# CCCLVI.—*Phototropic Amino-aryl Disulphoxides.*

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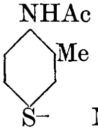
In a previous communication (J., 1924, **125**, 2359), it was shown that acetanilide *p*-disulphoxide (I) is phototropic, but examination of the material then available did not reveal the existence of other disulphoxides endowed with this property. Use has now been made of the various methods of synthesising disulphoxides in the exploration of this group, with the result that further information is available concerning the structural and physical conditions which determine the phototropic character. The orientation of the amino-groups is of importance; thus, whilst aniline and acetanilide *p*-disulphoxides may be obtained in the phototropic state, the property has not been observed with the *o*- and *m*-derivatives. Introduction of hydrocarbon groups in the aromatic nuclei of acetanilide *p*-disulphoxide does not profoundly influence the phototropic character, 1-*acetylaminonaphthyl* 4-*disulphoxide* (II) and

2-*acetylaminotolyl* 5-*disulphoxide* (as III) * having both been isolated as phototropic materials.



(III.)

$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NHAc$ (I.)

$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_6H_4Me$ (IV.)

$NHAc{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}S{\cdot}C_{10}H_6{\cdot}NHAc$ (II.)

$C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NHAc$ (V.)

Acylation of the amino-groups in aniline *p*-disulphoxide diminishes the sensitiveness of the material and may obliterate the phototropic character. The diacetyl derivative is less sensitive than the parent substance, but the *dicarbethoxy*- and the *dicarbomethoxy*-compounds appear to be devoid of phototropic character. Finally, two unsymmetrical disulphoxides containing one *p*-acetylamino-group have been examined, *viz.*, p-*tolyl* p-*acetylaminobenzenethiolsulphonate* (IV) and p-*acetylaminophenyl* p-*chlorobenzenethiolsulphonate* (V). Only the latter is phototropic, hence it seems that the presence of one amino-group in the thiol-substituted nucleus is sufficient to evoke the property. Other substances related to acetanilide disulphoxide have been examined, and among these *acetanilide* p-*disulphone* (VI) and p-*acetylaminophenyl* p-*acetylaminobenzenesulphonate* (VII) are not phototropic.

$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}NHAc$ (VI.)

$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}NHAc$ (VII.)

Of greater interest than these structural conditions attending the property is the fact that after thorough purification neither acetanilide *p*-disulphoxide nor aniline *p*-disulphoxide is phototropic; but when a pure inactive sample of either of these disulphoxides is mixed with a small quantity—about 0·1%—of the corresponding disulphide the material becomes phototropic, and with larger amounts of the disulphide—up to about 5%—the product acquires a permanent deep yellow colour. By no means all disulphides stimulate acetanilide *p*-disulphoxide in this manner; the effect appears to be confined to those disulphides containing the 4-amino- or substituted 4-amino-phenyl group, and it is remarkable that the 3-acetylamino- and 2-acetylamino-phenyl disulphides are without influence either on the corresponding disulphoxides or on the

* This derivative of *o*-toluidine was obtained by converting the corresponding sulphonic acid (Nevile and Winther, *Ber.*, 1880, **13**, 1941) into the disulphide and oxidising this with hydrogen peroxide. The disulphide, of which the orientation is thus known, is identical with the disulphide obtained by Hodgson (J., 1912, **101**, 1700) from the product of interaction of sulphur and *o*-toluidine hydrochloride at a high temperature. The constitution of this material has hitherto been uncertain.

4-acetylamino-phenyl isomeride. No theoretical interpretation of these facts is offered at present, but the relation between the phototropy of these disulphoxides and the presence of small quantities of the reduction products accords with the opinion of Stobbe (*Annalen*, 1908, **359**, 1) that phototropic change is accompanied by chemical change in the material. Moreover it is evident that support is forthcoming in aid of the opinion expressed by Gallagher (*Bull. Soc. chim.*, 1921, **29**, 961), who has claimed on other grounds a close connexion between the phenomena of phosphorescence and phototropy.

## EXPERIMENTAL.

*Aniline* p-*Disulphoxide.*—Recrystallised acetanilide-*p*-disulphoxide, prepared from hydrogen iodide and acetanilide-*p*-sulphinic acid, was hydrolysed with boiling hydrochloric acid, and the diluted solution made weakly acid (to thymol-blue) by addition of sodium carbonate. The precipitate was repeatedly crystallised from acetone with the aid of charcoal. The product formed colourless leaflets, m. p. 183° (Found: N, 10·2; S, 23·0. Calc.: N, 10·0; S, 22·9%). The material described (J., 1924, **125**, 2361) as yellow (m. p. 175°) contained disulphide. A pure inactive sample of acetanilide *p*-disulphoxide obtained by treating the purified base with acetic anhydride was colourless and had m. p. 236—237° (decomp.). These substances cannot be purified by means of hot alcohol (compare Hinsberg, *Ber.*, 1909, **42**, 1278), since this solvent generates the disulphides by reduction.

