Optical Activity in 1-*Phenylnaphthalene*-2′-*carboxylic Acid and Related Compounds.*

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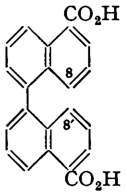
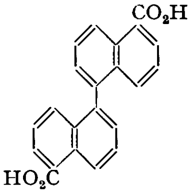
1-Phenylnaphthalene-2′-carboxylic acid and -2′ : 8-dicarboxylic acid have been obtained optically active. The active acids racemise in " B.P. " chloroform solution at 20° with half-life periods of 2 and 60 minutes respectively. The salts of these acids can undergo first- and second-order asymmetric transformations. The racemisation rates of 1 : 1′-dinaphthyl-5 : 5′- and -8 : 8′-dicarboxylic acid in aqueous sodium hydroxide solution have been compared.

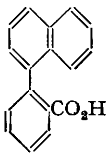
Diphenic acid undergoes rapid optical activation at —30° in chloroform solution in the presence of (+)-nor-ψ-ephedrine (Lesslie, Turner, and Winton, *J.*, 1951, 257), but the free acid has never been obtained optically active. Bell, Morgan, and Smyth (*Chem. and Ind.*, 1951, 634) recorded the isolation of optically active 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid (I*a* and I*b*) with $[\alpha]_D$ +66° in 0·1N-sodium hydroxide. The activity was said to be lost when the solution " was boiled for an hour." The relatively high optical stability suggested by this statement is surprising, since, although the 8- and the 8′-carbon atom clearly cannot pass each other without great distortion of the main structure (I*a*), very little interference would hitherto have been expected between the hydrogen atoms in the 2- and 8′- or in the 2′- and 8-positions (I*b*). Bell and his co-workers (*loc. cit.*; Crawford and Smyth, *J.*, 1952, 4133) also obtained 4 : 4′-diquinolyl and 5 : 5′-diquinolyl in optically active but evidently less optically stable forms. They associated the optical activity observed in these three compounds with steric interaction between the van der Waals envelopes of the 2- and the 8′-hydrogen atom.



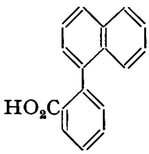
(I*a*)



(I*b*)



(II*a*)



(II*b*)

In order to obtain a more quantitative assessment of the optical stability of 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid, we have examined the acid in some detail. A brucine salt was obtained from aqueous 2-ethoxyethanol, and gave rise to an active acid with a half-life of 33 minutes in 0·1N-sodium hydroxide, at 60°.

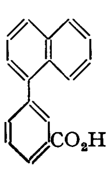
An acid intermediate between diphenic acid and 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid might be expected to be capable of exhibiting optical activity. Such an acid, 1-phenylnaphthalene-2′-carboxylic acid (II*a* and *b*) has been examined. In acetone solution, second-order asymmetric transformation was realised with cinchonidine and with brucine. The brucine (+)-acid salt had a half-life of 0·6 minute in chloroform solution at 20° and yielded optically active (+)-1-phenylnaphthalene-2′-carboxylic acid which had a half-life of 2 minutes in chloroform solution at 20°. Optical activation of the (±)-acid was observed in presence of three alkaloids in chloroform solution; with brucine the value for *k* of first-order asymmetric transformation was the same as that for the mutarotation of the salt obtained by second-order asymmetric transformation. The acid was activated by cinchonidine in chloroform but not in acetone solution.

For one position of the phenyl nucleus (as in II*a*), rotation about the 1 : 1′-bond is effectively prevented by interference between the carboxyl group and the 8-CH grouping. In the other position (as in II*b*), however, hindrance to rotation arises from the slight overlap of the 2′- and the 8-hydrogen atoms. The present results therefore support the assumption that hydrogen atoms are capable of impeding free rotation when they are attached to an aromatic nucleus.

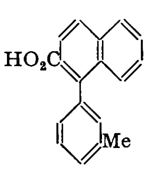
In order to investigate some of the limits of this effect, we examined 1-phenylnaphthalene-3′-carboxylic acid (III) and 3′-methyl-1-phenylnaphthalene-2-carboxylic acid (IV), in both of which the maximum blocking is provided by the slight overlap of the 2′- (or 6′-) and the 8-hydrogen atoms. With neither acid could evidence of optical activity be obtained, either by " addition curve " technique (Jamison and Turner, *J.*, 1938, **1646**; 1940, **264**) or by the achievement of a second-order asymmetric transformation. It may be noted that although (IV) appears similar to (II*b*), there is no position of (IV) comparable to (II*a*), in which passing of the *ortho*-groups is effectively prevented.

