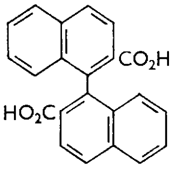
437. *Ground-state Strain and Other Factors Influencing Optical Stability in the* 1,1′-*Binaphthyl Series.*

By Ann S. Cooke (née Mellor) and Margaret M. Harris.

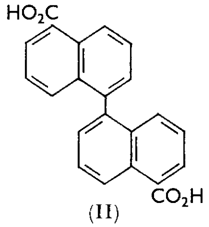
Arrhenius parameters and transition-state theory functions have been calculated from measurements of velocity constants for racemisation, and an explanation is advanced, based on this and other evidence, for the hitherto unexplained order of optical stabilities of 1,1′-binaphthyl-2,2′-, -5,5′- and -8,8′-dicarboxylic acid.

In the biphenyl series ample evidence has accumulated which supports the obstacle theory of optical stability: although there may be modification by other influences, the main factor determining optical stability is the size of the *ortho*-substituents. In the 1,1′-binaphthyl series the effect of blocking groups has been less easy to interpret. More than thirty years ago optically active 1,1′-binaphthyl-8,8′-dicarboxylic acid (III) was prepared almost simultaneously in three schools,[1-3] and the authors of two of the papers[2,3] commented on the surprisingly low optical stability of this acid (half-life 160 min. at 20° in aqueous sodium hydroxide) in comparison with the high stability of 1,1′-binaphthyl-2,2′-dicarboxylic acid (I).[4] Classical models indicate that the steric interference is very similar in acids (I) and (III).

The discovery in 1954 that 1,1′-binaphthyl-5,5′-dicarboxylic acid[5,6] (II), which has no carboxylic acid group in the interfering positions, was of comparable optical stability[7] (half-life 33 min. in 0·1N-sodium hydroxide at 60°) with the 8,8′-acid renewed interest in the problem of the 1,1′-binaphthyl carboxylic acids.



(I)



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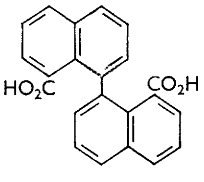

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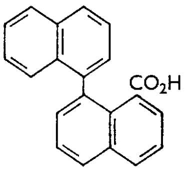

(IV)

The objects of the present work were to synthesise a variety of 1,1′-binaphthyl compounds in the optically active state, to measure their velocity constants for racemisation under similar conditions over a range of temperature, and to calculate Arrhenius parameters and transition-state theory functions for the racemisations; these should provide a basis

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[1] Corbellini, *Atti Accad. Lincei*, 1931, **13**, 702.
[2] Meisenheimer and Beisswenger, *Ber.*, 1932, **65**, 32.
[3] Stanley, *J. Amer. Chem. Soc.*, 1931, **53**, 3104.
[4] Kuhn and Albrecht, *Annalen*, 1928, **465**, 282.
[5] Crawford and Smyth, *Chem. and Ind.*, 1954, 346.
[6] Bell and Morgan, *J.*, 1954, 1716.
[7] Hall, Ridgwell, and Turner, *J.*, 1954, 2498.

for comparison of the various factors contributing to the free energies of racemisation in the different structures. The results are summarised in the Table.

Arrhenius parameters and transition-state theory functions for 1,1′-binaphthyl derivatives.

No.	Substituents				M. p. of (+)- or (−)-form	M. p. of (±)-form	Solvent
	8	8′	5	5′			
1	—	—	—	—	157—159°	145° * 157—159°	H·CO·NMe$_2$
2	—	—	CO$_2$H	CO$_2$H	—	360 †	,,
3	—	—	CO$_2$Me	CO$_2$Me	173—174	—	,,
4	CO$_2$H	—	—	—	227—230	246—248	,,
5	CO$_2$H	CO$_2$H	—	—	320	(304) 322—324	,,
6	CO$_2$H	CO$_2$Et	—	—	199	193—195	,,
7	CO$_2$Me	CO$_2$Me	—	—	123—125	145—147 § 155—157	,,
8	—	—	CO$_2^-$	CO$_2^-$	—	—	Aq. NaOH
9	CO$_2^-$	CO$_2^-$	—	—	—	—	,,
10	CO$_2^-$	CO$_2$Et	—	—	—	—	,,