The influence of disulphides on the properties of these and other disulphoxides was investigated by adding excess of water to cold acetic acid or acetone solutions containing measured quantities of the substances. Since these are insoluble in water, the required mixtures separated in the crystalline state. Mere admixture of the solid materials is not sufficient to induce phototropy and it is probable that the formation of mixed crystals is necessary to these phenomena of stimulation.

*Dicarbomethoxyaminodiphenyl* p-*disulphoxide*,

$$S_2O_2(C_6H_4{\cdot}NH{\cdot}CO_2Me)_2,$$

was obtained by boiling a solution of the crude base in acetone for ½ hour with methyl chloroformate and sodium carbonate. After purification it formed colourless needles, m. p. 186° (Found: C, 48·7; H, 4·3. $C_{16}H_{16}O_6N_2S_2$ requires C, 48·4; H, 4·0%). The *dicarbethoxy*-compound, $S_2O_2(C_6H_4{\cdot}NH{\cdot}CO_2Et)_2$, prepared in a similar manner, formed leaflets, m. p. 162° (Found: C, 50·7; H, 4·9; N, 6·8. $C_{18}H_{20}O_6N_2S_2$ requires C, 50·9; H, 4·7; N, 6·6%).

*Dicarbethoxyaminodiphenyl* p-*disulphide*, $S_2(C_6H_4{\cdot}NH{\cdot}CO_2Et)_2$, forms prisms, m. p. 136—137°, from alcohol (Found: C, 54·9; H, 5·2. $C_{18}H_{20}O_4N_2S_2$ requires C, 55·1; H, 5·1%).

p-*Acetylaminophenylmethylsulphone*, $NHAc{\cdot}C_6H_4{\cdot}SO_2Me$, prepared by methylation of the sulphinic acid, separated from hot water in needles, m. p. 183° (Found: N, 6·7. $C_9H_{11}O_3NS$ requires N, 6·5%).

*Acetanilide* p-*Disulphone* (VI).—Potassium permanganate (0·8 g.) was gradually added to a cooled, stirred solution of acetanilide-*p*-sulphinic acid (6 g.) in acetic acid (80 c.c.). The required material (1·2 g.), isolated after the addition of excess of sulphurous acid, was colourless, almost insoluble in the usual solvents, and had m. p. 245—250° (decomp.) (Found: C, 48·6; H, 4·4. $C_{16}H_{16}O_6N_2S_2$ requires C, 48·4; H, 4·1%). No evidence of phototropic properties of these sulphones and urethanes could be obtained.

p-*Acetylaminophenyl* p-*Acetylaminobenzenesulphonate* (VII).—A mixture of *p*-acetylaminobenzenesulphonyl chloride (4·6 g.), *p*-acetylaminophenol (3 g.), and dry pyridine (2 g.) was kept at 100° for ½ hour. The desired substance (3 g.) was isolated by treating the product with dilute sulphuric acid. Purified from alcohol, it had m. p. 218° (Found: C, 55·0; H, 4·8; S, 9·2. $C_{16}H_{16}O_5N_2S$ requires C, 55·1; H, 4·6; S, 9·2%).

*Acetanilide* o-*Disulphoxide*.—Aniline *o*-disulphide (Mohlau, *Ber.*, 1912, **45**, 134) was converted into the *diacetyl* derivative, which separated from dilute acetic acid in needles, m. p. 156° (Found: C, 57·6; H, 5·0. $C_{16}H_{16}O_2N_2S_2$ requires C, 57·8; H, 4·8%). A solution of this substance (2·8 g.) in acetic acid (28 c.c.) containing hydrogen peroxide (2 c.c. of 30% solution) was kept for 4 days and then added to water (150 c.c.). The material which separated crystallised from dilute acetic acid (charcoal) in colourless plates (1·5 g.), m. p. 140° (Found: C, 52·5; H, 4·5; N, 7·8. $C_{16}H_{16}O_4N_2S_2$ requires C, 52·7; H, 4·5; N, 7·7%). Poorer yields of the disulphoxide were obtained when larger quantities of material were used. The substance was not phototropic and was not stimulated when mixed with the corresponding disulphide.

