

and *p*-aminotolyl-*p'*-hydroxyphenylamine. Certain sulfurated derivatives of *p*-hydroxydiphenylamine were also prepared.

2. These dyes were purified and analyzed, and their properties and reactions were investigated.

3. The evolution of a part of the sulfur of these compounds as hydrogen sulfide upon their being heated with stannous chloride and strong acid was the most enlightening reaction encountered.

4. The respective units of which the aggregates of all four dyes are composed are apparently of a thiazine nature and bear polysulfide chains of varying sulfur content attached to the rings composing the nucleus. The longest polysulfide chain encountered contained four sulfur atoms.

5. Constitutional formulas for the four units involved are suggested.

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THE OPTICAL ROTATION OF *d*-TALONIC AMIDE AND OF CERTAIN SALTS OF *d*-TALONIC ACID

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d-Talonic amide has been prepared from γ -talonolactone.¹ Aqueous solutions of the amide were found to be levorotating in agreement with Hudson's amide rule of rotation.² This rule states that for the amides of the monobasic sugar acids the direction of rotation is determined by the configuration of carbon 2; when the hydroxyl is on the right of the structure, the amide is dextrorotatory, and conversely. Although talonic amide exhibits the expected levorotation, the numerical value of the molecular rotation, $[\text{M}] = -25.5^\circ (10)$,² is somewhat lower than the value calculated from the estimated molecular rotations of the individual asymmetric carbon atoms² in the amides of the hexonic sugar acids. A closely comparable molecular rotation of $-27.1^\circ (10)$ ² has been reported for *l*-ribonic amide,^{2a} in which the α , β and γ carbon atoms have the same configuration of H and OH groups as in *d*-talonic amide. Freudenberg and Kuhn³ have directed attention to the rather constant difference between the molecular rotations of sugar acids and the corresponding amides. This difference has an approximate value of 78° for the gluconic type and 48° for the gulonic type. Inasmuch as the configuration of talonic acid does not place it in either of the above groups, it is not surprising that the

¹ Cretcher and Renfrew, *THIS JOURNAL*, **54**, 1590 (1932).

² (a) Hudson and Komatsu, *ibid.*, **41**, 1141 (1919); (b) Hudson, "Reports on Carbohydrates," Tenth Conference of the International Union of Chemistry, p. 59, Liège, 1930.

³ Freudenberg and Kuhn, *Ber.*, **64**, 703 (1931).

molecular rotations of *d*-talonic acid, $[M] = +37.4^\circ (10)$,² and of talonic amide differ by a new value of 63° .

Talonic amide was prepared by the action of dry ammonia gas on *d*- γ -talono-lactone¹ dissolved in 30–50 volumes of absolute alcohol. The crude amide was obtained as a finely divided crystalline powder, which softened at 116° and melted at 118 – 120° . After repeated recrystallization from absolute alcohol, the melting point was 121° .

Anal. Calcd. for $C_6H_{13}O_6N$: N, 7.18. Found:⁴ N, 7.15, 7.23. *Optical Rotation.* $c = 1.926$; $l = 4$; $\alpha = -1.01^\circ$; $[\alpha]_D^{25} -13.1^\circ$; $[M] -25.5^\circ (10)^2$.

The initial levorotation of aqueous solutions of the amide slowly decreased, and after several days reached a zero or faintly dextro reading. That this mutarotation was probably due to the formation of the ammonium salt is indicated by a consideration of the observed rotation of the ammonium salt, and by the fact that a similar mutarotation was reported by Weerman⁵ for gluconic amide.

A second crystalline amide, melting at 100 – 102° , was obtained when 95% alcohol was used as a crystallizing solvent. This preparation was apparently amide with one mole of water of crystallization and could be converted into the anhydrous amide by recrystallization from absolute alcohol.

Anal. Calcd. for $C_6H_{13}O_6N \cdot H_2O$: N, 6.57. Found: N, 6.53, 6.65. *Optical Rotation.* $c = 2.208$ g.; $l = 1$; $\alpha = -0.27^\circ$; $[\alpha]_D^{25} -12.22^\circ$; $[M] -26.0^\circ (10)^2$.