No.	Temp. range for E	No. of k_s	10^4k_{rac} at 50°	$t_{\frac{1}{2}}$ (min.) at 50°	E_{rac} (kcal. mole^{-1})	$\log_{10} A$ (sec.$^{-1}$)	$\Delta F‡$ (kcal. mole^{-1}) at 50°	$\Delta H‡$ (kcal. mole^{-1})	$\Delta S‡$ (e.u.)
1	31—59°	7	7·94	14·5	22·5	12·1	23·5	21·6	−5·2
2	50—70	3	0·825	271·5	24·1	12·3	25·4	23·5	−5·9
3	49—70	3	1·48	101	23·8	12·2	24·8	23·2	−5·1
4	19—69	11	7·5	15·4	22·4	12·0	23·5	21·8	−5·5
5	14—90	14	2·24	51·5 ¶	22·1	11·3	24·4	21·5	−9·1
6	30—75	10	6·41	18·3	21·6	11·4	23·7	20·95	−8·4
7	30—75	17	4·94	23	22·0	11·6	23·8	21·4	−7·5
8	46—79	8	1·25	94	24·9	12·9	24·8	24·3	−1·5
9	17—52	16	38·5	3	26·0	15·2	22·5	25·4	+9·2
10	40—80	9	3·72	31	25·7	14·0	24·0	25·1	+3·2

* See Badar, Cheung King Ling, and Harris, unpublished work. † With decomp. § See Badar and Harris, unpublished work. ¶ This figure corrects an error by Harris and Mellor, *Chem. and Ind.*, 1961, 257.

It was not necessary to investigate 1,1′-binaphthyl-2,2′-dicarboxylic acid (I) again because Hall and Turner [8] have reported recently that, although it racemises on melting, they did not find it possible to racemise it in a solvent at temperatures at which it did not begin to decompose; it resisted racemisation in *N*-methylformamide at 175°, in boiling tetralin (2 hours), and in 0·1N-sodium hydroxide solution at 100° (10 hours) or 140° (5 hours). The optical stability of this acid can therefore be regarded as by far the greatest in the present series.

The compounds referred to in the Table are 1,1′-binaphthyl itself and derivatives in which it carries substituents in the 5,5′, the 8-, and the 8,8′-positions. All but one had been prepared previously in the racemic state; four of them had also been obtained optically active. Synthetic work is described in the Experimental section, together with the procedure used on this occasion for the resolution or asymmetric transformation of the acids. Optically active methyl esters were made by the action of diazomethane on the optically active acids.

1,1′-Binaphthyl, hitherto unknown in the optically active state, was made by deamination of (+)-4,4′-naphthidine [9] with hypophosphorous acid.[10] As the (+)-naphthidine has a half-life of less than 0·5 hour at 40°, it was necessary to find conditions under which

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

[9] Theilacker and Hopp, *Ber.*, 1959, **92**, 2293.

[10] Harris and Mellor, *Chem. and Ind.*, 1961, 1082.

deamination could be carried out swiftly and without heating. Bell and Morgan[11] had already tried to deaminate a naphthidine for this purpose, but in their experiments, with 2,2′-naphthidine, they obtained dark and indefinite products. The tetrazotised 4,4′-diamine gives a cleaner product which can be purified by chromatography on alumina and then still retains sufficient optical activity to allow measurements of velocity constants for racemisation.

Dimethylformamide was found to be a suitable solvent in which to study the racemisation of all the compounds listed, although in one case (1,1′-binaphthyl-5,5′-dicarboxylic acid) the specific rotation in dimethylformamide was so low that the progress of racemisation in this solvent had to be followed by making each measurement of optical rotation in sodium hydroxide solution. In addition, racemisation of three of the carboxylic acids was followed in aqueous sodium hydroxide solution.

The energy of activation for racemisation, E_{rac}, of the Arrhenius equation $k_{\text{rac}} = A \exp(-E_{\text{rac}}/\boldsymbol{R}T)$, was obtained from the measured racemisation velocity constants both by the graphical method and by least-squares calculation. A is the non-exponential frequency factor. In order to have strictly comparable figures at a single temperature, racemisation velocity constants at 50° were read from the graphs of $\log k_{\text{rac}}$ plotted against the reciprocal of the absolute temperature; 50° is a temperature at which all the compounds could be observed to racemise, although in some cases it is close to the upper or lower limit of accurate measurement.

$\Delta F^{\ddagger}$, the change in standard free energy, was calculated from the absolute reaction rate equation[12] $k_{\text{rac}} = \kappa(\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta F^{\ddagger}/\boldsymbol{R}T)$ in the form $\Delta F^{\ddagger} = 47{\cdot}22T - 4{\cdot}576T/(\log_{10} k_{\text{rac}}/T)$ and is given in the Table for 50°. $\Delta H^{\ddagger}$ was calculated from the relation $\Delta H^{\ddagger} = E - \boldsymbol{R}T$, and $\Delta S^{\ddagger}$ from $k_{\text{rac}} = \kappa(\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta H^{\ddagger}/\boldsymbol{R}T) \exp(\Delta S^{\ddagger}/\boldsymbol{R})$. The transmission coefficient κ was taken to be unity.

