# *The Optical Resolution of* 1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic Acid.*

By F. Bell and W. H. D. Morgan.

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1 : 1′-Dinaphthyl-5 : 5′-dicarboxylic acid has been resolved into optically active forms; the mechanism of racemisation is discussed.

Since 1 : 1′-dianthryl can be obtained in optically active forms of moderate stability (Bell and Waring, *J.*, 1949, 1579) it would be expected that 1 : 1′-dinaphthyl, also, could exist in optically active forms, although possibly of lower stability.

Attempts to resolve 4 : 4′-diamino-1 : 1′-dinaphthyl and 1 : 1′-dinaphthyl-4 : 4′-dicarboxylic acid yielded negative results (Bell and Morgan, *J.*, 1950, 1963) and attention was next directed to 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid. The bromine atom of ethyl

5-bromo-1-naphthoate, easily obtained from 1-nitronaphthalene, did not react with copper at 280°, and an Ullmann reaction with 5-bromo-1-nitronaphthalene required a temperature so high for initiation that decompostion ensued. The acid was obtained from 1-naphthoic acid by Seer and Scholl's method (*Annalen*, 1913, **398**, 83) and from 1-nitronaphthalene by that of Short and Wang (*J.*, 1950, 992), and independent resolution experiments were made on the two samples.

Experiments with quinidine, quinine, cinchonine, cinchonidine, and morphine failed, probably owing to the high solubilities of the salts. However, brucine gave a less soluble salt of the (+)-acid. The rotations of solutions of the partially active (+)- and (—)-acids in dilute aqueous sodium hydroxide were sensibly unchanged overnight but were reduced to zero by heating on a steam-bath for 1 hour. The optical stability of this substituted 1 : 1′-dinaphthyl appears to be of the same order as that of 1 : 1′-dianthryl and, rather surprisingly, also of 1 : 1′-dinaphthyl-8-carboxylic and -8 : 8′-dicarboxylic acid (Stanley, *J. Amer. Chem. Soc.*, 1931, **53**, 3104; Corbellini, *Atti R. Accad. Lincei*, 1931, **13**, 702; Meisenheimer, *Ber.*, 1932, **65**, 32), but much less than that of 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid (Kuhn and Albrecht, *Annalen*, 1928, **465**, 282) and 2 : 2′-diamino-1 : 1′-dinaphthyl (Kuhn and Goldfinger, *Annalen*, 1929, **470**, 183). Models of the Catalin type indicate that 1 : 1′-dinaphthyl-8-carboxylic and -8 : 8′-dicarboxylic acid, once optically active, should never racemise. Obviously the purely mechanical interpretation of the resolvability of diphenyls is an inadequate guide to racemisation results in this series. Such great distortion of the molecule would be required to allow free rotation about the 1 : 1′-linkage of these acids that it appears more probable that racemisation may be occasioned by a minute dissociation of such dinaphthyls into substituted naphthyl radicals. Such a process would probably be associated with a fairly high energy of activation and would agree with the observed great increase in rate of racemisation with rise of temperature.

Further, the production of a compound such as ethyl 6 : 6′-dinitrodiphenate from ethyl 1-iodo-6-nitrobenzene-2-carboxylate by an Ullmann reaction involves the union of two iodine-free residues in a specifically oriented arrangement and it is difficult to see how this could be achieved if the reaction involved any type of transition complex. Here reaction could most easily be interpreted as a union of free radicals. It must be admitted, however, that none of the reactions of the various dinaphthyls and dianthryls so far recorded in the literature appears to require for their interpretation the existence of free radicals, and, also, we failed to isolate any phenylanthracene from the product of interaction of 9 : 9′-dianthryl with dibenzoyl peroxide.

