5. *Diaryl-2 : 2'-disulphonic Acids and Related Compounds. Part III.* Optical Activity and Optical Stability in the 1 : 1'-Dinaphthyl Series.*

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

The mixture of the diastereoisomeric distrychnine salts of 1 : 1'-dinaphthyl-2 : 2'-disulphonic acid has been resolved. The disodium salt of the active acid possesses very high optical stability. The active 2 : 2'-disulphonyl dichlorides have been reduced to the active cyclic 2 : 2'-thiolsulphonates and 2 : 2'-disulphides. The thiolsulphonate exhibits anomalous optical dispersion. In boiling tetralin solution (206·8°) the thiolsulphonate has a half-life of 26 min., which is approximately equal to the half-life of " 4 : 6 : 4' : 6'-tetramethyldiphenyl-2 : 2'-thiolsulphonate " in boiling ethylbenzene (136°).

Diphenyl-2 : 2'-disulphonyl dichlorides which are unsubstituted in the 6 : 6'-positions are readily converted into 2 : 2'-dimercaptodiphenyls and thence into cyclic 2 : 2'-disulphides (dibenzo[*ce*]dithiins).[1] From 4 : 6 : 4' : 6'-tetramethyldiphenyl-2 : 2'-disulphonyl dichloride, however, polymeric material was obtained[2] instead of the

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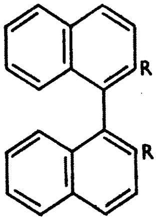
* Part II, *J.*, 1956, 3668.

[1] Part I, Armarego and Turner, *J.*, 1956, 1665.

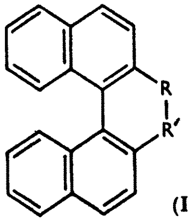
[2] *Idem, ibid.*, p. 3668.

expected dimercapto-derivative, and we failed to find a workable route to the corresponding cyclic 2 : 2′-disulphide. On the other hand, the tetramethyldiphenyldisulphonyl dichloride was readily reduced to the unstable 2 : 2′-disulphinic acid, which passed smoothly into the cyclic 2 : 2′-thiolsulphonate.

It appeared to us that a valuable addition to this set of facts might be obtained from an examination of compounds in which one of the rings in naphthalene was acting as the 6- and the 6′-substituent. Phenyl 1 : 1′-dinaphthyl-2 : 2′-disulphonate (I; R = $SO_2{\cdot}OPh$) was obtained by heating phenyl 1-iodonaphthalene-2-sulphonate with copper. Boiling *n*-butanolic sodium *n*-butoxide[2] converted the ester in high yield into the disodium salt (R = SO_3Na). The corresponding dipotassium salt was described by Barber and Smiles[3]



(I)



(II)

as resulting from the action of copper powder on boiling aqueous potassium 1-iodonaphthalene-2-sulphonate in presence of copper sulphate. The yield obtained was evidently low and later authors[4] failed to isolate any dinaphthyldisulphonate by this method. From the dipotassium salt, Barber and Smiles obtained 1 : 1′-dinaphthyl-2 : 2′-disulphonyl dichloride (I; R = SO_2Cl) and recorded that the latter, when reduced with zinc and hydrochloric acid, suffered reductive scission, giving 2-mercaptonaphthalene. This we regarded as unlikely and we have been unable to observe it. It seems probable that the disulphonyl dichloride used by Barber and Smiles contained naphthalene-2-sulphonyl chloride, which was the source of their 2-mercaptonaphthalene.

When equivalent aqueous solutions of disodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate and strychnine hydrochloride were mixed, the diastereoisomeric pair of alkaloidal salts was precipitated. The solid was dried, and repeatedly extracted with boiling methanol until the optical rotation of the residue became constant. The less soluble salt was almost pure (+)-acid (—)-base. From the methanolic extracts the almost pure (—)-acid (—)-base was isolated. From these two salts the two disodium salts were obtained and were, without purification, treated with phosphorus pentachloride. The (+)-disodium salt gave (—)-1 : 1′-dinaphthyl-2 : 2′-disulphonyl dichloride (I; R = SO_2Cl) with $[\alpha]^{21}_{5461}$ —26° ± 0·5° and $[\alpha]^{21}_{5791}$ —21° ± 0·5°. The (—)-disodium salt gave the (+)-dichloride, with $[\alpha]^{21}_{5461}$ +25·5° ± 0·5° and $[\alpha]^{21}_{5791}$ +21° ± 0·5°. Reduction of the (—)-dichloride with hydriodic–acetic acid gave (—)-disulphide (II; R = R′ = S) with $[\alpha]^{23}_{5461}$ —777° ± 1° and $[\alpha]^{23}_{5791}$ —748° ± 1°. The corresponding (+)-disulphide had $[\alpha]^{23}_{5461}$ +775° ± 1° and $[\alpha]^{23}_{5791}$ +748° ± 1°. Reduction of the (—)-dichloride with zinc and hydrochloric acid gave a mixture of (—)-2 : 2′-dimercapto-1 : 1′-dinaphthyl and the (—)-disulphide. No 1 : 1′-bond fission occurred. The (+)-disulphide was reduced by zinc and hydrochloric acid to (+)-2 : 2′-dimercapto-1 : 1′-dinaphthyl and this in turn was oxidised by ethanolic ferric chloride solution to strongly active (+)-2 : 2′-disulphide.

Reduction of the cyclic disulphide with zinc and hydrogen chloride in acetone gave the *SS-iso*propylidene derivative of 2 : 2′-dimercapto-1 : 1′-dinaphthyl (II; R — R′ = $\cdot S\cdot CMe_2\cdot S\cdot$). The optically active products from the (—)- and the (+)-2 : 2′-disulphide had $[\alpha]^{21}_{5461}$ —368° ± 1°, $[\alpha]^{21}_{5791}$ —329° ± 1°, and $[\alpha]^{20}_{5461}$ +367° ± 1°, $[\alpha]^{20}_{5791}$ +327° ± 1°, respectively.