*Acetanilide*-m-*sulphinic Acid*.—Finely-divided acetanilide-*m*-sulphonyl chloride was treated with an excess of sodium sulphite in aqueous alkaline solution until it dissolved. The required sulphinic acid (60% yield) was liberated by addition of sulphuric acid; after crystallisation from hot water, it had m. p. 145° (Found: N, 7·1. $C_8H_9O_3NS$ requires N, 7·0%).

When a solution of this sulphinic acid (20 g.) in water (800 c.c.) containing a few drops of hydriodic acid and an excess of sulphurous acid was kept at 90° for 2—3 hours, *acetanilide* m-*disulphoxide* was precipitated (30% yield). Crystallised from dilute acetic acid with the aid of charcoal, this substance was obtained colourless and had m. p. 212—213° (decomp.). It was not sensitive to light either in the pure condition or when mixed with the disulphide (Found: C, 52·3; H, 4·9; N, 7·7. $C_{16}H_{16}O_4N_2S_2$ requires C, 52·7; H, 4·5; N, 7·7%).

2-*Acetylaminotoluene*-5-*sulphonyl Chloride* (formula as III).—Thoroughly dried sodium 2-acetylaminotoluene-5-sulphonate (20 g.), which had been obtained from the aminosulphonate by treatment with acetic anhydride, was triturated with phosphorus pentachloride (20 g.) until the liquid material had solidified. After 1 hour, the product was treated in the usual manner; the dried sulphonyl chloride (16 g.) crystallised from benzene in needles, m. p. 159°, which were soluble in the usual media (Found: C, 43·3; H, 4·3; Cl, 14·4; S, 12·9. $C_9H_{10}O_3NClS$ requires C, 43·6; H, 4·1; Cl, 14·4; S, 12·9%).

2-*Acetylaminotoluene*-5-*sulphinic Acid*, $NHAc{\cdot}C_6H_3Me{\cdot}SO_2H$.—The sulphonyl chloride (18 g.) was shaken with an aqueous alkaline solution (100 c.c.) of sodium sulphite (50 g.), and dilute sulphuric acid (60%) added to the solution obtained. The *sulphinic acid* (70% yield), which separated crystalline, after recrystallisation from hot water, had m. p. 147° (Found: N, 6·6. $C_9H_{11}O_3NS$ requires N, 6·6%).

Attempts to convert this acid into the disulphoxide by means of dilute hydriodic and sulphurous acids failed, the only product isolated being a small quantity of the disulphide. 2-*Acetylaminotolyl* 5-*mercaptan*, $NHAc{\cdot}C_6H_3Me{\cdot}SH$, prepared by reducing an alcoholic solution of the sulphonyl chloride with zinc and hydrochloric acid (compare Zincke, *Ber.*, 1909, **42**, 3367), formed needles, m. p. 143°, from aqueous alcohol (Found: C, 59·6; H, 6·5; S, 17·5. $C_9H_{11}ONS$ requires C, 59·6; H, 6·1; S, 17·7%). 2-*Acetylamino*-5-*tolyl methyl sulphide*, $NHAc{\cdot}C_6H_3Me{\cdot}SMe$, obtained from the mercaptan and methyl sulphate, had m. p. 134° (Found: C, 61·2; H, 6·7. $C_{10}H_{13}ONS$ requires C, 61·4; H, 6·7%). Oxidation of the mercaptan in alcoholic solution with ferric chloride yielded 2-*acetylaminotolyl* 5-*disulphide*, $(S{\cdot}C_6H_3Me{\cdot}NHAc)_2$, which separated from acetic acid in leaflets, m. p. 222° (Found: C, 59·9; H, 5·2. $C_{18}H_{20}O_2N_2S_2$ requires C, 59·9; H, 5·5%). On hydrolysis with concentrated hydrochloric acid this substance was converted into 2-*aminotolyl* 5-*disulphide* (Found: C, 60·3; H, 5·6. $C_{14}H_{11}N_2S_2$ requires C, 60·8; H, 5·8%), which, after purification by means of aqueous alcohol, had m. p. 112°. This substance and its acetyl derivative were identified in the usual manner with the corresponding materials prepared from *o*-toluidine hydrochloride and sulphur by Hodgson's method (*loc. cit.*).