## EXPERIMENTAL

5-*Nitro*-1-*naphthoic acid*.—(a) *Ekstrand's method* (*J. pr. Chem.*, 1888, **38**, 156). 1-Naphthoic acid (*Org. Synth.*, **11**, 80; the 1-naphthylmagnesium bromide was poured on crushed carbon dioxide; yield, 57%) (87·5 g.) and concentrated nitric acid (230 c.c.) were heated on a steam-bath for 3—4 hr., then poured on ice. The precipitated solid was collected, washed, and extracted with boiling sodium carbonate (70 g.) solution. On acidification of the extract 90 g. of mixed nitro-acids were obtained. Crystallisation from alcohol (630 c.c.) gave, first, the 5-isomer, m. p. 234—235°, as fawn needles. Further small crops were obtained by evaporation and slow cooling (total yield, 18·5 g.).

(b) *Short and Wang's method* (*loc. cit.*). 1-Nitronaphthalene was converted successively into 1-chloromethyl-5-nitronaphthalene, 1-hydroxymethyl-5-nitronaphthalene, and 5-nitro-1-naphthoic acid. Amplification of Ekstrand's description (*loc. cit.*, p. 244) of the reduction of 5-nitro-1-naphthoic acid appears desirable. The nitro-acid (18·5 g.), in a small volume of dilute ammonia solution, was added slowly to a boiling solution of ferrous sulphate (200 g. in 240 c.c. of water). Aqueous ammonia (*d* 0·880; *ca.* 100 c.c.) was added cautiously until the mixture was alkaline as indicated by the precipitate becoming jet black. The mixture was boiled vigorously for 10 min. and then filtered into glacial acetic acid (30 c.c.), pale yellow 5-amino-1-naphthoic acid (12·2 g., 78%), m. p. 212—213°, being precipitated.

5-Amino-1-naphthoic acid was converted as described by Seer and Scholl (*loc. cit.*) into 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid (m. p. 351—355°) which after being boiled with acetic acid had m. p. 361°. The quinine, quinidine, cinchonine, cinchonidine, and morphine salts of this acid were non-crystallising and in solution had a strong green fluorescence.

*Resolution of* 1 : 1′-*Dinaphthyl*-5 : 5′-*dicarboxylic Acid.*—(a) *Acid from* 1-*naphthoic acid.* Brucine (1·77 g., 2 mols.) was added to a suspension of the acid (0·65 g.) in boiling ethanol (65 c.c.). The mixture was refluxed gently for ½ hr., the clear solution first obtained beginning to deposit crystals. After cooling, the insoluble portion (1·7 g.) was filtered off and the filtrate poured into dilute hydrochloric acid. The recovered 1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid, m. p. 355°, had $[\alpha]_D$ −20·4° (*c*, 1·08 in 0·1N-NaOH). The crop of the brucine salt was purified by extraction with boiling ethanol (65 c.c.) and then formed a pale yellow powder, m. p. 210° (decomp.), $[\alpha]_D$ −10·4° (*c*, 2·5 in $CHCl_3$). This was decomposed by trituration with dilute hydrochloric acid to give (+)-1 : 1′-dinaphthyl-5 : 5′-dicarboxylic acid, m. p. 355°, $[\alpha]_D$ +66° (*c*, 1 in 0·1N-NaOH).

(b) *Acid from* 1-*nitronaphthalene* (the authors are indebted to Mr. R. S. Williams for this material). The acid obtained as above from the more soluble salt had $[\alpha]_D$ −55° (*c*, 1 in 0·1N-NaOH). That obtained from the less soluble salt by trituration with dilute hydrochloric and subsequent reprecipitation from solution in sodium hydroxide had $[\alpha]_D$ +41° (*c*, 1·04 in 0·1N-NaOH). Rapid determination of the rotatory power of this acid is difficult because if precipitated from a solution of the sodium salt in the cold the acid separates as a bulky, gelatinous, almost unfilterable mass whilst precipitation near the b. p. adversely affects the rotatory power.

HERIOT-WATT COLLEGE, EDINBURGH.

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