Barber and Smiles[3] prepared the disulphide (II; R = R′ = S) by reducing the

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[3] Barber and Smiles, *J.*, 1928, 1141.

[4] Cummings and Muir, *J. Roy. Tech. Coll.* (*Glasgow*), 1937, **4**, 61.

disulphonyl dichloride with alkaline sodium sulphite, acidifying the mixture, and, without purifying the product, which they assumed was the cyclic thiolsulphonate, heating it with hydriodic–acetic acid. We find that their unpurified first product must in fact have been 1 : 1′-dinaphthyl-2 : 2′-disulphinic acid, and that this is only slowly affected by boiling dilute sulphuric acid, in which it is very sparingly soluble. Boiling in glacial acetic acid solution readily effected conversion into the 2 : 2′-thiolsulphonate. The optically active disulphonyl dichlorides led to disulphinic acids which were sufficiently soluble in boiling dilute sulphuric acid to pass smoothly in this reagent into the optically active 2 : 2′-thiolsulphonates. The latter exhibit marked anomalous dispersion, as is seen from the annexed figures.

	$[\alpha]^{25}_{6907}$	$[\alpha]^{25}_{5791}$	$[\alpha]^{25}_{5461}$	$[\alpha]^{25}_{4358}$
(—)-" 1 : 1′-Dinaphthyl-2 : 2′-thiolsulphonate " (c 0·1980 in $CHCl_3$)	−217° ± 2°	−204° ± 1°	−169° ± 1°	+1159° ± 5°
(+)-" 1 : 1′-Dinaphthyl-2 : 2′-thiolsulphonate " (c 0·2080 in $CHCl_3$)	+216° ± 2°	+204° ± 1°	+170° ± 1°	−1151° ± 5°

The rotation approached zero with the blue mercury lines (λ 4960, 4916).

(—)-Sodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate proved, as was expected,[2, 5] to have high optical stability. The rotation of an aqueous solution was unchanged at 190—200° for 10 hr. 1 : 1′-Dinaphth-2 : 2′-ylene disulphide, unfortunately, underwent chemical change in boiling ethylbenzene (137·6°) and in boiling *pseudo*cumene (171·2°). In the former solvent the rotation decreased during the first 2 hr. in a manner to be expected for a racemisation, but then increased linearly on heating further for 24 hr., reaching and then passing its original rotation in 9 hr. In the *pseudo*cumene the rotation decreased during the first 2 hr. but then remained constant. Schönberg, Rupp, and Gumlich[6] stated that diphenylene disulphide could dissociate reversibly into a biradical in solution. Hence it is very probable that the dinaphthylene disulphide dissociates into a biradical. This would be expected to have higher optical stability than the cyclic disulphide since in the latter the repulsive forces have been overcome during the formation of the S–S link. The *SS-iso*propylidene derivative of 2 : 2′-dimercapto-1 : 1′-dinaphthyl did not racemise in boiling mesitylene (166°) during 4½ hr. but lost 5% of its optical activity during 4½ hr. in boiling tetralin (207°). Similarly 1 : 1′-dinaphthyl-2 : 2′-thiolsulphonate underwent no racemisation in boiling ethylbenzene (136°) during 4 hr., but racemised completely in mesitylene at 200°, having lost half of its activity after about the first 30 min. In boiling tetralin (206·8°) the thiolsulphonate racemised with a half-life of 26 (±1) minutes. The half-life at 206·8° is thus approximately equal to that of " 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-thiolsulphonate " in boiling ethylbenzene (136°).

The preparation of dibenzothiophens by heating 2 : 2′-diarylene disulphides (dibenzo[*ce*]dithiins) with copper bronze was found to be satisfactory when diaryl-2 : 2′-thiolsulphonates (dibenzo[*ce*]dithiin 5 : 5-dioxides) were used.[1] The reaction of copper bronze and " 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-thiolsulphonate " (1 : 3 : 8 : 10-tetramethyldibenzo[*ce*]dithiin 5 : 5-dioxide) (III; R = Me) was investigated and the tetramethyldibenzothiophen was oxidised to a dioxide. The constitution of this dioxide was established by a different synthesis. Phenyl 4 : 6 : 2′ : 4′-tetramethyldiphenyl-2-sulphonate was prepared by an unsymmetrical Ullmann reaction on phenyl 2-iodo-3 : 5-dimethylbenzenesulphonate and 4-iodo-*m*-xylene. The ester was hydrolysed and the monosulphonic acid converted into 4 : 6 : 2′ : 4′-tetramethyldiphenyl-2-sulphonyl chloride. The latter cyclised to 2 : 4 : 5 : 7-tetramethyldibenzothiophen 9-dioxide (IV) which was identical with the previous thiophen dioxide.

The presence of the ·SO_2·S· groups in " diaryl-2 : 2′-thiolsulphonates " was demonstrated by the formation of these compounds by the direct oxidation of the disulphides[3, 1] and by mild reduction of the disulphides.[3] This group was thus shown to be present in (III;

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[5] Hall and Turner, *J.*, 1955, 1242.

[6] Schönberg, Rupp, and Gumlich, *Ber.*, 1933, **66**, 1932.

