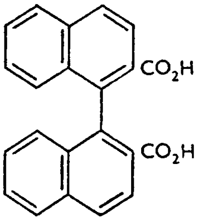
706. *Diaryl-2 : 2'-disulphonic Acids and Related Compounds. Part II.* The Optical Stability of a Cyclic 2 : 2'-Thiolsulphonate.*

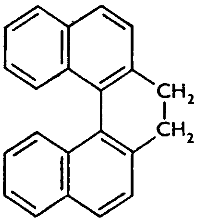
By W. L. F. Armarego and E. E. Turner.

The distrychnine salt of 4 : 6 : 4' : 6'-tetramethyldiphenyl-2 : 2'-disulphonic acid has been resolved. The disodium salt, the disulphonyl chloride, and the dianilide have high optical stability. The cyclic 2 : 2'-thiolsulphonate has a half-life of 24 minutes in boiling ethylbenzene and one of about 5 hours in boiling toluene. It is thus more stable than 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene.

1 : 1'-Dinaphthyl-2 : 2'-dicarboxylic acid (I) possesses very high optical stability. Yet active 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene (II), in which the energy of approach of two carbon atoms has been overcome, has the smaller, but still very considerable, optical stability which is represented by the statement that it has a half-life of 13 minutes in boiling ethylbenzene and about 3 hours in boiling toluene.[1] It seems probable therefore that since the active forms of diphenyl-2 : 2'-disulphonic acid (III; R = H) undergo complete racemisation in a few minutes in boiling aqueous solution,[2] derived cyclic types such as the 2 : 2'-thiolsulphonate (IV; R = H) or the 2 : 2'-disulphide (V; R = H) would have low configurational stability.



(I)



(II)

It appeared to us that the optical stability relationship between types (III) and (IV), or (III) and (V), could well be studied by using a disulphonic acid of high optical stability, and 4 : 6 : 4' : 6'-tetramethyldiphenyl-2 : 2'-disulphonic acid (III; R = Me) has been

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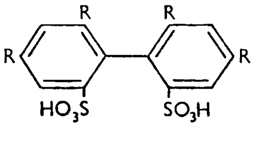
* Part I, *J.*, 1956, 1665.

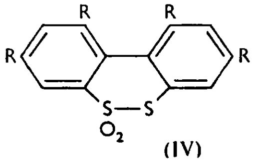
[1] Hall and Turner, *J.*, 1955, 1242; Hall, following note.

[2] Lesslie and Turner, *J.*, 1932, 2394.

selected for examination. It was synthesised from 2 : 4-xylidine ($NH_2 = 1$). This was sulphonated,[3] and the amino-group replaced by either bromine [3] or iodine. The derived sulphonyl chlorides were converted into phenyl 2-bromo(or 2-iodo)-3 : 5-dimethylbenzenesulphonate, which was heated with copper. The route through the iodo-compounds was the better. The phenyl 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonate so formed



(III)



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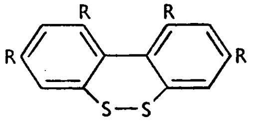

(V)

was, as expected, difficult to hydrolyse, but by using four molecular proportions of sodium *n*-butoxide in boiling butanol an 89% conversion into the sodium disulphonate was achieved. The alkali salts of 2-iodo-3 : 5-dimethylbenzenesulphonic acid gave very poor yields of the tetramethyldiphenyldisulphonates when their aqueous solutions were boiled in presence of copper powder and copper sulphate (see Part I).

4 : 6 : 4′ : 6′-Tetramethyldiphenyl-2 : 2′-disulphonyl chloride, obtained from the disodium salt and phosphorus pentachloride, could not be reduced to the 2 : 2′-dithiol. Use of an excess of zinc and hydrochloric acid, or hydriodic acid, gave polymeric material. It was therefore impossible to obtain the cyclic 2 : 2′-disulphide (V; R = Me) by the standard method of oxidising the dithiol. Reduction of the disulphonyl chloride with hot aqueous alkaline alkali sulphite gave the sodium disulphinate: on further heating after addition of excess of mineral acid, the precipitated unstable disulphinic acid passed into the thiolsulphonate (IV; R = Me). This compound was less conveniently obtained by the restricted reduction of the disulphonyl chloride with zinc and acid. By reduction of the thiolsulphonate with hydriodic–acetic acid the 2 : 2′-dithiol was produced in low yield, but attempted purification led to polymerised material. Reduction of the thiolsulphonate with lithium aluminium hydride in ether gave the 2′-mercapto-2-sulphinic acid, from which, by methylation, 4 : 6 : 4′ : 6′-tetramethyl-2-methylsulphonyl-2′-methylthiodiphenyl was formed.