The ammonium salt of talonic acid was obtained when talonic lactone was treated with concentrated aqueous ammonia. The reaction product was an oil which crystallized after standing for several days in contact with alcohol. The ammonium salt melted at 148° and showed a small dextro rotation with no mutarotation within a period of several days.

Anal. Calcd. for $C_6H_{13}O_7N$: N, 6.57. Found: N, 6.53, 6.72. *Optical Rotation.* $c = 2.746$ g.; $l = 1$; $\alpha = +0.08^\circ$; $[\alpha]_D^{25} +2.9^\circ$; $[M] +6^\circ (10)^2$.

That a slight dextrorotation characterizes certain salts of *d*-talonic acid in aqueous solution is further evidenced by the study of sodium *d*-talonnate. The sodium salt was prepared by titrating an aqueous solution of the lactone with a slight excess of *N*/*10* sodium hydroxide.

Optical Rotation. $c = 1.5844$ g. lactone which is equivalent to 1.9404 g. Na salt; $l = 2$; $\alpha = +0.10$; $[\alpha]_D^{25} +2.5^\circ$; $[M] +5.5^\circ (10)^2$.

Levene and Meyer⁶ have determined the optical rotation of a series of sodium salts of simple monocarboxylic sugar acids. In each case the salts were dextrorotatory when the hydroxyl group linked with the α -carbon was on the right of the carbon chain and conversely. Although the sodium and ammonium salts of talonic acid failed to show levorotation, the dextro value was small compared with the dextrorotation of solutions of the free acid. From the data thus far available as cited by Levene⁷ and from a consideration of the rotations observed for *d*-talonic salts, it may be said of hexonic monocarboxylic sugar acids that the rotation of the sodium salt is more dextro than the corresponding acid if the hydroxyl is on the right of the α -carbon—and the rotation is more levo if the hydroxyl is on the left.

⁴ All nitrogen analyses were micro Dumas determinations by Dr.-Ing. A. Schoeller, Berlin.

⁵ Weerman, *Rec. trav. chim.*, **37**, 16 (1917).

⁶ Levene and Meyer, *J. Biol. Chem.*, **26**, 355 (1916).

⁷ Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925, p. 41; *Chem. Rev.*, **2**, 179 (1925–1926).

Summary

1. *d*-Talonic amide is levorotating as would be predicted from Hudson's amide rule.

2. The sodium and ammonium salts of *d*-talonic acid show a small dextrorotation. The rotation is much less dextro than the rotation of solutions of the free acid.

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PYRIDINE BORON TRIFLUORIDE

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Boron trihalides are extremely reactive toward ammonia and amines, and Kraus and Brown¹ have recently studied a number of reactions with boron trifluoride. They showed that true addition compounds are formed with ammonia, ethylamine, diethylamine and triethylamine.

All of these compounds can be shown to be examples of coördinate covalency, in which the boron atom acts as acceptor and the nitrogen atom acts as donor. Since the nitrogen atom in pyridine has one lone pair of electrons it should be possible to prepare a similar compound of boron trifluoride and pyridine. The purpose of this investigation was to prepare and study such a compound. After the work was nearly completed, Bowlus and Nieuwland² reported experimental work in which they measured the absorption of boron trifluoride by pyridine, and obtained a solid product which they believe to contain two molecules of boron trifluoride to one of pyridine. While the existence of such a compound in the solid state is not inconsistent with modern valence theory, it is probably not simply a case of coördinate covalency. In the present investigation a compound of boron trifluoride and pyridine was prepared, in which the molecular ratio is 1:1.

Experimental

Preparation of Materials.—Boron trifluoride was prepared by heating a mixture of ammonium fluoborate and boric oxide with concentrated sulfuric acid. The boric oxide was prepared by fusing boric acid in an iron crucible.

The pyridine was twice redistilled through an efficient fractionating column, and a constant boiling fraction was used without further purification.

The benzene was likewise redistilled twice using a column in order to ensure the complete absence of water from the reaction chamber.

Preparation of the Compound.—The all-glass apparatus shown in Fig. 1, made of Pyrex glass, was thoroughly dried in an electric oven before use. Eighteen grams of an-

¹ Kraus and Brown, *THIS JOURNAL*, 51, 2690 (1929).

² Bowlus and Nieuwland, *ibid.*, 53, 3835 (1931).