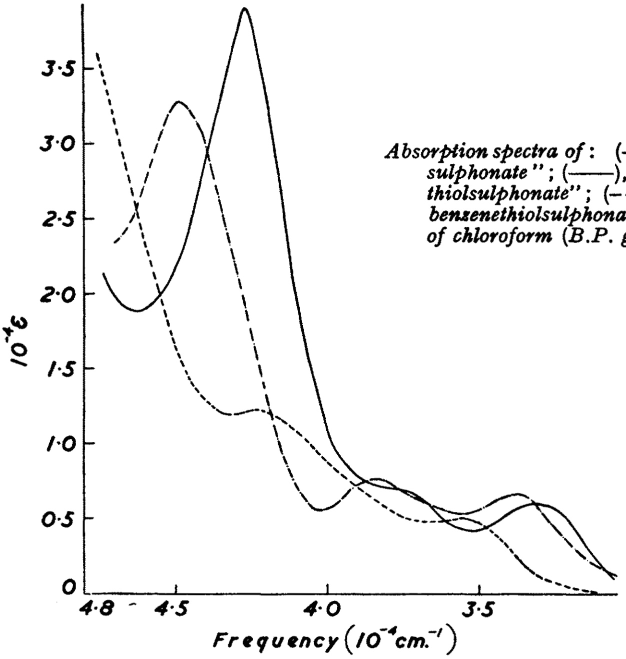
Ultraviolet absorption spectra.

(Wavelengths in parentheses denote inflections.)

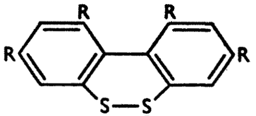
Compound	$\lambda_{\text{min.}}$	$\varepsilon_{\text{min.}}$	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	$\varepsilon_{\text{min.}}$
" Diphenyl-2 : 2′-thiolsulphonate " (III; R=H)	—	—	2230	32,900	2480	5550
" 4 : 6 : 4′ : 6′-Tetramethyldiphenyl-2 : 2′-thiolsulphonate " (III; R = Me)	2160	18,900	2338	38,000	—	—

Compound	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	$\varepsilon_{\text{min.}}$	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$
" Diphenyl-2 : 2′-thiolsulphonate " (III; R = H)	2610	7650	2810	5350	2960	6600
" 4 : 6 : 4′ : 6′-Tetramethyldiphenyl-2 : 2′-thiolsulphonate " (III; R = Me)	(2670)	(6850)	2835	4200	3020	5950

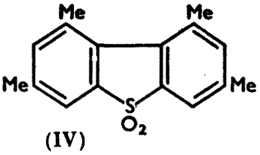
R = H) and (II; R = S, R′ = SO_2). Reduction of 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-disulphonyl dichloride was shown to give an unstable 2 : 2′-disulphinic acid [2] which cyclised to the corresponding 2 : 2′-thiolsulphonate. As 4 : 6 : 4′ : 6′-tetramethyl-2 : 2′-diphenylene disulphide could not be prepared [2] further evidence for the structure of (III; R = Me) was desirable. The optically active thiolsulphonate has a half-life period of 24 min.[2] at 136°, *i.e.*, about half that of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene at the same temperature,[5] and very much less than that of any of the diaryls with a seven-membered ring bridging the 2 : 2′-positions.[5, 7] Other evidence against structures such as –S·O·S– for the thiolsulphonate link involving higher-membered rings, *e.g.*, seven, was obtained from a comparative study of the ultraviolet absorption spectra of the compounds (III; R = H and Me) and (V).



Absorption spectra of: (—•—•—), " 1 : 1′-*diphenyl-2* : 2′-*thiolsulphonate* "; (——), " 4 : 6 : 4′ : 6′-*tetramethyldiphenyl-2* : 2′-*thiolsulphonate*"; (– – – –), 3 : 5-*dimethylphenyl* 3 : 5-*dimethylbenzenethiolsulphonate* (V); *in* 95% *ethanol containing* 1% *of chloroform* (*B.P. grade*).



(III)



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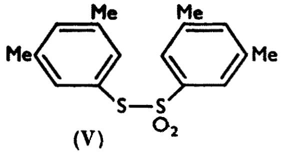

(V)

" Diphenyl-2 : 2′-thiolsulphonate " (III; R = H) shows a very high intensity band at

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[7] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

223 mμ and two bands of lower intensity at longer wavelengths (see Figure). The tetramethyl derivative (III; R = Me) shows a similar spectrum with a general shift towards longer wavelengths and an increase in intensity of the principal band such as might be expected to accompany the introduction of the four methyl groups. The similarity of the two spectra indicates that the same ring structure is almost certainly present in both compounds (III; R = H and Me).

EXPERIMENTAL

In all polarimetric readings $l = 2$; B.P. grade chloroform was used unless otherwise stated.

Phenyl 1-*Iodonaphthalene*-2-*sulphonate*.—526 G. of sodium 1-iodonaphthalene-2-sulphonate were prepared from 80 g. batches of sodium 1-aminonaphthalene-2-sulphonate. The yields were similar to those previously recorded.[3] All the former sodium salt was converted into the corresponding sulphonyl chloride by using an equivalent quantity of phosphorus pentachloride. It was practicable to use as much as 200 g. of the sodium salt in one batch. The crude iodosulphonyl chloride was crystallised from glacial acetic acid; it recrystallised from light petroleum (b. p. 100—120°) as colourless needles, m. p. 94—95 (yield 356 g., 68%). The second crystallisation removed a violet by-product.

An intimate mixture of 1-iodonaphthalene-2-sulphonyl chloride (176 g., 1 mol.), phenol (94 g., 2 mol.), and anhydrous sodium carbonate (79 g., 1½ mol.) was heated on a boiling-water bath for 1 hr. and then poured into ice-cold water. The precipitate was washed successively with dilute sodium carbonate, water, 2N-hydrochloric acid, and water. The dried *phenyl* 1-*iodonaphthalene*-2-*sulphonate* then crystallised from glacial acetic acid as flat colourless needles (yield from 311 g.: 352 g., 98%), m. p. 139° (Found: C, 46·3; H, 2·5. $C_{16}H_{11}O_3IS$ requires C, 46·8; H, 2·7%).