Evidently, therefore, in the series now under discussion, interference between the two nuclear hydrogen atoms, *without supporting collisions between other groups* in the molecule, does not hinder rotation about the 1 : 1′-bond sufficiently to give rise to observable optical activity.

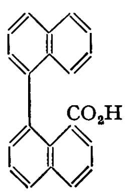
A comparative study of the relative optical stabilities of 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid (I*a* and I*b*), 1 : 1′-dinaphthyl-8-carboxylic acid (V), and 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid (VI) reveals an apparent anomaly. Meisenheimer and Beisswenger (*Ber.*, 1932, **65**, 32) resolved (V) and (VI) and determined the rates of racemisation of the acids in aqueous sodium hydroxide solution (see also Stanley, *J. Amer. Chem. Soc.*, 1931, **53**, 3104). The half-life periods found were : (V) 15 hours at 20° and (VI) 160 minutes at 20°, so that the order of stabilities appears to be (V) > (I) > (VI). [The half-life of (I) at 20° is not known, but an estimation from the value at 60° indicates that it will be between 300 and 700 minutes.] This order seemed to be contrary to expectation, and we therefore reinvestigated (VI) : our results agree closely with those of Meisenheimer. The order is no longer anomalous, however, if the stability of the monoethyl ester of (VI) is considered. Meisenheimer showed this compound to possess a half-life of 28 hours in aqueous sodium hydroxide at 18°. We thus have for stability order : Monoethyl ester of (VI) > (V) > (I). It appears to follow that the relatively low optical stability of the disodium salt of (VI) is due to the presence in the molecule of the two charged carboxylate ion groups in blocking positions. Even so, it is difficult to see why (VI) or its monoethyl ester should racemise at all readily. It appears from models that the considerable interference with free rotation about the 1 : 1′-bond in 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid is similar to that in 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid. But the latter compound is highly optically stable. Kuhn and Albrecht (*Annalen*, 1928, **465**, 282) failed to racemise it on heating a solution in aqueous sodium hydroxide solution for $4\frac{1}{2}$ hours on a boiling water-bath; we resolved the acid for another purpose (Hall and Turner, *Chem. and Ind.*, 1953, 1177) and confirmed this result. The rotation of the acid was unchanged after boiling in 0·1N-sodium hydroxide for 10 hours, followed by heating at 140° in a sealed tube for 5 hours.



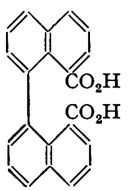
(III)



(IV)



(V)



(VI)

Attention may be drawn to the fact that certain active substituted diphenic acids are known for which the rates of racemisation in aqueous sodium hydroxide are greater than those in an organic solvent. Stanley, McMahon, and Adams (*J. Amer. Chem. Soc.*, 1933, **55**, 706) observed that 6 : 6′-dimethoxydiphenic acid (VII) racemised in boiling sodium ethoxide solution with a half-life of 11 hours, and in boiling 0·1N-sodium hydroxide with a half-life of 7 hours 50 minutes, whilst in boiling ethyl alcohol the half-life was 61·5 hours. Adams and Hale (*ibid.*, 1939, **61**, 2825) recorded that whilst 6-nitrodiphenic acid (VIII) racemised in boiling 0·1N-sodium hydroxide with a half-life of 4·6 minutes, the half-life of the acid in boiling *n*-butyl alcohol was 101 or 107 minutes.