DISCUSSION

1,1′-*Binaphthyl*.—It was of particular interest to be able to study the optical stability of this compound as it provides the skeletal framework for the others. Unlike biphenyl, 1,1′-binaphthyl itself, if rotation is restricted, is an asymmetric molecule and is capable of optical activity. Crawford and Smyth[13] have discussed the possibility that optical activity might be observed in 1,1′-binaphthyl in connection with their work on the biquinolyls and bi-isoquinolyls; they have prepared six of these compounds whose structure is based on the 1,1′-binaphthyl pattern, and found that they all show optical activity except for 8,8′-bi-isoquinolyl. The approximate half-life periods in hydrochloric acid solution vary from 2·5 hours to 12 minutes, except for 1,1′-biquinolyl which was observable only as the tartrate dissolved in aqueous hydrochloric acid. Only 4,4′-biquinolyl appears to have optical stability comparable with that of 1,1′-binaphthyl (2·5 hours at room temperature); all the others are less stable. It is difficult to make further, or more detailed, comparisons because it is not known whether the actual racemising species in the biquinolyls and bi-isoquinolyls is or is not protonated. Another compound which is optically labile and closely related, in its transition state for inversion, to 1,1′-binaphthyl is 1,1′-bianthryl,[14] which has a half-life period for racemisation of ~1 hour in boiling chloroform. This result is fairly close to, but somewhat larger than, that now obtained for 1,1′-binaphthyl.

The 1,1′-*Binaphthylcarboxylic Acids*.—(i) *Entropy factors*. One of the possibilities considered at the outset was that a large variation in the values of $\Delta S^{\ddagger}$ might, in some of the compounds, influence the values of $\Delta F^{\ddagger}$ so that the final order was not even

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[11] Bell and Morgan, *J.*, 1950, 1963.

[12] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

[13] Crawford and Smyth, *J.*, 1952, 4133; 1954, 3464.

[14] Bell and Waring, *J.*, 1949, 1579.

approximately that of the E_{rac} (or $\Delta H^{\ddagger}$) values.[15] A collection of experimental information has demonstrated[16] that entropy factors for racemisation of compounds having restricted rotation may vary over as large a range as from $+9{\cdot}2$ e.u. to $-20{\cdot}9$ e.u., corresponding to about 7 kcal. mole^{-1} in $\Delta F^{\ddagger}$. Inspection of the Table shows that for the racemisations in dimethylformamide the entropy factors in the present series vary only to a small degree and not in such a way as could be responsible for the order in which the optical stabilities lie.

(ii) *Activation energy for racemisation.* It is therefore necessary to concentrate on the E_{rac} (or $\Delta H^{\ddagger}$) values in an attempt to explain the relative results. The experimental energy of activation for racemisation by restricted rotation is normally considered to represent the energy barrier which has to be overcome when a molecule passes from the *R*- to the *S*-configuration. That this is reasonable is borne out by the agreement between calculated[17,18] and experimental[19] values of E_{rac} for the racemisation of 2,2′-dibromobiphenyl. However, there are factors in the structure of 2,2′-dibromobiphenyl which may make these findings not wholly representative of all molecules showing restricted rotation; one such factor is that it may not always be as easy to incorporate an acceptable figure for the gain in resonance energy in the transition state,[18] and another is that 2,2′-dibromobiphenyl in the ground state may be relatively strainless (although perhaps not entirely so). In a compound in which these two factors assume significant proportions the experimental E_{rac} will be made up thus:

$$E_{\text{rac}} = E_{\text{ster}} - E_{\text{r}} - E_{\text{gs}},$$

where E_{ster} is the energy due to strain and compression in the transition state, E_{gs} the ground-state energy, and E_{r} is the gain in resonance energy in the transition state.

(iii) E_{r}; *electron availability in the transition state.* The magnitude of E_{r} might be expected to depend on the degree of planarity of the transition state and also on the availability of electrons to the system. If 4,4′-naphthidine,[9] 1,1′-binaphthyl and 1,1′-binaphthyl-5,5′-dicarboxylic acid, being unsubstituted in the 8,8′-positions, had the same ground-state strain, and if the value of E_{ster} were the same for all three, then the differences in E_{rac} (21·4,* 22·5, and 24·1 kcal. mole^{-1}, respectively) might reflect differences in E_{r}. E_{r} would then apparently be greatest for the diamino-compound and least for the dicarboxylic acid, an order corresponding with the order of electron release $NH_2 > H > CO_2H$.