Diphenyl 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonate*.—Phenyl 1-iodonaphthalene-2-sulphonate (137 g.) was heated in a metal-bath kept at 150—160° and copper bronze (70 g.) stirred in, the temperature being kept below 300°. When the vigorous reaction was over, the ester was extracted with chlorobenzene. The extract was filtered and concentrated to a small volume. On cooling, *diphenyl* 1 : 1′-*dinaphthyl*-2 : 2′-*disulphonate* separated in small rhombs. After being recrystallised from glacial acetic acid it had m. p. 196—197° (yield from 352 g.: 202 g., 83%) (Found: C, 67·3; H, 4·0%; *M*, in boiling benzene, 551. $C_{32}H_{22}O_6S_2$ requires C, 67·8; H, 3·9%; *M*, 566).

Di-2-*naphthyl Disulphide*.—When 1-iodonaphthalene-2-sulphonyl chloride was reduced with excess of hydriodic acid (55% w/w) in boiling glacial acetic acid, the disulphide, m. p. 139° (lit., 139°), was obtained in 40% yield.

Disodium 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonate*.—To a boiling solution of diphenyl 1 : 1′-dinaphthyl-2 : 2′-disulphonate (56·6 g., 1 mol.) in butan-1-ol (2·5 l.) was added a solution of freshly cut sodium (9·2 g., 4 atom-equiv.) in butan-1-ol (500 ml.). The mixture was boiled for 45 min. Most of the disodium salt had then separated, but heating was continued for another 1½ hr. The solution was then concentrated to *ca.* 100 ml., poured into water (500 ml.), and acidified with 2N-hydrochloric acid. Phenol was extracted with ether, and the aqueous layer neutralised (Congo-red) with 10% sodium hydroxide solution and concentrated until a solid crystallised. Further concentration gave impure disulphonate. The overall yield from 202 g. of diester was 148 g. (anhydrous), 90%.

1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonyl Dichloride*.—This was obtained from the anhydrous disodium salt (43·0 g.), phosphorus pentachloride (43·0 g.), and phosphorus oxychloride (5 ml.). It crystallised from glacial acetic acid in long pale yellow needles, m. p. 203—204° (Barber and Smiles [3] gave 202—203°) (yield, 38·0 g., 89·5%).

1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide* (*Dinaphtho*[2,1-c, 1′,2′-e]*dithiin*) (II; R = R′ = S).—A solution of 1 : 1′-dinaphthyl-2 : 2′-disulphonyl dichloride (4·0 g.) in boiling glacial acetic acid (70 ml.) and hydriodic acid (55% w/w; 65 ml.) was allowed to cool to room temperature overnight. It was poured into water. The precipitate was freed from iodine by shaking it with warm sodium hydrogen sulphite solution; it crystallised from glacial acetic acid (250 ml.) as small bright yellow needles, m. p. 213—214° (Barber and Smiles [3] gave m. p. 214°) (2·5 g., 82%).

SS-iso*Propylidene Derivative of* 2 : 2′-*Dimercapto*-1 : 1′-*dinaphthyl* (4 : 4-*Dimethyldinaphtho*-[2, 1-b 1′, 2′-d][1, 3]*dithiepine*).—Through a solution of 1 : 1′-dinaphthylene 2 : 2′-disulphide (1·5 g.) in acetone (300 ml.; "AnalaR") containing zinc dust (2·0 g.) was passed a steady stream of dry hydrogen chloride. The gas did not react vigorously with the zinc and occasional heating on a water-bath was necessary to keep the solution boiling. After 20 min. the solution almost lost its yellow colour and the zinc had dissolved. In the next 20 min. the colour of the solution changed from pale yellow to orange and finally to scarlet. Heating and the passage of hydrogen chloride was continued for another 1½ hr. Acetone was distilled off and the residue poured into water (600 ml.), saturated with sodium chloride, and the organic layer that separated extracted with ether until the extracts were colourless. The ethereal extracts were washed twice with 10% sodium carbonate solution, then with brine, and dried (Na_2SO_4). The ether was distilled off and the residue allowed to cool. The solid *mercaptol* crystallised in large rhombs. This was triturated with small volumes of ethanol, filtered off, washed with ethanol, and recrystallised from butan-1-ol, forming colourless rhombs, m. p. 186—187° (0·90 g., 53%) (Found: C, 77·5; H, 5·3; S, 17·7. $C_{23}H_{18}S_2$ requires C, 77·0; H, 5·1; S, 17·9%).

1 : 1′-*Dinaphthyl*-2 : 2′-*disulphinic Acid*.—A mixture of 1 : 1′-dinaphthyl-2 : 2′-disulphonyl dichloride (5·0 g.), 30% aqueous sodium sulphite (400 ml.), and 10% aqueous sodium hydroxide (50 ml.) was shaken on a boiling-water bath for 2 hr. The solution obtained was filtered from a little unchanged disulphonyl dichloride, acidified with 4N-sulphuric acid (100 ml. excess), and heated on a boiling-water bath for 2 hr. The solid that separated was filtered off, washed with water, and dried (yield, 3·1 g., 71%). It could not be crystallised from common solvents and was partially soluble in cold 10% aqueous sodium hydroxide. It dissolved completely in the boiling alkali and was precipitated by dilute acid. The crude solid was crystalline (colourless needles) and melted at 165—167° with blackening and loss of sulphur dioxide [Found: C, 62·0; H, 3·6. $C_{20}H_{14}O_4S_2$ requires C, 62·8; H, 3·7%). Heating a suspension of this *disulphinic acid* (1·4 g., crude) in 4N-sulphuric acid (600 ml.) containing 55% w/w hydriodic acid (0·2 ml.) for 2½ hr. on a boiling-water bath did not convert it into the thiolsulphonate. Reduction with hydriodic–acetic acid converted it into the cyclic disulphide.

" 1 : 1′-*Dinaphthyl*-2 : 2′-*thiolsulphonate* " (*Dinaphtho*(2, 1-c, 1′, 2′-e]*dithiin* 3 : 3-*Dioxide*).—The above disulphinic acid (0·7 g.) could not be crystallised directly from glacial acetic acid but, after the acetic acid solution had been boiled for 10 min., the *thiolsulphonate* separated as pale yellow, highly refracting needles, m. p. 198—199° (0·5 g., 79%) (Found: C, 68·6; H, 3·6; S, 18·5. $C_{20}H_{12}O_2S_2$ requires C, 69·0; H, 3·5; S, 18·4%).

