348. *The Stereochemistry of 2 : 2′-Disubstituted Diphenyls. Part II. The Optical Resolution of Diphenyl-2 : 2′-disulphonic Acid.*

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In Part I (this vol., p. 2021) the optical activity of phenyl benzidine-2 : 2′-disulphonate was attributed to dissymmetry set up by the dynamic effect of the three oxygen atoms present in each of the SO_3Ph groups. It was desirable, however, to show that the phenyl radicals in these groups were at the most of subsidiary consequence, and we have therefore carried out experiments on the resolution of diphenyl-2 : 2′-disulphonic acid, which Stanley and Adams (*J. Amer. Chem. Soc.*, 1930, **52**, 4471) failed to obtain in optically active forms.

Since Part I was communicated, Pauling (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293) has discussed the atomic radii of the elements with which we are concerned in these compounds. His values, 1·04 Å. and 0·29 Å., respectively, for the atomic radii of sulphur and hydrogen do not differ greatly from those used in Part I, and, if anything, give greater security to the views there expressed.

Preliminary experiments showed that the brucine hydrogen salt of diphenyldisulphonic acid was optically heterogeneous, and a *l*-rotatory solution of the ammonium salt of the acid was obtained by decomposing one of the fractions. The brucine salt did not, however, lend itself to fractional crystallisation. Similar results were obtained with the distrychnine salt, by the decomposition of one fraction of which a *d*-rotatory ammonium salt resulted. The strychnine hydrogen salt proved moderately easy to deal with, and three pure components were isolated. When a solution of sodium diphenyl-2 : 2′-disulphonate was treated with a quarter molecule of strychnine hydrochloride, a sparingly soluble product separated. Systematic recrystallisation of this gave the very sparingly soluble *strychnine hydrogen* d-*diphenyl*-2 : 2′-*disulphonate* with $[\alpha]_{5791}^{20°}$ — 8·5° (in chloroform), and the less sparingly soluble *strychnine hydrogen*

dl-*diphenyl*-2 : 2′-*disulphonate* with $[\alpha]_{5791}^{20°}$ — 11·0°. Addition of another quarter molecule of strychnine hydrochloride to the first mother-liquor, followed by concentration, gave crops strikingly different from the previous ones, both in appearance and in solubility, and these on recrystallisation gave the readily soluble *strychnine hydrogen* l-*diphenyl*-2 : 2′-*disulphonate* with $[\alpha]_{5791}^{20°}$ — 13·8°.

As can be seen from the specific rotations of the above three salts, the rotation of the disulphonic acid must be very small. Conversion of the above salts into aqueous solutions of the corresponding ammonium salts showed that the acid components were respectively *d*-rotatory, inactive, and *l*-rotatory. These facts sufficiently establish the point we set out to prove, *viz.*, that diphenyl-2 : 2′-disulphonic acid is capable of exhibiting optical activity. The activity persisted in the cold, but was rapidly destroyed at 100°.

EXPERIMENTAL.

Preliminary Experiments.—(a) *With brucine.* A solution of sodium diphenyl-2 : 2′-disulphonate (Barber and Smiles, J., 1928, 1141) (7·2 g.) in H_2O (300 c.c.) was treated with brucine (3·9 g.) in the equiv. *N*-HCl. A salt, m. p. 209°, separated, which on decomposition gave an inactive acid. To the mother-liquor were added 3·9 g. of brucine in the equiv. HCl : 2 g. of salt, m. p. 197°, separated, which gave a solution of the ammonium salt having α_{5791} — 0·09°. Decomposition of a subsequent crop gave a solution (NH_4 salt) with α_{5791} — 0·11°.

(b) *With strychnine.* The distrychnine salt, prepared by dissolving the alkaloid in the free acid in boiling aq. solution, was well defined. Resolution was incomplete, but decomposition of 2 g. of a less sol. fraction having $[\alpha]_{5791}^{20°}$ — 20·3° gave an ammonium salt solution with α_{5791} + 0·09°.

