CLVI.—*The Optical Resolution of* 3 : 5-*Dinitro*-6-α-*naphthylbenzoic Acid.*

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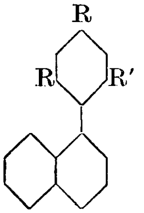
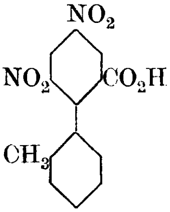
Although 2 : 2′-disubstituted 1 : 1′-dinaphthyl derivatives have been shown to exhibit molecular dissymmetry (compare Kuhn and Albrecht, *Annalen*, 1928, **465**, 282), it has not so far been established that a substituted phenyl-α-naphthyl derivative of type (I) is capable of resolution. We have recently described the resolution of 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acid (II) (J., 1930, 1758), from which it appeared necessary that a compound of type (I) should also exhibit stable dissymmetry.

(I.)





(II.)

When α-iodonaphthalene and ethyl 2-chloro-3 : 5-dinitrobenzoate were heated together in presence of copper-bronze, neither αα′-

dinaphthyl nor ethyl tetranitrodiphenate was formed, the sole product being *ethyl* 3 : 5-*dinitro*-6-α-*naphthylbenzoate* (I; R = R=NO_2, R′ = CO_2Et), which, like the previously described ethyl ester of (II), was difficult to hydrolyse, a fact in accord with its structure.

3 : 5-*Dinitro*-6-α-*naphthylbenzoic acid* was resolved through its brucine salt. The dl-*salt* could be crystallised from water or from ethyl alcohol without undergoing any separation into the two forms, but crystallisation from methyl alcohol effected moderately facile resolution. The less soluble diastereoisomeride was the brucine salt of the d-*acid*, having $[\alpha]_{5791}^{20^\circ}$ + 120·1° in chloroform, the readily soluble salt of the l-*acid* having $[\alpha]_{5791}^{20^\circ}$ − 114·0° in the same solvent. From these two salts were obtained the *d*-acid with $[\alpha]_{5791}^{20^\circ}$ + 63·4°, and the *l*-acid with $[\alpha]_{5791}^{20^\circ}$ − 63·3°, in acetone.

The optical stability of the dinitronaphthylbenzoic acid is considerable. A routine test for the optical stability of acids of the diaryl type has been to heat the alkaline solutions over periods of several hours, and note the racemisation produced. The *l*-form of the acid now described is not sensibly racemised in boiling *N*-sodium hydroxide in 4 hours.

We have, however, also applied a test of optical stability of a new and more drastic kind. The *d*-acid was heated with excess of thionyl chloride, and the d-3 : 5-*dinitro*-6-α-*naphthylbenzoyl chloride* obtained was hydrolysed at 100° with *N*-sodium hydroxide. Even after these two reactions, a virtually pure *d*-acid was obtained.

An attempt to include amide formation and hydrolysis in a second series of experiments failed, since, although the d-*amide* was readily obtained, it could not be hydrolysed.

EXPERIMENTAL.

Ethyl dl-3 : 5-*dinitro*-6-α-*naphthylbenzoate*. A mixture of 10 g. of ethyl 2-chloro-3 : 5-dinitrobenzoate and 10 g. of α-iodonaphthalene was kept at 210°, and 9 g. of copper-bronze were gradually added, with continuous stirring. Interaction proceeded vigorously, and satisfactorily if the temperature was carefully controlled, but above 210° tended to become explosively violent. When no further reaction occurred, the warm mixture was extracted with *o*-dichlorobenzene, most of the latter removed by distillation, and the residual solution treated with light petroleum (b. p. 60—80°) until no more crystallisation took place. The crude ester (7 g.) crystallised from aqueous alcohol in small yellow needles, m p. 109—110° (Found : C, 62·3; H, 4·1. $C_{19}H_{14}O_6N_2$ requires C, 62·3; H, 3·9%).

dl-3 : 5-*Dinitro*-6-α-*naphthylbenzoic acid*. A mixture of 20 g. of the ester, 100 c.c. of water, 200 c.c. of concentrated sulphuric acid, and 400 c.c. of glacial acetic acid was boiled under reflux for 2 hours. When the cooled solution was poured into water, a yellow solid separated, which was dissolved in sodium hydrogen carbonate solution. The filtered solution was treated with hydrochloric acid; the *acid* obtained crystallised from aqueous alcohol in fine, bright yellow needles, m. p. 184—185° (Found: C, 60·1; H, 3·2. $C_{17}H_{10}O_6N_2$ requires C, 60·3; H, 3·0%).

dl-3 : 5-*Dinitro*-6-α-*naphthylbenzamide*. The acid (0·6 g.) was heated with thionyl chloride (10 g.) under reflux on the water-bath. When evolution of hydrogen chloride ceased, the solution was left in a vacuum over soda-lime. The yellow solid obtained was dissolved in benzene and treated with dry ammonia. The filtered solution on evaporation gave the *amide*, which crystallised from benzene–light petroleum (b. p. 60—80°) in very small plates, m. p. 96—97° (Found: N, 12·5. $C_{17}H_{11}O_5N_3$ requires N, 12·5%).