Optical Resolution of Distrychnine 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonate*.—Disodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate (68·7 g., 1·5 mol.) in water (1 l.) was added to a boiling solution of finely powdered strychnine (100·3 g., 3 mol.) in 0·1N-hydrochloric acid (3 l., 3 mol.). The mixture was allowed to cool overnight and the distrychnine salt was then filtered off (yield, 118 g.). This crop " A " had $[\alpha]_{5461}^{23}$ −55·3°, $[\alpha]_{5791}^{23}$ −46·7°. It was extracted with methanol (3 l. in all) until the insoluble residue showed no decrease in specific rotation. It was almost pure (+)-*acid* (−)-*base*, m. p. 294—296° (decomp.) with darkening at 270° (yield 64·0 g.), $[\alpha]_{5461}^{22}$ −23° ± 0·5°, $[\alpha]_{5791}^{22}$ −18° ± 0·5° (*c* 1·1040) (Found: C, 64·9; H, 5·7; N, 4·9. $C_{62}H_{58}O_{10}N_4S_2,4H_2O$ requires C, 64·5; H, 5·8; N, 4·9%).

The methanolic solution was evaporated to dryness and the residue recrystallised from methanol to constant specific rotation. Thus almost pure (−)-*acid* (−)-*base* was obtained, having m. p. 296—300° (decomp.) with darkening at 280° (yield 37·0 g.), $[\alpha]_{5461}^{23}$ −127° ± 0·5°, $[\alpha]_{5791}^{23}$ −109° ± 0·5° (*c* 1·0820) (Found: C, 66·0; H, 5·4; N, 4·7. $C_{62}H_{58}O_{10}N_4S_2,3MeOH$ requires C, 66·2; H, 6·0; N, 4·75%).

The aqueous mother-liquor from the precipitation of " A " was concentrated and by recrystallisation from methanol of the crystalline solid that was isolated a further 10·0 g. of almost pure (−)-acid (−)-base was obtained. Further concentration of the aqueous filtrate gave mixtures containing the racemate.

(−)-1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonyl Dichloride*.—All crops of the (+)-acid (−)-base with $[\alpha]_{5461}^{22}$ −23° (62 g.) were dissolved in chloroform (500 ml.), shaken with 2% sodium hydroxide solution (250 ml.), and then again shaken with 2% sodium hydroxide solution (120 ml.). The alkaline extracts were combined and extracted with chloroform until the extract was optically inactive. This alkaline solution was carefully neutralised (pH 7·0), evaporated to dryness, and dried for 30 min. at 120—130° [yield of crude (+)-disodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate, 43·0 g.].

A mixture of anhydrous (+)-disodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate (43·0 g., crude) and phosphorus pentachloride (43·0 g.) was heated on a boiling-water bath for 30 min., then poured into ice-cold water. The precipitated *dichloride* was filtered and dried *in vacuo* (KOH).

It crystallised from glacial acetic acid in needles, m. p. 248—249° (decomp.) (13·0 g., 1st crop), $[\alpha]^{21}_{5461}$ −26° ± 0·5°, $[\alpha]^{21}_{5791}$ −21° ± 0·5° (*c* 1·0870) (Found: C, 52·9; H, 2·8. $C_{20}H_{12}O_4Cl_2S_2$ requires C, 53·2; H, 2·7%).

(+)-1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonyl Dichloride*.—All crops of (−)-acid (−)-base with $[\alpha]_{5461}$ higher than −122° (42 g.) were dissolved in chloroform (400 ml.) and extracted with 2% sodium hydroxide solution (240 ml. in all) and treated as in the previous experiment. The yield of dry crude (−)-disodium 1 : 1′-dinaphthyl-2 : 2′-disulphonate was 42 g. The (−)-disodium salt was treated with an equal weight of phosphorus pentachloride and the (+)-1 : 1′-*dinaphthyl*-2 : 2′-*disulphonyl dichloride* purified from glacial acetic acid, forming needles, m. p. 248—249° (decomp.) (12 g.), $[\alpha]^{22}_{5461}$ +25·5° ± 0·5°, $[\alpha]^{22}_{5791}$ +21° ± 0·5° (*c* 1·1950) (Found: C, 53·0; H, 2·6%).

Attempted Racemisation of (−)-*Disodium* 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonate*.—An aqueous solution of the (−)-disodium salt with α_{5461} −0·25° and α_{5791} −0·20° was heated in a sealed tube at 190—200° for 10 hr. The rotation of the solution was unchanged.

(−)-1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide*.—A solution of (−)-1 : 1′-dinaphthyl-2 : 2′-disulphonyl dichloride (5·4 g.) in boiling acetic acid (170 ml.) and 55% w/w hydriodic acid (130 ml.) was allowed to cool to room temperature during 24 hr. The *dithiin* was treated as in the case of the racemic compound and recrystallised to optical purity from a large volume of glacial acetic acid (*ca.* 700 ml.); it formed bright yellow needles, m. p. 262—263° (rapid heating) (3·4 g.), $[\alpha]^{23}_{5461}$ −777° ± 1°, $[\alpha]^{23}_{5791}$ −748° ± 1° (*c* 0·5140) (Found: C, 76·1; H, 3·7. $C_{20}H_{12}S_2$ requires C, 75·9; H, 3·8%).

(+)-1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide*.—The (+)-disulphonyl dichloride was treated with hydriodic–acetic acid as in the case of its enantiomorph, and the (+)-*disulphide* was crystallised from glacial acetic acid to optical purity, yielding bright yellow needles, m. p. 262—263° (rapid heating), $[\alpha]^{23}_{5461}$ +775° ± 1°, $[\alpha]^{23}_{5791}$ +748° ± 1° (*c* 0·4480) (Found: C, 76·1; H, 3·6%).