Resolution with Strychnine.—Strychnine hydrochloride dihydrate (16·4 g.) and sodium diphenyldisulphonate (29 g.) were dissolved together in boiling H_2O (4 l.). On standing, sparingly sol. glistening laminæ (*A*) (15·9 g.) separated, with $[\alpha]_{5791}^{20°}$ — 11·5° (in $CHCl_3$). After being recryst. from H_2O, the product had $[\alpha]_{5791}^{20°}$ — 9·2°; a second recrystn. gave 4·5 g. with m. p. 275—276° (decomp.; softening at 135°) (corr.) and $[\alpha]_{5791}^{20°}$ — 8·5° ($l = 2$; $c = 1·5110$; $\alpha_{5791}^{20°}$ = — 0·26°) in $CHCl_3$. A third recrystn. had no effect on the specific rotation. This salt is also sparingly sol. in $CHCl_3$, and is *strychnine hydrogen* d-*diphenyl*-2 : 2′-*disulphonate* (Found : C, 50·3; H, 5·2. $C_{33}H_{32}O_8N_2S_2,7·5H_2O$ requires C, 50·5; H, 6·0%). The salts were air-dried to const. wt.: after remaining for a day over conc. H_2SO_4, they had the same specific rotations, showing that the H_2O of crystn. was firmly held. The mother-liquors from the last two crystns. were concentrated; three successive crops had $[\alpha]_{5791}^{20°}$ — 10·4°, — 12·6°, and — 12·4°. The mother-liquor from which *A* separated was boiled and treated with strychnine (16·4 g.). On standing, 2·1 g. of needles separated, with $[\alpha]_{5791}^{20°}$ — 14·1°. Concentration of the mother-liquor produced no crystals until the vol. was 600 c.c.; slender needles then separated, with $[\alpha]_{5791}^{20°}$ — 15·3°, and at a somewhat smaller bulk more needles having $[\alpha]_{5791}^{20°}$ — 15·0°. Finally some strychnine hydrochloride separated.

All salts having $[\alpha]_{5791}^{20°}$ of about — 14° to — 15° were combined and crystal-

lised from H_2O until the specific rotation no longer changed; *strychnine hydrogen* l-*diphenyl*-2 : 2′-*disulphonate* was then obtained as readily sol. and highly characteristic slender needles, melting first at 143—145° and again at 209—210° (corr.), and having $[\alpha]_{5791}^{20°}$ — 13·8° ($l = 2$; $c = 1{\cdot}5945$; $\alpha_{5791}^{20°} =$ — 0·44°) in $CHCl_3$ (Found : C, 55·3; H, 5·9. $C_{33}H_{32}O_8N_2S_2,4H_2O$ requires C, 55·0; H, 5·6%). The salts examined were those obtained by air-drying to const. wt.

Recrystn. of salts having $[\alpha]_{5791}^{20°}$ of — 10° to — 12° until a const. specific rotation was shown gave pure *strychnine hydrogen* dl-*diphenyl*-2 : 2′-*disulphonate* in long rectangular plates, m. p. first 145° and then 265° (decomp.; corr.). This salt is less sparingly sol. than the *d*-salt, and had $[\alpha]_{5791}^{20°}$ — 11·0° in $CHCl_3$ ($l = 2$; $c = 1{\cdot}457$; $\alpha_{5791}^{20°} =$ — 0·32°) (Found : C, 50·2; H, 5·3; N, 3·5. $C_{33}H_{32}O_8N_2S_2,7{\cdot}5H_2O$ requires C, 50·5; H, 6·0; N, 3·6%). The salts examined were dried under conditions precisely similar to those used for the above salts. Particular care was necessary in this respect in view of the presence of H_2O of crystn. in all three salts.

The strychnine salts were decomposed by extracting their $CHCl_3$ solutions with dil. NH_3 aq. The NH_3 extracts were repeatedly extracted with $CHCl_3$ and then examined polarimetrically. Decomposition of 2 g. of the salt having $[\alpha]_{5791}^{20°}$ — 8·5° gave a solution ($l = 4$) with $\alpha_{5791}^{20°}$ + 0·27°. Decomposition of 1 g. gave a solution having α_{5791} + 0·14°. The rotation was unchanged after 3 days in the cold, but 10 mins.' boiling caused racemisation. Decomposition of 1 g. of the salt having $[\alpha]_{5791}^{20°}$ — 13·8° gave a solution (NH_4 salt) with $\alpha_{5791}^{20°}$ — 0·09° ($l = 2$), unchanged after 24 hrs. Inactive solutions were obtained when the salt having $[\alpha]_{5791}^{20°}$ — 11·0° was decomposed.

We desire to thank the Royal Society and the Chemical Society for grants.

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