We have also examined 1-phenylnaphthalene-2′ : 8-dicarboxylic acid (IX*a* and *b*). The brucine salt of this acid underwent first-order asymmetric transformation in chloroform solution at 20°. With two molecules of brucine to one of acid the rate of equilibration was considerably faster than with one molecule of each. Second-order transformation in benzene solution gave a monobrucine (+)-acid salt (even when two equivalents of brucine were used), having a half-life of 460 minutes in chloroform solution at 20°. Racemisation of the free (+)-acid was observed in chloroform solution at 20° ; the rate of racemisation was very sensitive to the presence of small quantities of ethyl alcohol, and half-life periods of 35 minutes (most alcohol), 60 minutes, and 220 minutes (least alcohol) were observed. This acid is thus intermediate in optical stability between 1-phenylnaphthalene-2′-carboxylic acid and 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid. It was not possible to observe racemisation in alkaline solution. The sodium salt is sparingly soluble and the acid dissolves so slowly in aqueous potassium hydroxide solution that polarimetric readings could not be taken until 15 minutes after wetting, by which time racemisation was complete. This result indicates qualitatively, however, that, as with (VI), the anion racemises faster than the free acid.

FIG. 1.

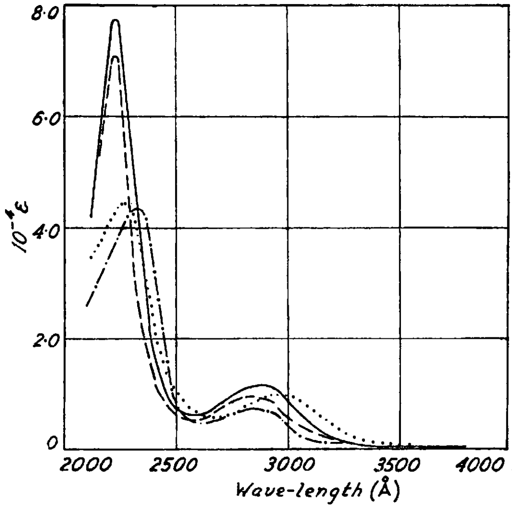


FIG. 2.

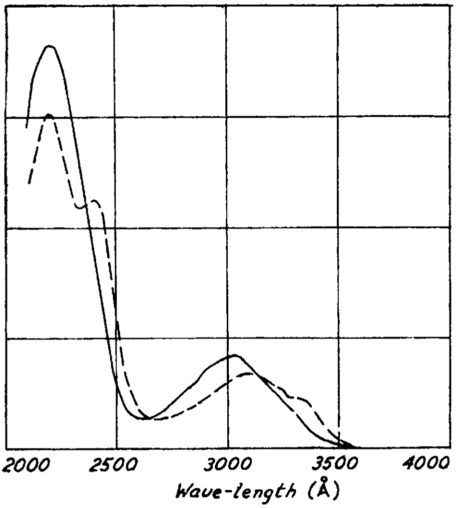


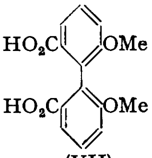
FIG. 1. ———————— 1-*Phenylnaphthalene*-3′-*carboxylic acid* (III).
— — — — — 1-*Phenylnaphthalene*-2′-*carboxylic acid* (II).
— · — · — 3′-*Methyl*-1-*phenylnaphthalene*-2-*carboxylic acid* (IV).
. . . . 1-*Phenylnaphthalene*-2′ : 8-*dicarboxylic acid* (IX).

FIG. 2. ———————— 1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic acid* (I).
— — — — — 1 : 1′-*Dinaphthyl*-8 : 8′-*dicarboxylic acid* (VI).

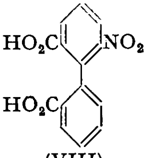
Ultra-violet absorption spectra.

	Short-wave band				Long-wave band	
Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
(I)	2216	74,000	2602	4800	3022	16,500
(VI)	2195	60,000	2675	4800	3092	13,800
	2395	44,500	—	—	3320	9,400
(II)	2225	68,500	2560	5100	2835	9,200
(III)	2230	77,500	2555	5400	2890	11,100
(IV)	2325	43,000	2600	3750	2840	6,800
(IX)	2262	43,500	2672	4900	2987	9,300