Attempted Racemisation of (−)-1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide*.—(*a*) A solution of the (−)-disulphide in boiling ethylbenzene (137·6°) with α_{5461} −7·16° was heated. The rotation decreased during the first 2 hr. to α_{5461} −5·95° and then increased steadily. After 15 hours' boiling α_{5461} was −7·67°. As heating was continued an offensive odour developed.

(*b*) In boiling *pseudo*cumene (171·2°) a solution with α_{5461} −2·14° showed a decrease in optical activity during the first 3 hr. to α_{5461} −1·49° but the rotation remained at that value when heating was continued for 13 hr.

(−)-SS-iso*Propylidene Derivative of* 2 : 2′-*Dimercapto*-1 : 1′-*dinaphthyl*.—Through a solution of (−)-1 : 1′-dinaphthylene 2 : 2′-disulphide (1·5 g.) in boiling acetone (300 ml., "AnalaR") containing zinc dust (2·0 g.) was bubbled dry hydrogen chloride, and the reaction was completed as in the case of the racemic compound. The dark orange paste obtained after removal of the ether did not crystallise, and dissolved completely in ethanol. The paste was dissolved in light petroleum (b. p. 60—80°; 150 ml.) and purified by passing it through a column of alumina (1·7 × 20 cm.) and developed with light petroleum (b. p. 60—80°). The purification was studied optically. Evaporation of the highly optically active light petroleum solutions gave a pale yellow paste which crystallised to colourless prisms overnight. These were triturated with ethanol, and filtered off; they crystallised from butan-1-ol as small prisms, m. p. 155—156° (1·0 g.). The yield was very low when all the solutions were concentrated by distilling off the solvent on a water-bath at 100°, and one chromatographic purification was insufficient. Better yields were obtained when the solutions were concentrated *in vacuo*. The *mercaptol* had $[\alpha]^{21}_{5461}$ −368° ± 1°, $[\alpha]^{21}_{5791}$ −329° ± 1° (*c* 0·4725) (Found: C, 76·7; H, 4·9. $C_{23}H_{18}S_2$ requires C, 77·0; H, 5·1%).

(+)-1 : 1′-Dinaphthyl-2 : 2′-disulphide gave the (+)-*mercaptol*, which crystallised from butan-1-ol in small prisms, m. p. 155—156°, $[\alpha]^{20}_{5461}$ +367° ± 1°, $[\alpha]^{20}_{5791}$ +327° ± 1° (*c* 0·3500) (Found: C, 76·5; H, 5·0%).

Attempted racemisation. (*a*) No racemisation took place after boiling (166°) a mesitylene solution (α_{5461} −3·37°) of the mercaptol for 4½ hr.

(*b*) When a solution of the (+)-compound in boiling tetralin (207°) with α_{5791} +2·25° was heated for 4½ hr. a small fall (*ca.* 5%) in rotation occurred.

(−)-2 : 2′-*Dimercapto*-1 : 1′-*dinaphthyl*.—The disulphonyl dichloride (2·5 g.; $[\alpha]^{22}_{5461}$ −23·8°) dissolved in boiling glacial acetic acid (400 ml.) containing excess of zinc dust (10 g.) was cooled and slowly treated with concentrated hydrochloric acid (50 ml.). After most of the zinc had dissolved, the solution was filtered, poured into ice-cold water (1 l.), and saturated with sodium chloride. The solution was extracted with ether, and the extract shaken with 10% aqueous sodium hydroxide until the ethereal layer was alkaline. The aqueous layer was acidified with concentrated hydrochloric acid, and the dithiol allowed to coagulate. The white solid was filtered off, washed with water, and dried *in vacuo* (yield 0·6 g., 36%; m. p. *ca.* 100°). This had $[\alpha]^{22}_{5461}$ −33° ± 1°, $[\alpha]^{22}_{5791}$ −32° ± 1° (*c* 0·4980).

The ethereal solution was dried ($CaCl_2$) and the ether distilled off. The yellow residue of disulphide crystallised in bright yellow needles (from glacial acetic acid), m. p. 258—260° (0·3 g., 18%), $[\alpha]^{22}_{5461}$ −631°, $[\alpha]^{22}_{5791}$ −595° (*c* 0·0990).

(+)-2 : 2'-*Dimercapto*-1 : 1'-*dinaphthyl*.—The disulphide (2·0 g.) in glacial acetic acid (400 ml.) was reduced with zinc dust (4·0 g.) and concentrated hydrochloric acid (25 ml.), filtered, and poured into water. The white alkali-soluble solid that separated was filtered off, washed, and dried; it had m. p. *ca.* 100° (1·3 g., 65%), $[\alpha]^{22}_{5461}$ +67° ± 1°, $[\alpha]^{22}_{5791}$ +66° ± 1° (*c* 0·5690).

Oxidation of (+)-2 : 2'-*Dimercapto*-1 : 1'-*dinaphthyl*.—A solution of the (+)-dithiol (0·2 g.) in boiling ethanol (50 ml.) was treated with anhydrous ferric chloride (3·0 g.) and heated on a boiling-water bath for ½ hr. On cooling, a solid separated. It was filtered off and dried; it crystallised from glacial acetic acid in bright yellow needles, m. p. 261—262° (0·14 g., 70%), $[\alpha]^{21}_{5461}$ +750°, $[\alpha]^{21}_{5791}$ +720° (*c* 0·1500).

" (−)-1 : 1'-*Dinaphthyl*-2 : 2'-*thiolsulphonate*."—Finely powdered (−)-1 : 1'-dinaphthyl-2 : 2'-disulphonyl dichloride (2·0 g.), 30% aqueous sodium sulphite (140 ml.), and 10% aqueous sodium hydroxide (20 ml.) were shaken at *ca.* 100° for 2 hr. The solution was filtered, acidified with 2N-sulphuric acid (100 ml.; excess), and heated on a boiling-water bath for 1½ hr. The solid that was precipitated was filtered off, washed, dried, and crystallised from methanol; it formed pale yellow needles (0·7 g.), m. p. 162°. The rotation approached zero with blue (mercury) light (Found: C, 68·4; H, 4·0. $C_{20}H_{12}O_2S_2$ requires C, 69·0; H, 3·5%). For rotations see p. 15.