If, on the other hand, E_{r} is insignificantly small, then the differences in E_{rac} must be attributed to differences in E_{ster} and perhaps in E_{gs}. These would be subtle steric differences, due to influences remote from the interfering groups.†

(iv) *Ground-state strain.* Since E_{rac} in the labile acids (II), (III), and (IV) does not vary by more than 3 kcal. mole^{-1}, some new factor which can assume significant proportions must be responsible for the closeness of their stabilities and striking difference from acid (I); it becomes interesting to examine the possibility that ground-state strain could be such a factor.

Optically active molecules which owe their asymmetry to " molecular overcrowding " have sometimes been reported to be more optically labile than would be expected when comparing them with structures, otherwise analogous, in which internal rotation can relieve the strain of overcrowding. Arrhenius parameters and other racemisation data,

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* This figure refers to acetone solution.

† This subject is being studied in the geometrically simpler system of 2,2′-di-iodobiphenyl and the results will shortly be published.

[15] Cagle and Eyring, *J. Amer. Chem. Soc.*, 1951, **73**, 5628.

[16] Hall and Harris, *J.*, 1960, 490.

[17] Westheimer, *J. Chem. Phys.*, 1947, **15**, 252; " Steric Effects in Organic Chemistry," ed. Newman, Wiley, New York, 1956.

[18] Howlett, *J.*, 1960, 1055, and personal communication.

[19] Harris, *Proc. Chem. Soc.*, 1959, 367; Harris and Mitchell, *J.*, 1960, 1905.

apart from some approximate half-lives, are not yet available for a series of such compounds, but several instances of optical lability have been described: for example, for 4,5,8-trimethyl-1-phenanthrylacetic acid,[20] 1,8-diamino-4,5-dimethylbenzocinnoline,[21] and 2,4,5,7-tetramethyl-1,8-phenanthroline.[22] A pertinent case is 3,4:5,6-dibenzophenanthrene-9,10-dicarboxylic acid which is optically labile,[23] whereas (+)-9,10-dihydro-3,4:5,6-dibenzophenanthrene, in which overcrowding is relieved by twisting, is optically stable; [8] the strain in the former can be estimated from the work of Coulson and Senent [24] who calculated the energy of distortion of 3,4:5,6-dibenzophenanthrene itself to be 28 kcal. mole^{-1}. A value for the dihydrodibenzphenanthrene is not yet available, but it is undoubtedly much smaller and is possibly insignificant.

Acids (I—IV) can now be viewed with the possibility of ground-state strain in mind; acid (II) can be considered to be normal, in comparison with 1,1'-binaphthyl itself: acid (I) is understandably more stable than (II): the anomalous members of the series are (III) and (IV); both of these have *peri*-substituted naphthalene residues.

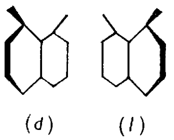
There is reliable evidence for steric repulsion between substituents in the 1,8-positions in naphthalene. Everard and Sutton,[25] from dipole-moment evidence on halogenomethoxynaphthalenes, suggested that in 1,5-dichloro-4,8-dimethoxynaphthalene the bonds to the chlorine atoms and methoxy-groups are displaced from the main plane of the naphthalene nucleus by as much as 18°. *X*-Ray crystallography showed that the 1,8-methyl groups in octamethylnaphthalene are 0·73 Å out of the main plane.[26] This deformation comes about because the two carbon atoms attached in the 1,8-positions in naphthalene on a classical planar model would be only 2·4 Å apart; the distortion (which is taken up in some degree all over the naphthalene system) makes them 2·98 Å apart, a distance generally accepted as tolerable.[27]

Strained Conformation of 8,8'-*Substituted* 1,1'-*Binaphthyls.*—A *peri*-substituted naphthalene unit, with its 1- and 8-bonds directed out of the main plane in opposite directions, can theoretically exist in two diastereoisomeric conformations (V*d*) and (V*l*); junction of these units in pairs leads to three structures, (*dd*), (*ll*), and (*dl*). Each of these structures, by rotation about the 1,1'-bond, can exist in an *R*- and an *S*-configuration. Such a set of six models represents 1,1'-binaphthyl-8,8'-dicarboxylic acid [28] (VI and VII, for example which are drawn near to passing positions). Passage from the *R*- to the *S*-configuration will be by the "*trans*"-route (all the formulæ I, II, III, and IV, VI, and VII are drawn in the "*trans*"-position), 8-CO_2H passing 2'-H, and 8'-CO_2H passing 2-H. Models incorporating the deformation show very much less steric resistance to $R \rightleftarrows S$ inversion than do classical models. [Classical models show very similar resistance to passing for the 2,2'-acid (I) and the 8,8'-acid (III); however, deformation in the ground state is not likely to be large in the 2,2'-acid, where the carbon atom of the CO_2H group is 2·9 Å distant from the 1'-carbon atom: the classical model can be regarded as giving an approximately satisfactory picture of this molecule.]