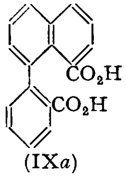
The ultra-violet absorption spectra of the acids (I—IV, VI, and IX) have been measured in 96% ethanol and the main features are recorded in the Table and in Figs. 1 and 2. The spectra of compounds (I) and (VI) differ from the spectrum of 1 : 1′-dinaphthyl, and those of (II), (III), and (IX) from that of 1-phenylnaphthalene to extents which are, in general, consistent with the expected effects of the substituents on the spectra of the parent compounds (Hirshberg and Jones, *Canad. J. Res.*, 1949, **27**, *B*, 437) and on the steric hindrance to coplanarity across the 1 : 1′-bonds (Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199). The low band intensities and the short-wave shift of the long-wave band in the spectrum of (IV) appear to be anomalous. There is a poor correlation between the relative degrees of conjugation across the 1 : 1′-bond, as inferred from the spectra, and the relative optical stabilities of the active isomers. The latter seem to be determined by the gross steric hindrance to coplanarity across the 1 : 1′-bond, in terms of the number and location of the adjacent substituent groups. The secondary effects of the substituents on the conjugation, and hence on the length of this bond, do not appear to have any further influence on the ease of rotation about it. This conclusion is contrary to the view taken by Calvin (*J. Org. Chem.*, 1939, **4**, 256) who has suggested that the shortening of the 1 : 1′-bond in diphenyls by resonance interaction of the appropriate 4 : 4′-substituents may be an important factor in determining optical stability. The lack of correlation between the spectra and optical stabilities of our compounds may perhaps be associated with the possibility that some of the compounds have non-coplanar ground states and coplanar excited stated (cf. Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117), so that the substituents affect the spectra by altering the transition probabilities for the excited states and have little influence on the ground states.



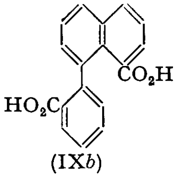
(VII)



(VIII)



(IX*a*)



(IX*b*)

It may be pointed out that the interpretation of the spectra is almost certainly complicated by the sensitivity of the long-wave fine-structure to the state of ionisation of the carboxyl groups. Detailed studies of this effect and spectrophotometric measurements of p*K*'s are envisaged. The results should provide additional evidence on the coplanarity or otherwise of the carboxyl groups with the aromatic rings to which they are attached.

EXPERIMENTAL

In all polarimetric observations $l = 2$ unless otherwise stated.

5-*Amino*-1-*naphthoic Acid*.—This was prepared as described by Ekstrand (*J. pr. Chem.*, 1888, **38**, 241). More precise conditions for the nitration of 1-naphthoic acid were worked out. Finely ground 1-naphthoic acid (90 g.) was added gradually with stirring to nitric acid (*d* 1·42; 600 c.c.) at 80° and heating continued for a further ½ hr. The cooled solution was poured on ice, and a small quantity of 1-nitronaphthalene removed by treating the product with sodium carbonate solution and reprecipitating the mixed 5- and 8-nitronaphthoic acids. Two recrystallisations from ethanol gave 5-nitro-1-naphthoic acid (20 g., 16%) with m. p. 238—239°.

1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic Acid* (I).—This was prepared from 5-amino- *via* 5-iodo-1-naphthoic acid as described by Seer and Scholl (*Annalen*, 1913, **398**, 82). After the methyl ester had been heated with copper bronze in an atmosphere of carbon dioxide the mixture was extracted whilst hot with *o*-dichlorobenzene, and the crude ester was hydrolysed. 1 : 1′-Dinaphthyl-5 : 5′-dicarboxylic acid, crystallised twice from ethanol, had m. p. 358° (block) (50% yield).

Brucine Salt of (+)-1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic Acid*.—The acid (0·684 g., 1 mol.) and anhydrous brucine (1·576 g., 2 mols.) were dissolved in boiling 2-ethoxyethanol (40 c.c.), and hot water (80 c.c.) was added. The solution was boiled and cooled. It deposited prisms (1·29 g., 58% of total solid). From the re-heated mother-liquor a further 0·32 g. was obtained by the addition of water.

(+)-1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic Acid*.—The first crop of salt was ground with hydrochloric acid and dissolved in 0·1N-sodium hydroxide, and the solution was shaken with chloroform to remove traces of brucine. The solution had α^{20}_{5461} +0·51°. Its concentration was determined by precipitation of the acid from a known volume; the acid was thus found to have $[\alpha]^{20}_{5461}$

+27·2° (*c*, 0·8260 in 0·1N-sodium hydroxide). Racemisation at 60° gave k = 0·024 min.$^{-1}$. Similar treatment of the second crop gave acid with $[\alpha]^{20}_{5461}$ +56·1° (*c*, 0·3210 in 0·1N-sodium hydroxide), k for racemisation at 60°, 0·020 min.$^{-1}$.