Resolution of 3 : 5-*Dinitro*-6-α-*naphthylbenzoic Acid*.—Preliminary experiments showed that brucine was more satisfactory for this purpose than quinine or strychnine. Recrystallisation of the *dl*-brucine salt from water or ethyl alcohol effected no separation into the diastereoisomerides. Attempted resolution starting with the ammonium salt of the *dl*-acid and brucine sulphate in aqueous solution met with no success. The following method was finally adopted (all rotations were measured in chloroform solutions). When an ethyl-alcoholic solution of the *dl*-acid (7 g.) was added to a solution of brucine (8·5 g.) in the same solvent, almost quantitative precipitation of the brucine *dl*-salt of the acid occurred. It was dissolved in hot methyl alcohol (700 c.c.). The cold solution deposited 7 g. of deep yellow, glassy, square plates which had $[\alpha]_{5791}^{20^\circ}$ + 96·0° (c = 1·000). From the mother-liquor were obtained 2 g. having $[\alpha]_{5791}^{20^\circ}$ + 45·8° (c = 1·09), and after removal of most of the solvent a third fraction (6 g.) was obtained having $[\alpha]_{5791}^{20^\circ}$ − 99·1° (c = 7·22).

Repeated recrystallisations of the first crop from methyl alcohol gave the brucine salt of the *d*-acid (4 g.), having $[\alpha]_{5791}^{20^\circ}$ + 120·1° (c = 0·6310). It crystallised in clumps of small, square, bright yellow plates, and was very sparingly soluble in most solvents, but readily soluble in chloroform.

The pure brucine salt of the *l*-acid (2·3 g.) was similarly obtained by recrystallisation of the third crop from methyl alcohol and had $[\alpha]_{5791}^{20^\circ}$ − 114·0° (c = 0·5220).

On recrystallising from methyl alcohol the middle fraction having $[\alpha]_{5791}^{20^\circ}$ + 45·8°, a small amount of the racemic acid salt was obtained as small yellow needles having $[\alpha]_{5791}^{20^\circ}$ + 3·8° (c = 0·5280).

The free acids were obtained from their brucine salts by adding the calculated amount of *N*-ammonium hydroxide to an aqueous suspension of the salt, together with a little chloroform. The chloroform solution of brucine was then removed, and after two or three extractions of the aqueous layer with chloroform, the free acid was precipitated with dilute hydrochloric acid.

d-3 : 5-*Dinitro*-6-α-*naphthylbenzoic acid* crystallised from aqueous ethyl alcohol in very fine, yellow needles, m. p. 179—180°, and had $[\alpha]_{5791}^{20^\circ}$ + 63·4° in acetone ($l = 2$; $c = 0{\cdot}615$; $\alpha_{5791}^{20^\circ} = +\ 0{\cdot}78^\circ$) (Found : C, 60·2; H, 3·2. $C_{17}H_{10}O_6N_2$ requires C, 60·3; H, 3·0%). It is sparingly soluble in water and in light petroleum, but readily dissolves in alcohol, acetone or benzene.

The sodium salt had $[\alpha]_{5791}^{20^\circ}$ + 67·6° in water ($l = 2$; $c = 0{\cdot}629$; $\alpha_{5791}^{20^\circ}$ + 0·85°), unchanged after 48 hours. When the solution was decomposed with dilute hydrochloric acid, the free acid obtained had $[\alpha]_{5791}^{20^\circ}$ + 63·0° for $c = 0{\cdot}167$ in acetone, showing that no racemisation had occurred.

l-3 : 5-*Dinitro*-6-α-*naphthylbenzoic acid* was similar to its *d*-isomeride. It had $[\alpha]_{5791}^{20^\circ}$ − 63·3° for $c = 0{\cdot}560$ in acetone (Found : C, 60·1; H, 3·2%).

Action of N-*Sodium Hydroxide Solution on the* l-*Acid*.—A solution of 0·1 g. of the *l*-acid in 20 c.c. of *N*-sodium hydroxide solution was heated under reflux on a water-bath for 4 hours. The alkaline solution was acidified with dilute hydrochloric acid, and the free acid dried; it had $[\alpha]_{5791}^{20^\circ}$ − 62·8° for $c = 0{\cdot}3340$ in acetone.

Action of Thionyl Chloride on the d-*Acid*.—The *d*-acid was converted, by the method used for the *dl*-compound, into the *acid chloride*, which crystallised from light petroleum (b. p. 60—80°) in clusters of small, yellow, rectangular plates, m. p. 132—133°. It had $[\alpha]_{5791}^{20^\circ}$ + 42·6° for $c = 0{\cdot}540$ in benzene (Found : N, 7·7. $C_{17}H_9O_5N_2Cl$ requires N, 7·9%).

Action of N-*Sodium Hydroxide Solution on the Acid Chloride*.—0·1 G. of the *d*-acid chloride, heated on the water-bath with 20 c.c. of *N*-sodium hydroxide solution, dissolved after about 10 minutes. Addition of dilute hydrochloric acid precipitated the free acid, which had $[\alpha]_{5791}^{20^\circ}$ + 61·3° for $c = 0{\cdot}286$ in acetone.

d-3 : 5-*Dinitro*-6-α-*naphthylbenzamide*.—The *d*-acid chloride (0·5 g.) was converted as described under the *dl*-compound into the *amide* (0·5 g.), which crystallised from benzene–light petroleum (b. p. 60—80°) in very small, rectangular, yellow needles, m. p. 168—169°, and had $[\alpha]_{5791}^{20^\circ}$ + 38·4° for $c = 0{\cdot}508$ in benzene (Found : N, 12·6. $C_{17}H_{11}O_5N_3$ requires N, 12·5%).

Sodium nitrite (3 mols.) had no action on the amide (1 mol.) dissolved in glacial acetic acid (cold or hot); after 3 days the amide was recovered on addition of water. The amide was also recovered unchanged after being heated with *N*-sodium hydroxide solution or 75% sulphuric acid.

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