

sequently added. The acetylated triphenylmethyl derivative of turanose neutralized 16.8 cc. of decinormal alkali, whereas the value calculated for tri-(triphenylmethyl)-turanose pentaacetate is 15.9.

The triphenylmethyl estimation was carried out by the method of Josephson,¹⁰ 0.1525 g. of substance was dissolved in 0.5 cc. of cold glacial acetic acid and mixed with 0.4 cc. of glacial acetic acid saturated at 0° with hydrogen bromide. After a transitory halochromic coloration due to the formation of a double compound between triphenyl carbinol and hydrogen bromide, triphenylbromomethane separated from the cold liquid. The crystals were collected on a Jena glass filter and washed by means of a pipet with 0.4 cc. of glacial acetic acid. After being dried over solid potassium hydroxide in a vacuum desiccator to constant weight, the triphenylbromomethane formed weighed 0.1088 g., which is 94.13% of the theoretical amount required for tri-(triphenylmethyl)-turanose pentaacetate.

Summary

Two different formulas for both turanose and melezitose are recorded in the literature. Evidence is submitted to show that turanose has three primary alcoholic groups in its molecule in that a tri-(triphenylmethyl)-turanose and its pentaacetate could be prepared. This fact together with certain methylation experiments of former investigators leads to the conclusion that the formulas of turanose (I) and melezitose (III) originally suggested by G. Zemplén and G. Braun should be chosen for these rare compound sugars.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MUNICH
AND THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE RESOLUTION OF 8,8'-DICARBOXY-1,1'-DINAPHTHYL

By W. M. STANLEY¹

RECEIVED MAY 28, 1931

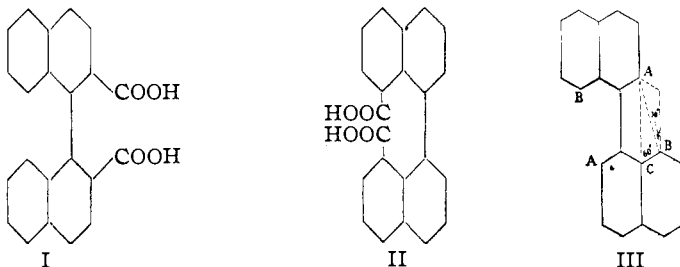
PUBLISHED AUGUST 5, 1931

The resolution of 2,2'-dicarboxy-1,1'-dinaphthyl² (I) demonstrated that the 2,2'-carboxyl groups and the 8,8'-hydrogen atoms are sufficiently large to interfere with each other and thus allow resolution into optical isomers. This indicates that a carboxyl group and a hydrogen atom are large enough to interfere across the space AB (III) which may be calculated as 2.51 Å. by assuming the usual angles in the benzene ring. The fact that this compound was found to be quite stable toward racemization indicates that this interference is fairly large. The compound in which the carboxyl groups and the hydrogen atoms are interchanged, 8,8'-dicarboxy-1,1'-dinaphthyl (II), should also be resolvable, since the 8,8'-carboxyl groups and the 2,2'-hydrogen atoms should interfere across the space AB as in the previous compound, assuming that no additional fac-

¹ National Research Fellow in Chemistry.

² Kuhn and Albrecht, *Ann.*, **464**, 282 (1928).

tors enter the case. This compound (II) is of unusual interest since it may be readily seen that it is an example of an α,α' -disubstituted diphenyl derivative. Although the resolution of α,α' -disubstituted diphenyl derivatives has been predicted,³ attempts at resolution, up to the present time, have been unsuccessful.



In the present investigation 8,8'-dicarboxy-1,1'-dinaphthyl was resolved into its optical isomers by fractionation of the monoquinine salt from benzene. Pyridine solutions of the *d*- and *l*-acids gave $[\alpha]_D^{20} + 198.1^\circ$ and $[\alpha]_D^{20} - 185.8^\circ$, respectively. Practically complete racemization occurred in pyridine solution on standing for five weeks at 19° , and complete racemization occurred in 2 *N* ammonium hydroxide solution on standing at 19° for fifteen hours. The optically active acids were also completely racemized by heating in pyridine solution at 100° for thirty minutes or by heating in 0.1 *N* sodium hydroxide at 90° for thirty minutes.

The correct explanation as to why 8,8'-dicarboxy-1,1'-dinaphthyl is readily racemized while 2,2'-dicarboxy-1,1'-dinaphthyl is quite stable toward racemization is not yet clear. The difference in stability may be due to the fact that the peri-substituted carboxyl groups in 8,8'-dicarboxy-1,1'-dinaphthyl render the molecule more labile and more capable of distortion than when the carboxyl groups are in the 2,2' positions.