In a second series of experiments, crystallisation of the brucine salt was brought about at 80° by gradual addition of water to a solution in 2-ethoxyethanol. The first crop (45·5% of total solid) had $[\alpha]^{20}_{5461}$ −16·3° in $CHCl_3$ and gave an acid with $[\alpha]^{20}_{5461}$ +56·6° in 0·1N-sodium hydroxide. A second crop (33·4% of total solid) was obtained by adding more water at 80° and allowing the solution to cool. It had $[\alpha]^{20}_{5461}$ −23·1° in chloroform and gave an acid with $[\alpha]^{20}_{5461}$ +45·3° in 0·1N-sodium hydroxide. For these two acids the rate constants of racemisation at 60° in 0·1N-sodium hydroxide were, respectively, k = 0·019 and 0·020 min.$^{-1}$.

The average value of k from all these racemisations is 0·020 min.$^{-1}$, whence half-life = 33 min.

1-*Phenylnaphthalene*-2′-*carboxylic Acid* (II).—This was prepared by heating a mixture of 1-iodonaphthalene, methyl *o*-iodobenzoate, and copper bronze and hydrolysing the product (Baddar and Warren, *J.*, 1938, 401). The acid had m. p. 159·5—161°.

Second-order Asymmetric Transformation of Brucine Salt.—1-Phenylnaphthalene-2′-carboxylic acid (1·5081 g., 1 mol.) and anhydrous brucine (2·5100 g., 1 mol.) were dissolved together in 100 c.c. of boiling acetone. The solution was filtered hot and the filtrate evaporated to about 30 c.c. The crystalline material which separated was filtered, washed with acetone, and dried in a vacuum [yield 3·66 g., representing 91% of the total solids originally taken; m. p. 105° (decomp.)].

The mutarotation of the brucine (+)-acid salt was twice followed in " B.P. " chloroform at 20°. Readings were started (1) 1·75 min. and (2) 2·1 min. respectively after wetting of the solids with solvent.

Experiment (1).

Time after wetting with solvent (min.)	1·75	2·2	2·7	3·3	4·1	4·75	12·0	∞
α^{20}_{5461}	+0·03	−0·10	−0·20	−0·26	−0·30	−0·31	−0·32	−0·32
k (min.$^{-1}$)	—	1·03	1·13	1·14	1·22	1·18	—	—

Average k, 1·1 min.$^{-1}$, whence half-life = 0·6 min.

(+)-1-*Phenylnaphthalene*-2′-*carboxylic Acid.*—The brucine (+)-acid salt was ground with excess of formic acid at about 5°. The suspension was poured into a large bulk of ice-cold dilute hydrochloric acid. The precipitated (+)-*acid*, washed and dried in a vacuum, had m. p. 162° (Found: C, 82·15; H, 4·9. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%).

Racemisation of (+)-1-*Phenylnaphthalene*-2′-*carboxylic Acid.*—A solution (20 c.c.) of the acid (0·2130 g.) in " B.P. " chloroform was studied at 20° on two separate occasions. k found: (1) 0·355, (2) 0·36 min.$^{-1}$, whence average half-life = 2·0 min.

Second-order Asymmetric Transformation of Cinchonidine Salt.—The acid (0·2462 g., 1 mol.) and cinchonidine (0·2942 g., 1 mol.) were dissolved together in 2·5 c.c. of boiling acetone. The (filtered) solution deposited 0·425 g. of *salt* (77% of total), m. p. 148—150° (decomp.) (Found: C, 79·7; H, 6·3. $C_{36}H_{34}O_3N_2$ requires C, 79·0; H, 6·3%). The mutarotation of the salt was followed in chloroform solution at 20°. The observed angle changed from 5·07° to 4·33°. k = 1·3 min.$^{-1}$, half-life = 0·5 min.

First-order Asymmetric Transformations.—(a) *With brucine.* A chloroform solution was made up to contain 0·1546 g. (1 mol.) of (±)-acid and 0·2455 g. (1 mol.) of anhydrous brucine in 20 c.c. at 20°. The solution was examined polarimetrically, the first reading being made 1·6 min. after wetting. The observed angle of rotation changed from −0·40° to −0·31° during 4 min. A second experiment gave similar figures, and the log plot of the combined readings gave a value of k approximately equal to the more accurate one derived from the second-order asymmetric transformation.