" (+)-1 : 1'-*Dinaphthyl*-2 : 2'-*thiolsulphonate* " was prepared as its enantiomorph from the (+)-disulphonyl dichloride and formed pale yellow needles, m. p. 162° (Found: C, 69·0; H, 3·5%). For rotations see p. 15.

Racemisation. (*a*) No racemisation occurred when a solution of the (+)-compound in boiling ethylbenzene (135·8°) with α_{5791} +1·69° was heated for 4½ hr.

(*b*) A solution of the (−)-compound in mesitylene with α_{5791} 1·13° racemised completely after 2 hr. when heated in a sealed tube at 200° (±2°). It lost about half its activity after the first 30 min.

(*c*) The rate of racemisation in boiling tetralin (206·8°) was measured by using a solution (25 ml.) of the (+)-compound. This was raised rapidly to its b. p. and after suitable intervals was cooled rapidly with water. Polarimetric readings were taken at 20° and the solution returned to the flask and re-heated for a further period. α_{5791} fell from +0·80° to 0° during 2 hr.: k was 2·7(±0·2) × 10^{-2} min.$^{-1}$ and the half-life 26 ± 1 min.

(*d*) The rate of racemisation in boiling tetralin (207·7°) was repeated with the (−)-enantiomorph: k was 2·8(±0·2) × 10^{-2} min.$^{-1}$ and $t_{0.5}$ 25 ± 1 min.

2 : 4 : 5 : 7-*Tetramethyldibenzothiophen*.—4 : 6 : 4' : 6'-" Tetramethyldiphenyl-2 : 2'-thiolsulphonate "[2] (1·0 g.) was heated with copper bronze (2·0 g.) at 250—260° for 2 hr. Sulphur dioxide was evolved. Distillation at 20 mm. gave a yellow oil which slowly became a waxy yellow solid. This *dibenzothiophen* crystallised from light petroleum (b. p. 60—80° and 80—100°) in long pale yellow needles, m. p. 121—122° (0·3 g., 37%) (Found: C, 80·0; H, 7·1. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%).

Phenyl 4 : 6 : 2' : 4'-*Tetramethyldiphenyl*-2-*sulphonate*.—Phenyl 2-iodo-3 : 5-dimethylbenzenesulphonate [2] (38·8 g., 1 mol.) was heated in 4-iodo-*m*-xylene (46·4 g., 2 mol.; prepared from *m*-4-xylidine) with copper bronze (50 g.) in a bath at 180—190°. The vigorous reaction was over in 10 min. After extraction with hot chloroform and separation of insoluble material the crude product was obtained as a residue by distilling off the chloroform. This was poured into water and excess of iodoxylene removed by steam-distillation. The solid residual *ester* was filtered off, dried, and crystallised several times from ethanol and finally from butan-1-ol, forming short colourless needles, m. p. 90—91° (19·0 g., 52%) (Found: C, 72·0; H, 6·3. $C_{22}H_{22}O_3S$ requires C, 72·1; H, 6·1%).

4 : 6 : 2' : 4'-*Tetramethyldiphenyl*-2-*sulphonyl Chloride*.—A mixture of phenyl 4 : 6 : 2' : 4'-tetramethyldiphenyl-2-sulphonate (12·2 g., 1 mol.) in absolute ethanol (100 ml.) with a solution

of sodium ethoxide (1·5 g., 2 mol., of sodium in 50 ml. of alcohol) was boiled under reflux. After 2 hr. the reaction was not complete since a portion of the solution gave a white precipitate with water. A further quantity of sodium ethoxide (2 mol.) in ethanol was added and boiling continued for another 2 hr. Ethanol was distilled off, the residue poured into water and acidified, phenol extracted with ether, and the aqueous layer concentrated to a small volume. A solid crystallised in silver flakes (5·2 g.; anhydrous).

The sulphonic acid (5·2 g.) was heated with phosphorus pentachloride (5·2 g.) on a water-bath for 10 min. The mixture was poured into water and the pasty *sulphonyl chloride* isolated and dried in a vacuum-desiccator (KOH). It crystallised from toluene in fine white needles, m. p. 128—130° (0·9 g., 16%) (Found: S, 10·4. $C_{16}H_{17}O_2ClS$ requires S, 10·4%).

2 : 4 : 5 : 7-*Tetramethyldibenzothiophen* 9 : 9-*Dioxide*.—(*a*) A mixture of 4 : 6 : 2′ : 4′-tetramethyldiphenyl-2-sulphonyl chloride (0·50 g.), tetrachloroethane (25 ml.), and anhydrous aluminium chloride (0·35 g.) was heated on a boiling-water bath for 30 min. The reaction was vigorous at first and the solution became pale green with violet fluorescence. The reaction was completed by keeping at room temperature for 4 hr. The solution was then diluted with water (100 ml.) and tetrachloroethane distilled off in steam. The residue was cooled and the solid product collected, dried, and crystallised from glacial acetic acid, forming long white needles, m. p. 304—305° (0·3 g., 68%) (Found: C, 71·0; H, 6·2; S, 11·6. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9; S, 11·8%).

(*b*) A solution of 2 : 4 : 5 : 7-tetramethyldibenzothiophen (0·12 g.), obtained from (II; R = Me), in boiling glacial acetic acid (10 ml.) was added to 3% aqueous potassium permanganate (10 ml.), and the mixture kept for 10 min. The solution was decolorised with sodium hydrogen sulphite solution, and the white solid dioxide filtered off and crystallised from glacial acetic acid, forming long white needles (0·1 g., 74%), m. p. 304—305° (mixed m. p. 303—305°).