The set of interference values which has been suggested³ was designed primarily to enable estimation of the interferences between 2,6 and 2',6' groups in diphenyl derivatives. In such compounds the interfering groups were assumed to be at an angle of 60° from the line of nearest approach (AC). However, in the case of 8,8'-dicarboxy-1,1'-dinaphthyl the 2,2'- and the 8,8'-groups cause the interference and these groups may be assumed to be at an angle of 30° from the line of nearest approach (AB). The effective diameter of the groups would probably be a little larger since they are directed more toward each other (by 30°); consequently in compounds of this type the interference values would probably need to be slightly increased.

The author wishes to express his sincere thanks to Professor Ludwig Kalb for the 8,8'-dicarboethoxy-1,1'-dinaphthyl used in this investigation.

³ Stanley and Adams, THIS JOURNAL, 52, 1200 (1930); 53, 2364 (1931).

Experimental Part

8,8'-Dicarboxy-1,1'-dinaphthyl.—A mixture of 0.65 g. of 8,8'-dicarboethoxy-1,1'-dinaphthyl⁴ and 2 g. of potassium hydroxide in 50 cc. of amyl alcohol was refluxed for seven hours. About 45 cc. of alcohol was then removed by distillation under vacuum and 100 cc. of water added to the residue. The acid was then precipitated by the addition of concentrated hydrochloric acid, removed by filtration and dissolved in 50 cc. of dilute aqueous ammonia. This solution was treated with animal charcoal to give a colorless solution, from which the acid was precipitated by the addition of hydrochloric acid. The yield was 0.5 g. (91%) of a product melting at 298–300° to a red liquid. Upon recrystallization from ethyl alcohol the melting point was raised to 306–307°. The 8,8'-dicarboxy-1,1'-dinaphthyl is insoluble in xylol, acetone, ether and chloroform, slightly soluble in ethyl alcohol, ethyl acetate and acetic acid, and soluble in pyridine and hot acetic anhydride. The ester was only partially saponified by the use of methyl or ethyl alcoholic potassium hydroxide.

Anal. Subs., 5.025 mg.: CO₂, 14.20 mg.; H₂O, 1.89 mg. Calcd. for C₂₂H₁₄O₄: C, 77.17; H, 4.12. Found: C, 77.07; H, 4.21.

Resolution of 8,8'-Dicarboxy-1,1'-dinaphthyl.—To a cloudy solution of 0.4367 g. of 8,8'-dicarboxy-1,1'-dinaphthyl in 150 cc. of absolute ethyl alcohol was added 0.4138 g. (1 equivalent) of quinine. The solution, which became perfectly clear upon the addition of the quinine, was evaporated to dryness. The mono-quinine salt is very soluble in methyl alcohol, ethyl alcohol, acetone and chloroform, slightly soluble in benzene and insoluble in ether and water. The mono-quinine salt was taken up in 20 cc. of benzene and a few drops of ethyl alcohol was added to make the solution clear. The solution was then boiled for five minutes and allowed to stand. After standing for two days at room temperature, the clear solution was decanted from a thin glassy film (0.24 g.) which had formed on the sides and bottom of the flask.

Rotation. 0.0566 g. made up to 3 cc. with chloroform at 20° gave $\alpha_D -0.45^\circ$; $l = 1$; $[\alpha]_D^{20} -23.9^\circ$.

After standing two more days a mass of fine crystals (0.25 g.) and two large clusters of fine needles (0.1 g.) had separated from the decanted solution. These were removed and dried. The melting point of the 0.1-g. portion was 195° with sintering at 175°.

Rotation of the 0.1 g. portion: 0.0548 g. made up to 3 cc. with chloroform at 20° gave $\alpha_D -3.1^\circ$; $l = 1$; $[\alpha]_D^{20} -169.7^\circ$.

The 0.1-g. portion was recrystallized from benzene. The melting point was unchanged.

Rotation. 0.0292 g. made up to 2 cc. with chloroform at 20° gave $\alpha_D -2.42^\circ$; $l = 1$; $[\alpha]_D^{20} -165.8^\circ$.

Rotation of the 0.25-g. portion: 0.0604 g. made up to 3 cc. with chloroform at 20° gave $\alpha_D -2.75^\circ$; $l = 1$; $[\alpha]_D^{20} -136.6^\circ$.