(b) *With cinchonidine.* A chloroform solution (20 c.c.) containing the (±)-acid (0·1415 g.) and cinchondine (0·1676 g.) was examined at 20°; α^{20}_{5461} changed from +4·18° to +4·32° in about 3 min.

(c) *With quinidine.* A solution (25 c.c.) of the (±)-acid (0·2014 g.) and quinidine (0·2627 g.) in chloroform mutarotated through +0·10°.

1-*Phenylnaphthalene*-3′-*carboxylic Acid* (III).—Copper bronze (27 g., 6 atom-equiv.) was added gradually to a stirred mixture of 1-iodonaphthalene (18·2 g., 1 mol.) and methyl *m*-iodobenzoate (18·8 g., 1 mol.) at 270°. The temperature rose to 300°. After ½ hr. the mixture was allowed to cool to 150° and extracted with hot *o*-dichlorobenzene. After removal of the solvent, the residual oil was hydrolysed by boiling with 10% alcoholic potassium hydroxide (200 c.c.) for

6 hr. The alcohol was removed and the residue extracted with water. After being shaken with benzene, the aqueous extract was acidified, and the precipitated acids were extracted with cold benzene. The benzene was removed, and the residue crystallised four times from methanol. 1-*Phenylnaphthalene*-3′-*carboxylic acid* (3·2 g., 17%) was obtained as prisms, m. p. 185·5—188° (Found : C, 82·2; H, 5·2. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%).

Brucine Salt of 1-*Phenylnaphthalene*-3′-*carboxylic Acid*.—The acid (0·1000 g., 1 mol.) and anhydrous brucine (0·1184 g., 1 mol.) were dissolved in boiling *cyclo*hexane (80 c.c.). The cooled solution deposited the *salt* (0·2000 g.), m. p. 144° (decomp.) (Found : C, 74·5; H, 6·5; N, 4·0. $C_{40}H_{38}O_6N_2$ requires C, 74·8; H, 6·0; N, 4·4%). The salt showed no mutarotation at 5° in chloroform solution, and on decomposition gave an inactive acid.

3′-*Methyl*-1-*phenylnaphthalene*-2-*carboxylic Acid* (IV).—This was prepared by heating *m*-iodotoluene and methyl 1-bromo-2-naphthoate with copper bronze (Baddar and Gindy, *J.*, 1948, 1231). After hydrolysis and partial separation of the product, the acid was esterified with methanol and hydrogen chloride (Baddar and Gindy used diazomethane), and the ester distilled. The fraction boiling at 187—195°/4 mm. was hydrolysed and the 3′-methyl-1-phenylnaphthalene-2-carboxylic acid crystallised from aqueous ethanol.

Brucine Salt of 3′-*Methyl*-1-*phenylnaphthalene*-2-*carboxylic Acid*.—The acid (0·3000 g., 1 mol.) and anhydrous brucine (0·4506 g., 1 mol.) were dissolved together in boiling acetone (40 c.c.), and ether (80 c.c.) was added. The cooled solution deposited the *salt* (0·5517 g.), m. p. 198° (Found : C, 74·4; H, 6·25; N, 4·0. $C_{41}H_{40}O_6N_2$ requires C, 75·0; H, 6·1; N, 4·3%). The salt showed no mutarotation at 5° in chloroform solution, and on decomposition gave an inactive acid.

1 : 1′-*Dinaphthyl*-8 : 8′-*dicarboxylic Acid* (VI).—Methyl 8-bromo-1-naphthoate was prepared from 8-bromo-1-naphthoic acid (Rule, Pursell, and Brown, *J.*, 1934, 168) *via* the acid chloride. It had m. p. 35—37°. Rule and Barnett (*J.*, 1932, 175) give m. p. 33°. By heating this ester with copper bronze at 300° for ½ hr. and extracting the resulting mixture in a Soxhlet apparatus with acetone, *methyl* 1 : 1′-*dinaphthyl*-8 : 8′-*dicarboxylate* (50%), m. p. 155—159°, was obtained (Found : C, 77·8; H, 5·2. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%). Hydrolysis of the ester with solid potassium hydroxide gave 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid, m. p. 300—304°. (Meisenheimer and Beisswenger, *loc. cit.*, used ethyl 8-chloro-1-naphthoate.)