It can be seen from a model that if the two sulphur atoms in the unsubstituted thiolsulphonate (IV; R = H) have approximately the same radius (1·0 Å) that they would have in the cyclic disulphide (V; R = H), a strainless form is obtained when the angle of twist between the (collinear) benzene nuclei is about 35° and the sulphur angle is about 90°. Into such a molecule two methyl groups can be put into the 6- and 6′-positions only with some strain.

Treating an aqueous solution of one mol. of sodium 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonate with an aqueous solution of two mols. of strychnine hydrochloride gave the almost pure (—)-base (—)-acid salt, and by evaporation of the mother-liquor crude (—)-base (+)-acid salt was obtained, initially as an oil. The less soluble salt became optically pure after one crystallisation from methanol and had $[\alpha]_{5461}^{19\cdot2}$ —100·0° (±0·5°), $[\alpha]_{5791}^{19\cdot2}$ —96·0° (±0·5°) (in $CHCl_3$).

Treatment with sodium hydroxide gave the sodium (—)-disulphonate, which after crystallisation from ethanol had $[\alpha]_{5461}^{20}$ —39·0° (±0·5°), $[\alpha]_{5791}^{20}$ —35·0° (±0·5°) (in H_2O). Crystallisation from ethanol of the sodium disulphonate obtained from the more soluble strychnine salt gave the sodium (+)-disulphonate with $[\alpha]_{5461}^{20}$ +40·5° (±0·5°), $[\alpha]_{5791}^{20}$ +35·0° (±0·5°) (in H_2O). The sign of rotation of the sodium salts was reversed in ethanol: the values of the rotation for various ethanol–water mixtures are given in the Experimental section.

By the action of phosphorus pentachloride on the (—)-sodium salt, 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonyl chloride was obtained with $[\alpha]_{5461}^{20}$ —94·5° (±0·5°), $[\alpha]_{5791}^{20}$ —83·5° (±0·5°) (in $CHCl_3$): the (+)-disulphonyl chloride, from the (+)-sodium

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[3] Junghahn, *Ber.*, 1912, **35**, 3747.

salt, had $[\alpha]^{20}_{5461}$ +95·0° (±0·5°), $[\alpha]^{20}_{5791}$ +83·5° (±0·5°) (in $CHCl_3$). The (−)- and the (+)-disulphonyl chloride gave, respectively, a (+)-, $[\alpha]^{22}_{5461}$ +238° (±1°), and a (−)-disulphonanilide, $[\alpha]^{22}_{5461}$ −237° (±1°). The (−)-disulphonyl chloride was heated with aqueous alkaline sodium sulphite until it had all dissolved, excess of dilute mineral acid was added and the mixture heated. The cyclic thiolsulphonate so obtained was strongly dextrorotatory, with $[\alpha]^{20}_{5461}$ +253° (±1°) and $[\alpha]^{20}_{5791}$ +188° (±1°) (in $CHCl_3$). From the (+)-disulphonyl chloride there was similarly obtained the (−)-thiolsulphonate, $[\alpha]^{20}_{5461}$ −252° (±1°), $[\alpha]^{20}_{5791}$ −190° (±1°).

The optically active sodium 4 : 6 : 4' : 6'-tetramethyldiphenyl-2 : 2'-disulphonate underwent no measurable racemisation in aqueous solution when heated in a closed vessel for 26 hours at 180—200°. The active disulphonyl chloride did not racemise during half an hour at 170—175° in a vacuum. The active disulphonanilides remained unchanged when their solutions in *m*-nitrotoluene were boiled for 1½ hours. The (−)-thiolsulphonate had a half-life of 24 minutes in boiling ethylbenzene solution, that is about twice the half-life (13 min.) of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene in the same solvent at the same temperature. The half-life of the (+)-thiolsulphonate in boiling toluene was 291 (±2) min. The activation energy calculated from the two rate determinations is 31 kcal./mole.

EXPERIMENTAL

Polarimetric readings were made with $l = 2$. The chloroform used was of B.P. grade.