Anal. Calcd. for C₄₂H₃₈O₈N₂: C, 75.64; H, 5.75. Found: C, 75.47; H, 5.71.

The remaining salt solution was evaporated to dryness and gave 0.25 g. of salt which sintered at 173° and melted at 190°.

Rotation. 0.0570 g. made up to 3 cc. with chloroform at 20° gave $\alpha_D = +3.65^\circ$; $l = 1$; $[\alpha]_D^{20} +192.1^\circ$.

The first portion (0.24 g.) of salt which was obtained in the fractionation consisted mainly of the *d,l*-salt. Upon refractionation from benzene the partially pure *d*- and *l*-salts were obtained.

***d*-8,8'-Dicarboxy-1,1'-dinaphthyl.**—To 0.24 g. of salt having a rotation of +192.1° in chloroform was added 10 cc. of 0.5 *N* hydrochloric acid. After stirring for ten

⁴ Kalb, *Ber.*, **47**, 1724 (1914).

minutes the mixture was filtered. This treatment was repeated twice and the precipitated acid was dissolved in 15 cc. of 0.1 *N* sodium hydroxide and extracted twice with 5 cc. of chloroform. The active acid was then precipitated from the alkaline solution with dilute hydrochloric acid. After drying, the product melted to a red liquid at 305–306°.

Rotation. (a) 0.0210 g. made up to 2 cc. with pyridine at 20° gave $\alpha_D +2.08^\circ$; $l = 1$; $[\alpha]_D^{20} +198.1^\circ$. (b) 0.0336 g. made up to 15 cc. with 0.1 *N* sodium hydroxide gave $\alpha_D -0.28^\circ$; $l = 0.5$; $[\alpha]_D^{20} -250.0^\circ$. (c) 0.0190 g. made up to 5 cc. with 2 *N* aqueous ammonia gave $\alpha_D -0.35^\circ$; $l = 0.5$; $[\alpha]_D^{20} -184.2^\circ$.

A portion of the *d*-salt having a rotation of +44.5° in chloroform was hydrolyzed in a similar manner to give partially pure *d*-acid.

Rotation. (a) 0.0250 g. made up to 9 cc. with 0.5 *N* aqueous ammonia gave $\alpha_D -0.12^\circ$; $l = 1$; $[\alpha]_D^{20} -43.2^\circ$. (b) 0.0240 g. made up to 2 cc. with pyridine at 20° gave $\alpha_D +0.88^\circ$; $l = 1$; $[\alpha]_D^{20} +73.1^\circ$.

It was necessary to use dilute alkaline solutions of the *d*-acid since concentrated alkaline solutions of the *d*-acid were always cloudy. Repeated solution in alkali, extraction with chloroform and precipitation with hydrochloric acid did not change this property.

l-8,8'-Dicarboxy-1,1'-dinaphthyl.—A portion of *l*-salt having a rotation of -169.7° in chloroform was hydrolyzed by treatment with three 5-cc. portions of 0.5 *N* hydrochloric acid and extraction of the alkaline solution with chloroform. The *l*-acid so obtained melted to a red liquid at 304.5–305.5°.

Rotation. 0.0240 g. made up to 2 cc. with pyridine at 20° gave $\alpha_D -2.25^\circ$; $l = 1$; $[\alpha]_D^{20} -185.8^\circ$.

Anal. Subs., 4.447 mg.: CO₂, 12.57 mg.: H₂O, 1.68 mg. Calcd. for C₂₂H₁₄O₄: C, 77.17; H, 4.12. Found: C, 77.02; H, 4.23.

A portion of *l*-salt having a rotation of -136.6° in chloroform was hydrolyzed by treatment with three 10-cc. portions of 0.5 *N* hydrochloric acid, solution in 0.5 *N* aqueous ammonia and immediate precipitation with dilute hydrochloric acid.

Rotation. 0.0225 g. made up to 2 cc. with pyridine at 20° gave $\alpha_D -2.02^\circ$; $l = 1$; $[\alpha]_D^{20} -179.6^\circ$.

The *l*-acid was precipitated from the pyridine solution by the addition of concentrated hydrochloric acid at 0°. The rotation was again taken.

Rotation. 0.0187 g. made up to 2 cc. with 2 *N* ammonium hydroxide at 20° gave $\alpha_D +0.31^\circ$; $l = 1$; $[\alpha]_D^{20} +33.1^\circ$.

Racemization Experiments

1. A solution of 0.0210 g. of *d*-acid in 2 cc. of pyridine at 20° gave $\alpha_D +2.08^\circ$; $l = 1$; $[\alpha]_D^{20} +191.1^\circ$. Heating the solution at 100° for thirty minutes caused complete racemization of the acid.

