation from benzene and then ethanol gave the *bisethoxymethyl compound* (0·85 g.), m. p. 80—81° (Found: C, 84·45; H, 7·05; O, 8·5. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1; O, 8·6%). This compound was also obtained by boiling the bisbromomethyl compound with alcoholic potash; m. p. and mixed m. p. 80—81°.

(±)-8,8′-*Bismethoxymethyl*-1,1′-*binaphthyl* (Ih).—This was prepared similarly, using methanol in place of ethanol, and dried in a vacuum; the (±)-*bismethoxymethyl compound* melted at 71—73° (Found: C, 84·6; H, 6·4; O, 9·2. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·5; O, 9·3%).

(±)-8-*Bromomethyl*-8′-*methoxycarbonyl*-1,1′-*binaphthyl* (Ii).—8-Hydroxymethyl-8′-methoxycarbonyl-1,1′-binaphthyl (Id) (0·3 g.), treated with hydrobromic acid in hot glacial acetic acid, gave a yellow solid, m. p. 120—124° (0·25 g.); (±)-8-*bromomethyl*-8'-*methoxycarbonyl*-1,1'-*binaphthyl* had m. p. 133—134° (from acetone) (Found: C, 68·5; H, 4·3; Br, 20·8. $C_{23}H_{17}O_2Br_2$ requires C, 68·2; H, 4·2; Br, 19·8%).

(±)-8,8'-*Dimethyl*-1,1'-*binaphthyl* (Ij).—(±)-8,8'-Bisbromomethyl-1,1'-binaphthyl (5 g.; 1M) in sodium-dried ether (500 c.c.) was added, with stirring, to lithium aluminium hydride (1·4 g.; 3·3M) and heated under reflux for 2 hr. Normal working-up gave 3·15 g. (*ca.* 100%), m. p. 123—127°; recrystallisation from ether gave (±)-8,8'-*dimethyl*-1,1'-*binaphthyl*, m. p. 129—130°, in colourless needles (Found: C, 93·5; H, 6·4. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%).

(+)-8,8'-*Dimethyl*-1,1'-*binaphthyl*.—(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl, $[\alpha]^{19}$ +470° (2·0 g.), treated as above, gave (+)-8,8'-*dimethyl*-1,1'-*binaphthyl* (1·3 g.), m. p. 129—130°, $[\alpha]^{17\cdot5}$ +231° (Found: C, 93·3; H, 6·4%).

Racemisation in NN-*dimethylformamide solution.*

Temp. (°c)	100	105	110	115	120	125	130
10^5k (sec.$^{-1}$)	1·50	2·32	3·84	6·08	8·80	13·8	24·3
$t_{\frac{1}{2}}$ (min.)	679	499	301	190	131	83·6	48·2

whence E_{rac} = 27·6 kcal. mole^{-1} (graphical), 27·4 (least-squares calculation).

An approximately equal mixture of the (±)- and the (+)-8,8'-dimethyl-1,1'-binaphthyl melted about 10° lower than either; on successively heating to 200° and cooling, the mixed melting point gradually approached that of the racemic compound.

(−)-8,8'-*Dimethyl*-1,1'-*binaphthyl*.—A similar preparation, starting from (−)-8,8'-bisbromomethyl-1,1'-binaphthyl, $[\alpha]^{21}$ −358°, gave the (−)-*dimethyl compound*, m. p. 129—130° $[\alpha]^{21}$ −207°.

(±)-1,1'-*Binaphthyl*-8,8'-*bis*(*methylenequinolinium*) *Dibromide* (Ik).—(±)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g.) was dissolved in hot quinoline. The needles (1·65 g.) which separated overnight were crystallised from water to give the *bis*(*methylenequinolinium*) *dibromide*, m. p. 178—182° (Found: C, 68·7; H, 4·6; Br, 23·0; N, 3·9. $C_{40}H_{30}Br_2O_2$ requires C, 68·8; H, 4·3; Br, 22·9; N, 4·0%).

(+)-1,1'-*Binaphthyl*-8,8'-*bis*(*methylenequinolinium*) *Dibromide*.—This (0·75 g.) was similarly prepared from the (+)-bisbromomethyl compound (0·5 g.); it had m. p. 212—213°, $[\alpha]^{17}$ +294°. Racemisation could not be followed as the compound decomposes in hot solvents.

Racemisation of 4,4'-*Diamino*-1,1'-*binaphthyl in* NN-*Dimethylformamide Solution*.—The diamine was resolved as previously described.[3]

Temp. (°c)	13·5	16·1	17·95	21·8	25·4	30·4	34·6	40·0
10^4k (sec.$^{-1}$)	2·85	3·92	4·49	7·00	12·4	21·2	35·6	74·4
$t_{\frac{1}{2}}$ (min.)	405	294	257	165	93·1	54·5	32·4	15·5

whence E_{rac} = 21·9 kcal. mole^{-1}, $\log_{10} A = 12\cdot1$, $\Delta F^{\ddagger}$ = 22·8 kcal. mole^{-1}, $\Delta H^{\ddagger}$ = 21·2 kcal. mole^{-1}, $\Delta S^{\ddagger} = -5\cdot0$ e.u.

The authors thank the Central Research Funds Committee of the University of London for a polarimeter, Imperial Chemical Industries Limited for assistance with the cost of analyses, the Pakistani Department of Scientific and Industrial Research for study leave (Y. B.), and the D.S.I.R. for a research grant (M. M. H.). Part of the work on the naphthidine was carried out in the University of Malta (A. S. C.).

BEDFORD COLLEGE, UNIVERSITY OF LONDON,
REGENT'S PARK, LONDON N.W.1.

[*Received, July 3rd,* 1964.]