Phenyl 2-Bromo-3 : 5-dimethylbenzenesulphonate.—2 : 4-Xylidine was sulphonated with some modification of the procedure described by Junghahn.[3] By recovering and sulphonating unchanged base, a 68% yield was obtained. The solid diazo-sulphonate was heated at 70° with 48% hydrobromic acid, and the sodium sulphonate was salted out with sodium chloride. After treatment of the dehydrated sodium salt with phosphorus pentachloride, the bulk of the phosphoryl chloride was removed by distillation before the addition of ice-water. The sulphonyl chloride was filtered off and dried in a vacuum.

The sulphonyl chloride (56 g., 1 mol.) was dissolved in dry pyridine (100 c.c.), and phenol (40 g., 2 mol.) added. The dark reddish solution was heated at 100° for ½ hr., then cooled and poured into ice-water. The pale yellow oil that separated was washed with dilute hydrochloric acid and with dilute alkali. The solid *ester* obtained crystallised from ethanol as flat prisms, m. p. 96—97° (48 g., 71%) (Found : Br, 23·1. $C_{14}H_{13}O_3BrS$ requires Br, 23·4%).

An alternative procedure, which gave a purer crude product, was to heat the sulphonyl chloride (1 mol.) with phenol (2 mol.) and anhydrous sodium carbonate (1·5 mol.) for 1·5 hr. at 100°.

2 : 4-*Dinitrophenyl* 4-*Bromo*-3 : 5-*dimethylbenzenesulphonate.*—To a solution of 2 : 4-dinitrophenol (2·3 g.) in chloroform (35 c.c.) was added a solution of the above sulphonyl chloride (7 g.) in dry pyridine (2·2 c.c.). The mixture was boiled under reflux for 2 hr. The chloroform was distilled off and the residue treated with cold water. The *ester* crystallised from a large bulk of methanol or ethanol in long yellow needles, m. p. 147—148° (19%) (Found : N, 6·55. $C_{14}H_{11}O_7N_2Br$ requires N, 6·5%).

Phenyl 4 : 4' : 6 : 6'-*Tetramethyldiphenyl*-2 : 2'-*disulphonate.*—*Method A.* Phenyl 2-bromo-3 : 5-dimethylbenzenesulphonate (30 g.) was heated at 240—260°, and copper bronze (60 g.) added at such a rate that the temperature of the mixture did not rise above 280°. When the reaction was complete, the somewhat cooled mixture was treated with chlorobenzene and filtered, and the copper washed with chlorobenzene. The solvent was distilled off and the residual *disulphonate* was crystallised from butan-1-ol or glacial acetic acid, forming flat rhombs, m. p. 180—181° (39%; overall yield on xylidinesulphonic acid 12%) (Found : C, 63·7; H, 5·0; S, 12·3%; *M*, ebullioscopic in benzene, 536. $C_{28}H_{26}O_6S_2$ requires C, 64·3; H, 5·0; S, 12·4%; *M*, 523).

2-*Iodo*-3 : 5-*dimethylbenzenesulphonyl Chloride.*—The above diazo-sulphonate (160 g., 1 mol.) was added to a solution of potassium iodide (160 g., 1½ mol.) in 25% v/v sulphuric acid (800 c.c.) and heated on a boiling-water bath until evolution of nitrogen ceased. On cooling, the sulphonic acid separated as plates, and more was obtained by vacuum-evaporation of the mother-liquor. The acid was dried in a vacuum over H_2SO_4. It lost iodine when exposed to light. The yield was 231 g.

The acid (156 g.) was gradually treated with phosphorus pentachloride (156 g.) with ice-water cooling. After 1 hr., most of the phosphoryl chloride was distilled off under vacuum and the residue treated with ice-cold water. The dried *sulphonyl chloride* crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 86—87° (66%) (5·245 mg. gave 5·820 mg. of AgI + AgCl. $C_8H_8O_2ClIS$ requires 5·991 mg.).

The *sulphonamide*, resulting from the interaction of the chloride and concentrated aqueous ammonia, crystallised in needles from dilute ethanol (Found: I, 40·2; N, 4·2. $C_8H_{10}O_2INS$ requires I, 40·8; N, 4·5%).