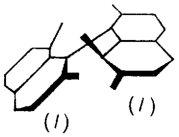
A figure of 7·9 kcal. mole^{-1} has been estimated for the energy due to steric compression in 1,8-dimethylnaphthalene; [29] a compression of a similar kind involving carbon atoms attached in the 1- and the 8-position, occurs twice in 1,1'-binaphthyl-8,8'-dicarboxylic acid. It would perhaps therefore be reasonable to suggest that a lower limit for the ground-state strain energy in this compound is about 15 kcal. mole^{-1}.

[20] Newman and Hussey, *J. Amer. Chem. Soc.*, 1947, **69**, 3023.
[21] Theilacker and Baxman, *Annalen*, 1953, **581**, 117.
[22] Wegner, 1956, reported in ref. 21.
[23] Bell and Waring, *J.*, 1949, 2689.
[24] Coulson and Senent, *J.*, 1955, 1819; Coulson, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publns., London, 1958, p. 61.
[25] Everard and Sutton, *J.*, 1949, 2317.
[26] Donaldson and Robertson, *J.*, 1953, 17.
[27] Harnik and Schmidt, *J.*, 1954, 3295.
[28] Harris and Mellor, *Chem. and Ind.*, 1961, 557.
[29] Packer, Vaughan, and Wong, *J. Amer. Chem. Soc.*, 1958, **80**, 905.

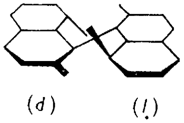
Mesoid and Racemoid Transition Paths.—The graphs drawn by plotting k_{rac} against $1/T$ showed no significant deviations from linearity in all the cases quoted in the Table, over the stated temperature range. In the molecules studied there are, in principle, two obstructions to planarity and therefore two potentially labile and potentially observable causes of molecular asymmetry, *viz.*, restricted rotation about the 1,1′-bond and hindered wagging of interfering groups; evidently the lability of one is in the present observable range and that of the other is not. The unobserved lability must be fast rather than very slow, because the racemisations all proceed to $\alpha = 0°$ with an unchanging velocity constant, within the limits of our experimental observation. It seems most probable that the decline in optical rotation observed polarimetrically represents the change $R \rightleftarrows S$, irrespective of the conformation of the individual halves of the molecule, and that the wagging (*d*) $\rightleftarrows$ (*l*) is too fast to affect the linearity of the Arrhenius plots: nevertheless, it can be significant in the transition path.



(V)



(VI) Racemoid



(VII) Mesoid

Because of the deformations (*d*) and (*l*), three possible "*trans*"-transition paths for rotation about the 1,1′-bond to bring about the $R \rightleftarrows S$ change can be envisaged.[30] Two of these hypothetical paths, $R(dd) \rightleftarrows S(dd)$ or $R(ll) \rightleftarrows S(ll)$, the racemoid ones, are mirror images of each other and have equal energy barriers; in each of them 8-CO_2H passes 2′-H at the same time as 8′-CO_2H passes 2-H; there is a single high energy barrier: these transition states still retain asymmetry. By the remaining path, $R(dl) \rightleftarrows S(dl)$, the mesoid, the two pairs of obstacles are not encountered simultaneously, but one after the other; between the two energy barriers lies an energy minimum representing an intermediate state (VII), the configuration of which is neither *R* nor *S*, nor is it flat; it has a centre of symmetry.

As less energy is required for a mesoid inversion, this will be the path used:

$$\begin{tikzcd}
R(dd) \arrow[r, shift left] & R(dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & R(ll) \arrow[l, shift left] \\
S(dd) \arrow[r, shift left] & S(dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[u, shift left] & S(ll) \arrow[l, shift left]
\end{tikzcd}$$

An energy diagram (Figure) represents the racemoid (*a*) and mesoid (*b*) inversion paths for an 8,8′-disubstituted 1,1′-binaphthyl, with a 2,2′-disubstituted 1,1′-binaphthyl (*c*) for comparison. The diagram is simplified in the sense that it makes no allowance for E_r and it assumes that there is no significant ground-state strain energy in the 2,2′-compound. All the *cis*-inversion paths are impossibly high. E_{gs} represents the ground-state energy for the 8,8′-compound, and E_{rac} measures the observed energy required for racemisation of the 8,8′-acid by the lower, mesoid path, E'_{rac} the energy barrier for the 2,2′-acid.