2. A solution of 0.0240 g. of *l*-acid in 2 cc. of pyridine at 20° gave $\alpha_D -2.25^\circ$; $l = 1$; $[\alpha]_D^{25} -185.8^\circ$. Standing for five weeks at room temperature caused almost complete racemization since the rotation was -5° : $\alpha_D -0.06^\circ$; $l = 1$; $[\alpha]_D^{20} -5.0^\circ$.

3. A solution of 0.0187 g. of *l*-acid in 2 cc. of 2 *N* aqueous ammonia at 20° gave $\alpha_D +0.31^\circ$; $l = 1$; $[\alpha]_D^{20} +33.1^\circ$. After standing at 19° for fifteen hours the rotation was zero.

4. A solution of *l*-acid in 2 *N* aqueous ammonia having $\alpha_D +0.24^\circ$ was allowed to stand at 19°; after two hours $\alpha_D +0.18^\circ$; after four hours $\alpha_D +0.13^\circ$; after six hours $\alpha_D +0.08^\circ$; after ten hours $\alpha_D 0^\circ$.

5. A solution of 0.0336 g. of *d*-acid in 15 cc. of 0.1 *N* sodium hydroxide gave $\alpha_D -0.28^\circ$; $l = 0.5$; $[\alpha]_D^{20} -250.0^\circ$. After heating the solution at 90° for thirty minutes the rotation was zero.

6. A portion of 0.0314 g. of acid having a rotation of -179° in pyridine was added to 3 cc. of acetic anhydride. The mixture was heated to boiling during one minute to effect solution and then immediately cooled to 20° . The rotation of the acetic anhydride solution was zero. The acetic anhydride was removed below 20° by means of a stream of air under vacuum and the residue dissolved in 2 cc. of pyridine. The rotation of the pyridine solution was zero.

The material recovered from the pyridine solution was recrystallized from benzene and had a melting point of $179-180^\circ$. It was insoluble in cold alkali and but slowly soluble in hot alkali, from which solution the original acid of m. p. $306-307^\circ$ was obtained upon acidification. An analysis proved it to be the mixed acid anhydride of one molecule of 8,8'-dicarboxy-1,1'-dinaphthyl and two molecules of acetic acid.

Anal. Subs., 5.063 mg.: CO_2 , 13.66 mg.; H_2O , 1.89 mg. Calcd. for $\text{C}_{26}\text{H}_{18}\text{O}_6$: C, 73.21; H, 4.25. Found: C, 73.58; H, 4.18.

When this mixed acid anhydride was heated above its melting point (180°) bubbles were evolved from the light yellow liquid and at $198-202^\circ$ the liquid was converted to a red colored solid. After washing with hot dilute sodium hydroxide and recrystallization from chloroform this material melted at about 340° . This compound proved to be the anthanthron which was previously prepared by Kalb⁴ by the action of concentrated sulfuric acid on 8,8'-dicarboethoxy-1,1'-dinaphthyl. Solution in concentrated sulfuric acid caused a bright green coloration.

Anal. Subs.: 2.619 mg.: CO_2 , 8.26 mg.; H_2O , 0.77 mg. Calcd. for $\text{C}_{22}\text{H}_{10}\text{O}_2$: C, 86.25; H, 3.29. Found: C, 86.01; H, 3.29.

Summary

1. 8,8'-Dicarboxy-1,1'-dinaphthyl has been resolved into optical isomers by fractionation of the monoquinine salt from benzene.
2. This compound is the first α,α' -disubstituted diphenyl derivative which has been resolved.
3. The optically active acids were readily racemized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 74]

SIGNIFICANT TEMPERATURES IN THE PYROLYSIS OF CERTAIN PENTANES AND PENTENES¹

BY JAMES F. NORRIS AND GEORGE THOMSON

RECEIVED MAY 29, 1931

PUBLISHED AUGUST 5, 1931

Previous determinations in this Laboratory of the temperatures at which certain ethers² and a number of alkyl derivatives of malonic acid³ begin to decompose when heated under definite conditions showed that these temperatures could be determined in independent experiments that gave results which agreed within ± 2 degrees. The values obtained made it possible to correlate the temperatures at which certain bonds were broken

¹ From the thesis presented by George Thomson in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1930.

² Norris and Young, *THIS JOURNAL*, **52**, 753 (1930).

³ Norris and Young, *ibid.*, **52**, 5066 (1930).