Phenyl 2-*Iodo*-3 : 5-*dimethylbenzenesulphonate*.—The iodo-sulphonyl chloride (265 g., 1 mol.) was heated at 100° with phenol (2 mol.) and sodium carbonate (1½ mol.). After the standard procedure, the *ester* crystallised from ethanol as plates, m. p. 105—106° (94%) (Found: C, 43·2; H, 3·5. $C_{14}H_{13}O_3IS$ requires C, 43·3; H, 3·4%).

Phenyl 4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonate*.—*Method B*. The iodo-ester (129 g.) was heated at 170—180° with copper bronze (100 g.). The yield of disulphonate was 70 g. (80%) (the overall yield calculated on xylidinesulphonic acid was 41·5%).

Di-(2-*iodo*-3 : 5-*dimethylphenyl*) *Disulphide*.—A solution of the iodo-sulphonyl chloride (5·9 g.) in boiling glacial acetic acid (60 c.c.) was treated with 55% (w/w) hydriodic acid (50 c.c.). After an hour at room temperature the mixture was poured into a saturated aqueous solution of sodium hydrogen sulphite. The solid *disulphide* was collected, washed, dried, and crystallised from glacial acetic acid; it formed long pale yellow needles, m. p. 160—161° (4·0 g., 85%) (Found: I, 48·4. $C_{16}H_{16}I_2S_2$ requires I, 48·2%). At 190—220° the disulphide reacted with copper bronze with uncontrollable vigour, and no tetramethylthianthren could be isolated.

Sodium and Barium Salts of 4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonic Acid*.—Sodium (3 g., 4 atom-equivs.) was dissolved in butan-1-ol (100 c.c.), and the solution added to one of phenyl 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonate (16·7 g., 1 mol.) in butan-1-ol (160 c.c.). The mixture was boiled under reflux for 3 hr., and then distilled until the residual volume was about 75 c.c. The liquid was poured into water (200 c.c.), and the solution boiled, filtered, and acidified with 2N-hydrochloric acid. Phenol was removed by extraction with ether, and the aqueous solution, after being neutralised (to Congo-red) with 10% aqueous sodium hydroxide, was filtered and concentrated to about 50 c.c. On cooling, the *sodium salt* crystallised in platelets (88% yield of anhydrous salt, after drying at 120°) (Found: S, 15·8. $C_{16}H_{16}O_6S_2Na_2$ requires S, 15·5%). The salt was hygroscopic and was soluble in ethanol. When only 2 mol. of sodium butoxide were used, 30% of unchanged ester was recovered after 12 hours' boiling.

The barium salt separated in fine needles when a 5% solution of barium chloride was added to a warm aqueous solution of the sodium disulphonate. The *barium salt* was very sparingly soluble in water and did not react under normal conditions with phosphorus pentachloride (Found: Ba, 24·7, 24·5. $C_{16}H_{16}O_6S_2Ba,3H_2O$ requires Ba, 24·6%).

4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonyl Chloride*.—A mixture of the sodium disulphonate (anhydrous; 31·0 g., 1 mol.) with phosphorus pentachloride (32·0 g., 2 mol.) was heated at 100° for 10 min. The cooled liquid was poured into water and the resulting yellow solid *dichloride* was washed and dried and crystallised from glacial acetic acid, forming needles, m. p. 164° (23 g., 77%) (Found: C, 47·0; H, 4·1; S, 15·9. $C_{16}H_{16}O_4Cl_2S_2$ requires C, 47·2; H, 3·9; S, 15·7%). With phenol in dry pyridine it gave the diphenyl disulphonic ester, m. p. 181°, in 31% yield and with aniline it gave 4 : 6 : 4′ : 6′-*tetramethyldiphenyl*-2 : 2′-*disulphonanilide* (37%), cubic crystals, m. p. 208—209° (from ethanol) (Found: N, 5·7. $C_{28}H_{28}O_4N_2S_2$ requires N, 5·4%).