It seems probable that one of the six conformers is obtained in crystalline form as a result of optical resolution or asymmetric transformation, and racemisation represents the attainment of an equilibrium mixture containing equal concentration of *R*- and *S*-molecules, but an excess of the preferred conformation, racemoid or mesoid, within these two configurations. There are indications that a study of molecular structure in the crystal in the 1,1′-binaphthyl series would yield interesting results: dimethyl 1,1′-binaphthyl-8,8′-dicarboxylate crystallises in two forms,[31] plates, m. p. 145—147°, and

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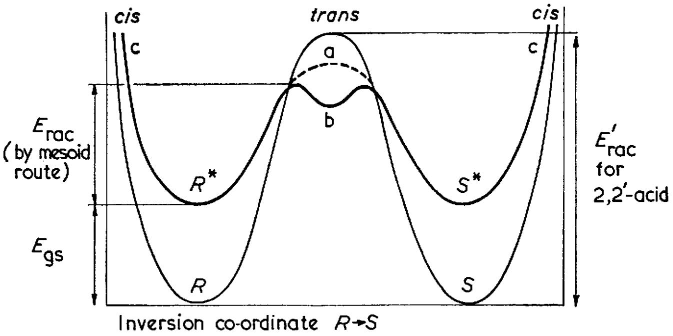
[30] Cheung King Ling and Harris, *Chem. and Ind.*, 1962, 1378.

[31] Badar and Harris, unpublished work.

elongated prisms, m. p. 155—157°; 1,1'-binaphthyl itself shows two crystalline modifications[32] and has been the subject of a preliminary *X*-ray crystallographic investigation;[33] in addition, the wide variation in observed melting points of the 8,8'-acid may be due to the occurrence of different crystalline modifications. It is possible that different conformations of the molecules in the crystals are responsible for some of these results.

Racemisation in Aqueous Sodium Hydroxide.—Nos. 8—10 in the Table show the figures obtained from racemisations carried out in sodium hydroxide solution. Here the $\Delta S^{\ddagger}$ values are positive or only slightly negative. Solvation by water molecules could account for these differences, which are most marked for the 8,8'-acid; if this acid is solvated, in its ionic state, the water molecules must be dropped in order that inversion can take place. E_{rac} for this compound has the high value of 26 kcal. mole^{-1}, but, compensated for by the positive entropy factor, the half-life period (3 min. at 50°) is the lowest of all those recorded here.



Schematic energy diagram representing optical-inversion paths for 1,1'-binaphthyl-2,2'- and -8,8'-dicarboxylic acids.

(a) 1,1'-Binaphthyl-8,8'-dicarboxylic acid, racemoid route.
(b) ,, 8,8'- ,, ,, mesoid ,,
(c) ,, 2,2'- ,, ,, .

* In order to emphasise the main arguments, this diagram is simplified in the following sense: the troughs R^* and S^* have no closely defined meaning on the inversion co-ordinate, except that the configuration is R or S. On the energy co-ordinate, the point R^* represents the energy of the equilibrium mixture $R(dd) \rightleftarrows R(dl) \rightleftarrows R(ll)$ in the ground state. The transition state, at (a), has the conformation (*dd*) or (*ll*); the intermediate, at (b), has the conformation (*dl*), the humps on either side of it are $R(dl)$ and $S(dl)$. Between R^* and the hump $R(dl)$ a molecule which started in the $R(dd)$ or $R(ll)$ form has changed to $R(dl)$ [in order to show this part of the inversion process it would be necessary to introduce a third co-ordinate, to represent the progress of the wagging, and to make assumptions about the relative magnitude of the ground-state energies of (*dd*)- and (*dl*)-molecules.]

In conclusion, a study of this set of compounds provokes speculation regarding the way in which a half-life period for racemisation (the ultimate criterion of optical stability) can be influenced by the steric barrier to restricted rotation, by the gain in resonance energy in the transition state, by the entropy of activation, by the conformation of the transition state, and by the ground-state strain of the molecule. It would be interesting, in this context, to have E_{rac} figures for other molecules, known to be strained in the ground-state in such a way that the strain energy could lower the barrier to racemisation. Another interesting possibility is that in a suitable molecule both

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[32] Badar, Cheung King Ling, and Harris, unpublished work.
[33] Brown, Trotter, and Robertson, *Proc. Chem. Soc.*, 1961, 115.

wagging and $R \rightleftharpoons S$ configurational inversion should be detectable polarimetrically in one system.