Optical Resolution of 1 : 1′-*Dinaphthyl*-8 : 8′-*dicarboxylic Acid*.—This was carried out on lines similar to those described by Meisenheimer and Beisswenger (*loc. cit.*) and the racemisation of the active acids followed in 0·1N-sodium hydroxide at 20°. *k* for (−)-acid was : (1) 0·0043 min.$^{-1}$, (2) 0·0042 min.$^{-1}$. *k* for (+)-acid was: (1) 0·0040 min.$^{-1}$, (2) 0·0044 min.$^{-1}$, whence half-life is 165 min.

1-*Phenylnaphthalene*-2′ : 8-*dicarboxylic Acid* (IX).—This was prepared by the general method described by Rule, Pursell, and Barnett, *J.*, 1935, 751.

First-order Asymmetric Transformations with Brucine : Acid–Base Ratio 1 : 1.—A chloroform solution (20 c.c.) containing acid (0·1000 g.) and anhydrous brucine (0·1347 g.) and 0·5 c.c. of ethyl alcohol was examined polarimetrically at 20° and showed mutarotation from α^{20}_{5461} −0·29° to +0·45°. In two separate experiments, $k =$ 0·0012 and 0·0013 min.$^{-1}$, half-life = 550 min.

Acid–Base Ratio 1 : 2.—A chloroform solution (20 c.c.) containing acid (0·1000 g.), anhydrous brucine (0·2695 g.), and ethyl alcohol (0·5 c.c.) was examined polarimetrically at 20°. In two experiments the observed angle changed from −2·01° (−2·13°) to −1·40° (−1·47°). $k =$ 0·0049 and 0·0049 min.$^{-1}$; half-life = 140 min.

Second-order Asymmetric Transformation.—The acid (0·5000 g., 1 mol.) and anhydrous brucine (0·6735 g., 1 mol.) were dissolved in 150 c.c. of benzene, and the solution was evaporated to 30 c.c. The *salt* obtained (0·9520 g., 75% of total solids) had m. p. 205°, $[\alpha]^{20}_{5461}$ +66° (*c*, 0·500 in $CHCl_3$) (Found : C, 72·4; H, 5·8; N, 4·0. $C_{41}H_{38}O_8N_2$ requires C, 71·7; H, 5·6; N, 4·1%). A solution of the salt (0·1000 g.) and 0·5 c.c. of ethyl alcohol in chloroform was made up to 20 c.c. and examined polarimetrically at 20°. *k* for equilibration in two separate experiments = 0·0015 and 0·0015 min.$^{-1}$, half-life = 460 min.

(+)-1-*Phenylnaphthalene*-2′ : 8-*dicarboxylic Acid*.—The brucine salt was ground with dilute hydrochloric acid, and the liberated acid washed with hydrochloric acid and water and dried. The acid was examined polarimetrically in chloroform solution at 20°. (*a*) A solution (10 c.c.) containing 0·0500 g. of acid was shaken three times with dilute hydrochloric acid and once with water before being examined polarimetrically (1-dm. tube). The low observed angles render the value. for *k* subject to a considerable experimental error. $k \sim$ 0·0030 min.$^{-1}$; half-life = 230 ± 40 min.

(*b*) A similar solution was examined without further washing (*i.e.*, the " B.P." chloroform contained the normal amount of alcohol). The first reading was made 2·5 min. after wetting of the acid solvent and the first observed angle was +0·16° ($l = 1$). $k = 0{\cdot}0115$ min.$^{-1}$; half-life = 60 ± 8 min.

(*c*) 0·1000 g. of acid and 0·5 c.c. of ethyl alcohol were dissolved in chloroform and the volume made up to 20 c.c. The first reading (4·5 min. after wetting) was +0·35°. $k = 0{\cdot}020$ min.$^{-1}$; half-life = 35 ± 2 min.

Absorption Spectra.—Spectra were determined in 96% ethanol (1·25 × 10^{-5}M-solutions) on a Unicam S.P. 500 Spectrophotometer.

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