Reduction of 4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonyl Chloride*.—(a) *With alkaline sodium sulphite*. The disulphonyl chloride (7·8 g.) was shaken at 100° with 30% sodium sulphite solution (250 c.c.) and 10% sodium hydroxide solution (20 c.c.). With intermittent shaking, the suspended chloride dissolved in 8—10 hr. The yellow solution was acidified with excess of 2N-sulphuric acid and heated on a boiling-water bath until all the material that separated had coagulated. The cyclic *thiolsulphonate* (1 : 3 : 8 : 10-*tetramethyldibenzo*[ce]*dithiin* 5 : 5-*dioxide*; Ring Index no. 1936) was collected, dried, and crystallised from glacial acetic acid (prisms, m. p. 177—178°) or from butan-1-ol (needles, m. p. 177—178°) (yield, 4·2 g.) (Found: C, 62·9; H, 4·9; S, 21·4%; *M*, ebullioscopic in benzene, 316. $C_{16}H_{16}O_2S_2$ requires C, 63·1; H, 5·2; S, 21·0%; *M*, 304).

(b) *With zinc dust and hydrochloric acid*. The disulphonyl chloride (4 g., 1 mol.) was dissolved in hot absolute ethanol (50 c.c.), zinc dust (5 g., 8 atom-equivs.) added, and the mixture cooled to 10°. Concentrated hydrochloric acid (20 c.c.) was added at such a rate that the temperature did not rise above 20°. The mixture was heated at 100° for 10 min., filtered, and poured into water (200 c.c.). The solid separating crystallised from glacial acetic acid as prisms (2·0 g.), m. p. 177° undepressed by admixture with the thiolsulphonate from (a).

When reduction was attempted with a large excess of zinc dust and hydrochloric acid, a white polymeric substance was obtained.

(c) *With hydriodic–acetic acid.* A solution of the disulphonyl chloride (2 g.) in boiling glacial acetic acid (30 c.c.) was treated with hydriodic acid (*d* 1·7) (20 c.c.) and glacial acetic acid (20 c.c.). The mixture was boiled and then left to cool for 24 hr. The product resembled that obtained by using excess of zinc and hydrochloric acid.

Reduction of the Thiolsulphonate.—(*a*) The thiolsulphonate (0·5 g.) was dissolved in boiling glacial acetic acid (10 c.c.), and 55% w/w hydriodic acid (10 c.c.) added. After 5 min. the mixture was cooled and 4 : 6 : 4′ : 6′-*tetramethyldiphenyl*-2 : 2′-*dithiol* crystallised. It separated from glacial acetic acid in rectangular plates, m. p. 138—139° (Found: C, 71·2; H, 6·7; S, 22·1. $C_{16}H_{18}S_2$ requires C, 70·0; H, 6·6; S, 23·4%). It was soluble in alkali but readily oxidised in air to an alkali-insoluble product.

(*b*) Reduction with lithium aluminium hydride in ethereal solution gave 2′-*mercapto*-4 : 6 : 4′ : 6′-*tetramethyldiphenyl*-2-*sulphinic acid* (Found: C, 63·7; H, 6·1; S, 20·4. $C_{16}H_{18}O_2S_2$ requires C, 63·1, H, 5·9; S, 20·9%). Methylation of this substance with methyl sulphate in alkaline solution gave *methyl* 4 : 6 : 4′ : 6′-*tetramethyl*-2′-*methylthio*-2-*diphenylyl sulphone*, plates, m. p. 146—147 (from butan-1-ol) (Found: C, 65·0; H, 6·7. $C_{18}H_{22}O_2S_2$ requires C, 64·7; H, 6·6%).

Optical Resolution of Strychnine 4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonate.*—Strychnine (66·88 g., 2 mol.) was dissolved in water (2 l.) containing concentrated hydrochloric acid (7·3 g., 2 mol.) by boiling. Anhydrous sodium 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonate (41·4 g., 1 mol.), dissolved in water (400 c.c.), was added to the hot solution. A precipitate suddenly separated. The mixture was kept overnight and then filtered. The solid was dried in a vacuum at 67° and crystallised from methanol (10 l.) as rhombs (25 g.), m. p. 340° (decomp.), $[\alpha]_{5461}^{19\cdot2}$ −100·0° (±0·5°), $[\alpha]_{5791}^{19\cdot2}$ −96·0° (±0·5°) (*c* 1·0310 in $CHCl_3$). Recrystallisation of this (−)-*base* (−)-*acid salt* from a large volume of methanol did not affect the specific rotation (Found: C, 65·2; H, 6·3. $C_{58}H_{62}O_{10}N_4S_2,2CH_3\cdot OH$ requires C, 65·3; H, 6·4%).