EXPERIMENTAL

(±)-Dimethyl 1,1′-binaphthyl-8,8′-dicarboxylate was prepared in a second crystalline *form*: the Ullmann reaction on methyl 8-bromo-1-naphthoate, as previously described,[7] gave a cleaner product when it was carried out below 200°.[31] It crystallised from ethanol in two forms, plates m. p. 145—147° (Found: C, 77·7; H, 4·8; O, 17·2. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9; O, 17·3%), and elongated prisms,[30] m. p. 155—157° (Found: C, 77·9; H, 4·9; O, 16·9%), interconvertible by dissolution and appropriate inoculation.

(+)- *and* (—)-*Dimethyl* 1,1′-*Binaphthyl*-8,8′-*dicarboxylate*.—Finely ground (—)-1,1′-binaphthyl-8,8′-dicarboxylic acid (2·5 g.) was added gradually to cold ethereal diazomethane (0·61 g. in 35 c.c.). Each portion of acid dissolved, with effervescence, and the (—)-*ester* (1·8 g.) separated at the bottom of the flask. It melted at 123—125°, solidified, and re-melted at 157° (Found: C, 77·9; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%). The (+)-ester was prepared similarly from the (+)-acid.

(±)-1,1′-Binaphthyl-8,8′-dicarboxylic acid, prepared by the hydrolysis of the dimethyl ester,[7] melted with decomposition at a point varying between 306° and 324°, depending on the crystallinity of the sample and the rate of heating (previous workers have recorded 304°,[2] 306—307,[3] 300—304°[7]) (Found: C, 77·1; H, 4·1; O, 18·7. Calc. for $C_{24}H_{14}O_4$: C, 77·2; H, 4·1; O, 18·7%).

(+)- and (—)-1,1′-binaphthyl-8,8′-dicarboxylic acid were obtained as brucine salts by the method of Meisenheimer and Beisswenger;[2] brucine (+)-acid, $[\alpha]_{5461}^{21\cdot4}$ —481°, m. p. 260—275° (lit.,[2] $[\alpha]_D$ —395°, m. p. 255—262°); brucine (—)-acid, $[\alpha]_{5461}^{21\cdot4}$ +483°, m. p. 220—250° (lit., $[\alpha]_D$ +377°, m. p. 228—234°). The active acids were obtained by shaking a chloroform solution of the corresponding salt with aqueous sodium hydroxide: the aqueous extract, if washed and freed from traces of chloroform with a stream of nitrogen, could be used directly for observation of racemisation or treated with dilute hydrochloric acid to precipitate the (+)- or the (—)-acid, m. p. 320°.

(±)-Ethyl hydrogen 1,1′-binaphthyl-8,8′-dicarboxylate, m. p. 194—195°, was described by Meisenheimer and Beisswenger,[2] with an analysis of the brucine salt. Repetition by their method gave the *acid ester*, m. p. 193—195° (Found: C, 77·9; H, 4·8; O, 17·2. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9; O, 17·3%).

(—)-Ethyl hydrogen 1,1′-binaphthyl-8,8′-dicarboxylate was obtained by using brucine but by a different procedure from that described.[2] The (±)-acid ester (2·3 g., 1 mol.), dissolved in boiling 2-ethoxyethanol (20 c.c.), was added to brucine (2·6 g., 1 mol.) in the same solvent (5 c.c.). After filtration while hot, hot water (15 c.c.) was added. Slow crystallisation gave a single diastereoisomer (3·9 g., 80%), m. p. 193°, by asymmetric transformation, $[\alpha]_{5461}^{21\cdot4}$ —419° in chloroform containing 2½% of ethanol. The (—)-acid, m. p. 199°, recovered from this salt, had $[\alpha]_{5461}^{17}$ —336·1° in dimethylformamide and is dextrorotatory in aqueous sodium hydroxide.

Methyl 1,1′-binaphthyl-8-carboxylate was prepared in yield improved over that previously described,[2] by an Ullmann reaction between methyl 8-bromo-1-naphthoate (25 g., 1 mol.), 1-iodonaphthalene (24 g., 1 mol.), and copper bronze (50 g.) at 260°; the mixture was heated for 10 min. at 220° after all the copper had been added. Extraction with chloroform, followed by fractional crystallisation from acetone and then from ethanol, gave the ester (3·6 g.), m. p. 118—121° (12%) (Found: C, 84·4; H, 5·3. Calc. for $C_{22}H_{16}O_2$: C, 84·6; H, 5·2%).