3 : 5-*Dimethylbenzenesulphonyl Chloride*.—2-Diazo-3 : 5-dimethylbenzenesulphonate was reduced with absolute ethanol containing *ca.* 1 g. of copper bronze and sodium 3 : 5-dimethylbenzenesulphonate was isolated in the usual manner. The anhydrous salt and an equal weight of phosphorus pentachloride were heated together on a boiling-water bath for 20 min., then poured into cold water, and the solid sulphonyl chloride was isolated, dried, and crystallised from light petroleum (b. p. 60—80°); it formed yellow needles, m. p. 94° (Moschner[8] gave m. p. 89—90°; Armstrong and Wilson[9] gave m. p. 94°). The overall yield of the sulphonyl chloride from 62 g. of diazo-salt was 41%.

Phenyl 3 : 5-*dimethylbenzenesulphonate* was obtained from the sulphonyl chloride and phenol in dry pyridine. It crystallised from ethanol in rhombs, m. p. 68—69° (Found: S, 11·7. $C_{14}H_{14}O_3S$ requires S, 12·2%).

3 : 5-*Dimethylphenyl* 3 : 5-*Dimethylbenzenethiolsulphonate* (V).—3 : 5-Dimethylbenzenesulphonyl chloride (1·8 g.) was shaken with a solution of sodium sulphite (40 ml. containing 8 g.) and made alkaline with 10% sodium hydroxide solution (30 ml.). The mixture was kept at *ca.* 100° until all the solid dissolved. The solution was then filtered and acidified with dilute hydrochloric acid (10 ml.; 50% excess). The whole was kept at *ca.* 100° until all the solid coagulated. The *dioxide* was then filtered off and dried; it crystallised from glacial acetic acid as colourless needles, m. p. 116—117° (0·9 g.) (Found: C, 62·4; H, 5·7; S, 20·8. $C_{16}H_{18}O_2S_2$ requires C, 62·8; H, 5·9; S, 20·9%). Ultraviolet absorption: $\lambda_{\text{min.}}$ 232 mμ, ε 12,000; $\lambda_{\text{max.}}$ 236·5 mμ, ε 12,300; $\lambda_{\text{min.}}$ 275 mμ, ε 4800; $\lambda_{\text{max.}}$ 281 mμ, ε 5000.

1 : 3 : 8 : 10-*Tetramethyldibenzo*[ce]*dithiin*.—(*a*) A solution of 3 : 5-dimethylbenzenesulphonyl chloride (5·0 g.) in ethanol (100 ml.) containing zinc dust (19·6 g.) was cooled to 0°. Concentrated hydrochloric acid (25 ml.) was added slowly and the temperature of the solution kept at 10°. The mixture was kept at room temperature for 4 hr., then heated on a boiling-water bath for 30 min., and anhydrous ferric chloride (10 g.) was added. Pouring the whole into water precipitated an oil, which solidified, and was filtered off, washed, and dried. It crystallised from ethanol in waxy prisms, m. p. 35—36° (1·5 g., 45%).

(*b*) The sulphonyl chloride (2·0 g.) in boiling acetic acid (20 ml.) was added to hydriodic acid (*d* 1·7; 20 ml.) and left in the dark for 24 hr. The solution was poured into ice-cold water saturated with sulphur dioxide, and the waxy solid collected, dried, and crystallised from ethanol; the *dithiin* formed prisms, m. p. and mixed m. p. 36—37° (1·0 g., 38%) (Found: C, 69·7; H, 6·6; S, 23·8. $C_{16}H_{16}S_2$ requires C, 70·0; H, 6·6; S, 23·4%).

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[8] Moschner, *Ber.*, 1901, **34**, 1257.

[9] Armstrong and Wilson, *Chem. News*, 1901, **83**, 46.

(*c*) A solution of the thiolsulphonate (0·5 g.) in boiling acetic acid (10 ml.) and 55% w/w hydriodic acid (10 ml.) was boiled for 5 min., and kept at room temperature for 2 hr. The mixture was treated as in (*b*) and the product was extracted with ether, as it could not be isolated as a solid. The extract was dried ($CaCl_2$) and the ether distilled off. The oily residue solidified on cooling (yield, 0·35 g., 77%) and had m. p. and mixed m. p. 35—36°.

Reduction of 4 : 8-*Dimethyldibenzo*[ce]*dithiin followed by Condensation of the Dithiol with Carbon Disulphide.*—The disulphide (2·0 g.) in ethanol (150 ml.) was reduced with zinc dust and concentrated hydrochloric acid until the yellow colour of the solution was discharged. The alcoholic solution was poured into water (600 ml.) and treated with 2N-hydrochloric acid; the excess of zinc was washed with ethanol, and the washings were added to the aqueous solution. The oil that separated was extracted with ether, the ethereal solution dried (Na_2SO_4), and the ether distilled off. The residual oil solidified when cooled with solid carbon dioxide.

The oil was dissolved in 10% sodium hydroxide solution (40 ml.), and excess of carbon disulphide (20 ml.) was added. The mixture was boiled under reflux for 2 hr. and excess of carbon disulphide distilled off. Cooling of the alkaline solution caused 4 : 4′-*dimethyl*-2 : 2′-*diphenylene trithiocarbonate* to separate as a red solid. This was filtered off, dried, and crystallised from ethanol or glacial acetic acid, forming orange-red needles, m. p. 177—178° (0·4 g., 18%) (Found: C, 62·4; H, 4·2; S, 32·8. $C_{15}H_{12}S_3$ requires C, 62·5; H, 4·2; S, 33·3%).

Ultraviolet Absorption Spectra.—The compounds used were dissolved in chloroform (1 ml.; " B.P. grade ") and the solutions made up to 100 ml. with 95% ethanol. The spectra were measured on a Unicam S.P. 500 spectrophotometer.

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