The first aqueous filtrate was concentrated to 400 c.c. An oil separated. This was isolated by decanting off the mother-liquor and washing the residue twice with a little water. The washings were added to the mother-liquor, and the solution was concentrated to 200 c.c. More oil separated. The combined oils, after being washed, were then dried in a vacuum. The almost pure solid (−)-*base* (+)-*acid salt* so obtained was very soluble in water and in cold methanol {yield 25 g.; m. p. 270° (decomp.; softening at 250°), $[\alpha]_{5461}^{18\cdot2}$ −70·5° (±0·5°), $[\alpha]_{5791}^{18\cdot2}$ −61·0° (±0·5°) (*c* 1·0905 in $CHCl_3$)} (Found: C, 61·2; H, 6·4. $C_{58}H_{62}O_{10}N_4S_2,6H_2O$ requires C, 61·2; H, 6·2%).

Sodium (−)-4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonate.*—A chloroform solution of the (−)-base (−)-acid salt (22 g.) was thrice extracted with 10% aqueous sodium hydroxide (in all about 400 c.c.). The combined alkaline solutions were extracted with chloroform until the latter had no optical activity. The alkaline solution was neutralised with concentrated hydrochloric acid and evaporated in a vacuum on a water-bath. The residual solid was dried at 120—130° for 2 hr. and then extracted with hot absolute ethanol until the extract ceased to possess optical activity. The ethanol solution (about 1 l.) was filtered and concentrated to about 150 c.c. On cooling, the disodium (−)-salt separated as needles (8·5 g.). After being dried in a vacuum it had $[\alpha]_{5461}^{18}$ −39·0° (±0·5°), $[\alpha]_{5791}^{20}$ −35·0° (±0·5°) (*c* 1·1015 in H_2O), and $[\alpha]_{5461}^{18}$ +9·5° (±0·5°), $[\alpha]_{5791}^{20}$ +8·0° (±0·5°) (*c* 0·968 in absolute EtOH). Evaporation of the ethanolic mother-liquor gave 3·0 g. of almost pure (−)-salt.

Sodium (+)-4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonate.*—From the (−)-base (+)-acid salt (22 g.), sodium (+)-salt was obtained, having $[\alpha]_{5461}^{20}$ +40·5° (±0·5°), $[\alpha]_{5791}^{20}$ +35·0° (±0·5°) (*c* 1·0870 in H_2O), and $[\alpha]_{5461}^{18}$ −9·5° (±0·5°), $[\alpha]_{5791}^{18}$ −9·0° (±0·5°) (*c* 0·9680 in EtOH).

Rotations in aqueous ethanol are tabulated.

A solution of the sodium salt in water, with α_{5461} +0·56° and α_{5791} +0·49° ($l = 2$), was heated for 26 hr. in a sealed tube at 180—200° and although the resulting solution was slightly turbid the rotation was unchanged.

Active 4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonyl Chlorides.*—Anhydrous sodium (−)-tetramethyldiphenyldisulphonate (6 g.) was treated with an equal weight of phosphorus

Effect of adding water to absolute ethanol solutions (20 *ml.*; *c* 0·968; $l = 2$) *of sodium* 4 : 6 : 4′ : 6′-*tetramethyldiphenyl*-2 : 2′-*disulphonates.*

Added water (ml.)	(−)-Salt		(+)-Salt		Added water (ml.)	(−)-Salt		(+)-Salt	
	α^{20}_{5461}	α^{20}_{5791}	α^{18}_{5461}	α^{18}_{5791}		α^{20}_{5461}	α^{20}_{5791}	α^{18}_{5461}	α^{18}_{5791}
0·0	+0·18°	+0·15°	−0·19°	−0·17°	2·5	−0·41°	−0·39°	+0·40°	+0·35°
0·1	+0·13	+0·10	−0·12	−0·12	3·0	−0·42	−0·40	+0·41	+0·36
0·3	+0·02	0·00	—	—	3·5	−0·43	−0·41	—	—
0·5	−0·07	−0·06	0·00	+0·01	4·0	−0·44	−0·41	+0·43	+0·39
0·7	−0·13	−0·13	+0·09	+0·06	5·0	−0·42	−0·39	+0·40	+0·35
1·0	−0·22	−0·21	+0·19	+0·15	7·0	−0·39	−0·37	+0·37	+0·32
1·5	−0·32	−0·31	+0·30	+0·25	9·0	−0·36	−0·34	+0·34	+0·31
2·0	−0·39	−0·37	+0·36	+0·31	11·0	−0·32	−0·31	+0·32	+0·29

Error ± 0·01°.

pentachloride, the procedure being as for the (±)-material. The (−)-*chloride* crystallised from glacial acetic acid in yellow needles (2·7 g.), m. p. 165°, $[\alpha]^{20}_{5461}$ −94·5° (±0·5°), $[\alpha]^{20}_{5791}$ −83·5° (±0·5°) (*c* 1·0300 in $CHCl_3$) (Found: C, 46·7; H, 4·1%).