This ester was hydrolysed by heating it with 30% alcoholic potassium hydroxide for 15 min., distilling off the alcohol, and heating the residue at 130—140° for a further 15 min. Repeated crystallisation from ethanol gave the (±)-acid, m. p. 246—248° (lit.,[2] 242°) in 56% yield (Found: C, 84·2; H, 4·85; O, 11·2. Calc. for $C_{21}H_{14}O_2$: C, 84·5; H, 4·7; O, 10·7%). The (±)-acid was resolved both through its brucine salt,[2] m. p. 150—155°, $[\alpha]_{5461}^{23}$ —159·2°, and its strychnine salt, m. p. 227—230°, $[\alpha]_{5461}^{23}$ —240°. The (—)-acid recovered from either of these salts had m. p. 227—230°.

(±)-1,1′-Binaphthyl-5,5′-dicarboxylic acid, m. p. 360°, was prepared as described by Hall, Ridgwell, and Turner[7] (Found: C, 77·0; H, 4·1; O, 18·9. Calc. for $C_{22}H_{14}O_4$: C, 77·1; H, 4·2; O, 18·7%).

(+)-1,1'-Binaphthyl-5,5'-dicarboxylic acid, obtained through its brucine salt,[7] had m. p. 367°, $[\alpha]_{5461}^{17}$ +68·8° in dimethylformamide.

(+)-*Dimethyl* 1,1'-*binaphthyl*-5,5'-*dicarboxylate*, prepared by the action of diazomethane on the above (+)-acid, had m. p. 173—174° (Found: C, 77·5; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%).

(+)-1,1'-*Binaphthyl*.—(+)-Naphthidine,[9] m. p. 204—205°, $[\alpha]_{5791}^{20}$ +46·5° in acetone (2 g.), was tetrazotised between −20° and −15° and poured, with stirring, into 20% aqueous hypophosphorous acid (50—100 c.c.) at 0°. After 30 min. the deep yellow precipitate was filtered off and extracted with benzene (200 c.c.); the deep red benzene solution was washed with dilute aqueous sodium hydroxide, dilute hydrochloric acid, and water, then diluted with its own volume of light petroleum (b. p. 40—60°), and run on a column of alumina. The product was eluted with 9 : 1 light petroleum–ether. The solvents were removed from the eluent in a current of air, leaving (+)-1,1'-binaphthyl (0·65 g., 26%), m. p. 157—159°, α_{5791}^{22} 0·682°, $[\alpha]_{5791}^{22}$ +245·3° (c 0·189, l 2).

Racemic 1,1'-binaphthyl, which can be recovered from the solution after racemisation, crystallises in two forms, m. p. 145° and 157—159°.[31]

Polarimetric Work.—Unless otherwise stated, readings were made for the mercury green line, λ = 5461 Å. In all cases a 2-dm., centre-filling, jacketed, polarimeter tube with fused end-plates was used (except for the 1,1'-binaphthyl-8,8'-dicarboxylic acid, for which a similar 1 dm. tube was used). A fast stream of water, pumped from a thermostat-bath (Circotherm) through the jacket, controlled the higher temperatures; for the lower temperatures the apparatus described by Harris and and Mitchell[19] was used. A standard thermometer was fitted into the central opening of the polarimeter tube.

Determinations of k_{rac} were made over as large a range of temperature as was consistent with accurate measurement. The only departure from straightforward observation of undisturbed solutions in the tube was made in the case of 1,1'-binaphthyl-5,5'-dicarboxylic acid which has a low rotation in dimethylformamide; a concentrated solution in dimethylformamide was sealed in ampoules in 5 c.c. portions and kept in a thermostat-bath. Ampoules were removed at suitable times and cooled quickly, the solution was shaken with 0·1N-sodium hydroxide (15 c.c.), and the rotation of the aqueous solution was measured at 15°.

Accurate determination of the specific rotation of optically labile compounds is not possible: extrapolation of measured rotations to zero time is meaningful only if the substance under investigation dissolves instantaneously in the solvent at the required temperature.

Solvents.—Chloroform used when measuring the rotation of alkaloidal salts contained 2½% of ethanol by volume; dimethylformamide was purchased from British Drug Houses Ltd., and had n_D^{20} = 1·4280; aqueous sodium hydroxide was 0·1N and, when used, was always present in sufficient quantity to make the full sodium salt of the acid under investigation.

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BEDFORD COLLEGE, LONDON, N.W.1.

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