The (+)-*chloride*, obtained from the sodium (+)-sulphonate and phosphorus pentachloride, had m. p. 165°, $[\alpha]^{20}_{5461}$ +95·0° (±0·5°), $[\alpha]^{20}_{5791}$ +83·5° (±0·5°) (*c* 1·0415 in $CHCl_3$) (Found: C, 47·5; H, 4·2%).

4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*disulphonanilides*.—(−)-4 : 6 : 4′ : 6′-Tetramethyldiphenyl-2 : 2′-disulphonyl chloride was heated in previously distilled aniline for ½ hr. at 100°. The mixture formed was poured into dilute hydrochloric acid, and the solid filtered, washed, and dried. The (+)-*anilide* crystallised from ethanol in prisms, m. p. 218—219°, $[\alpha]^{22}_{5461}$ +238° (±1°) (*c* 0·4220 in $CHCl_3$) (Found: N, 5·2%).

The (−)-*anilide* had m. p. 218—219°, $[\alpha]^{22}_{5461}$ −237·0° (±1°) (*c* 0·4250 in $CHCl_3$) (Found: N, 5·2%).

A solution of the (+)-dianilide in *m*-nitrotoluene with α_{5461} +0·43° and α_{5791} +0·35° was boiled under reflux for 2½ hr. The cooled solution had unchanged rotation.

4 : 6 : 4′ : 6′-*Tetramethyldiphenyl*-2 : 2′-*thiolsulphonate* (1 : 3 : 8 : 10-*Tetramethyldibenzo*[ce]-*dithiin* 5 : 5-*Dioxide*).—Finely powdered (−)-4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonyl chloride (1·8 g.) was shaken at the temperature of a boiling-water bath with 30% aqueous sodium sulphite solution (100 c.c.) and 10% aqueous sodium hydroxide (10 c.c.), dissolving completely in 3 hr. The solution was filtered, cooled, acidified with 50% sulphuric acid (about 100 c.c.), and heated on a boiling-water bath until all the oil that separated had solidified (about ½ hr.). The mixture was cooled and the solid filtered off, dried in a vacuum, and crystallised from butan-1-ol (about 10 c.c.). The (+)-*thiolsulphonate* so obtained, after being dried in a vacuum (0·7 g.), had m. p. 178—178·5°, $[\alpha]^{20}_{5461}$ +253·0° (±1°), $[\alpha]^{20}_{5791}$ +188·0° (±1°) (*c* 0·5705 in $CHCl_3$) (Found: C, 62·9; H, 5·6%).

The (−)-*thiolsulphonate* (0·7 g. from 1·7 g.) had m. p. 178—178·5°, $[\alpha]^{20}_{5461}$ −252°, $[\alpha]^{20}_{5791}$ −190° (±1°) (*c* 0·5385 in $CHCl_3$) (Found: C, 63·0; H, 5·3%).

The rate of racemisation in boiling ethylbenzene was measured for a solution (25 c.c.) containing 0·0833 g. of (−)-thiolsulphonate. The temperature was rapidly raised to the b. p. and after a suitable interval the solution was rapidly cooled to room temperature. Polarimetric readings were taken at 21° and the solution then rapidly heated to the b. p., and so on. α_{5461} ($l = 2$) fell from −1·49° to 0°, and α_{5491} from −1·12° to 0° in 143 min. From a logarithmic plot, *k* was found to be 2·8 (±0·2) × 10^{-2} min.$^{-1}$ and the half-life 24 ± 1 min.

The rate of racemisation in boiling toluene was measured for a solution (25 c.c.) containing 0·0878 g. of the (+)-thiolsulphonate. From a logarithmic plot, *k* was found to be 2·38 (±0·02) × 10^{-3} min.$^{-1}$ and the half-life 291 ± 2 min.

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