2-*Acetylaminotolyl* 5-*disulphoxide* (as III) was obtained by the action of hydrogen peroxide (30% solution) on a mixture of the disulphide and acetic acid (20 parts). After 8 days, the solution was treated with water and the material which separated was purified in the usual manner. The substance, m. p. 183° (decomp.), separated from hot alcohol in yellow needles (Found: C, 54·9; H, 5·3. $C_{18}H_{20}O_4N_2S_2$ requires C, 55·1; H, 5·1%). This colour was undoubtedly due to the presence of a small quantity of the disulphide, but sufficient material was not available for treatment by the method applied to the acetanilide derivative.

1-*Acetylaminonaphthalene*-4-*sulphinic Acid*, $NHAc{\cdot}C_{10}H_6{\cdot}SO_2H$.—1-Acetylaminonaphthalene-4-sulphonyl chloride (Schroeter, *Ber.*, 1906, **39**, 1559; Zincke and Schutz, *Ber.*, 1912, **45**, 473) (30 g.) was shaken with sodium sulphite (110 g.) and water (200 g.) until it dissolved. The required *acid* was isolated in the usual manner; after crystallisation from dilute alcohol, it had m. p. 176° (decomp.) (Found: C, 57·6; H, 4·2. $C_{12}H_{11}O_3NS$ requires C, 57·8; H, 4·4%).

1-*Acetylaminonaphthyl* 4-*disulphoxide* (III) was obtained (25% yield) from the sulphinic acid by treatment in aqueous alcohol with sulphurous and hydriodic acids in the usual manner. The *disulphoxide*, which separated very slowly, was collected at intervals to avoid the inclusion of a more soluble blue material which was simultaneously formed (compare Reissert, *Ber.*, 1922, **55**, 858). It crystallised from acetic acid in pale yellow needles, m. p. 234° (decomp.) (Found: C, 61·8; H, 4·6. $C_{24}H_{20}O_4N_2S_2$ requires C, 62·0; H, 4·3%). It is probable that the substance contained a trace of the disulphide. The orange tint developed by exposing the material to sunlight was rapidly destroyed at 100°. Proof that the substance contains the disulphoxide structure was obtained by the action of 2 : 5-dibromophenyl mercaptan (compare Gibson and Smiles, J., 1924, **125**, 178), 1-acetylaminonaphthalene-4-sulphinic acid and the following unsymmetrical disulphide being produced.

2 : 5-*Dibromophenyl* 4-*acetylaminonaphthyl disulphide*,

$$NHAc{\cdot}C_{10}H_6{\cdot}S{\cdot}S{\cdot}C_6H_3Br_2,$$

separates from alcohol in colourless needles, m. p. 189° (Found: Br, 33·2. $C_{18}H_{13}ONBr_2S_2$ requires Br, 33·1%).

*Acetanilide*-p-*sulphonyl iodide*, $NHAc{\cdot}C_6H_4{\cdot}SO_2I$, was prepared by adding the requisite amount of iodine, dissolved in alcohol, to a dilute aqueous solution of sodium acetanilide-*p*-sulphinate. It was purified by the addition of light petroleum to an ethereal solution and formed yellow needles, m. p. 97° (decomp.) (Found: I, 39·1. $C_8H_8O_3NIS$ requires I, 39·0%).

p-*Tolyl* p-*acetylaminobenzenethiolsulphonate* (IV) was obtained (10% yield) by the interaction of silver *p*-tolyl mercaptide and acetanilide-*p*-sulphonyl iodide in presence of dry ether (compare Miller and Smiles, J., 1925, **127**, 229). The soluble *p*-tolyl disulphide also formed was readily separated from the required *disulphoxide*, this being sparingly soluble in alcohol. It was colourless, had m. p. 169° (decomp.), and was not phototropic (Found : C, 56·1; H, 4·6. $C_{15}H_{15}O_3NS_2$ requires C, 56·0; H, 4·7%).

p-*Acetylaminophenyl* p-*Chlorobenzenethiolsulphonate* (V).—When the requisite amount of bromine was added to acetanilide *p*-disulphide (m. p. 215°) suspended in carbon tetrachloride, an orange, crystalline material was formed. This was evidently acetanilide *p*-sulphur bromide, since it was converted by alcohol and similar agents into the original disulphide, but it was not sufficiently stable to permit isolation for analysis. This material was triturated with an excess of silver *p*-chlorobenzenesulphinate in presence of carbon tetrachloride. The insoluble portion was collected and treated with alcohol, which dissolved the required disulphoxide and acetanilide disulphide. These were separated in the usual manner. The unsymmetrical *disulphoxide* was obtained in colourless needles, m. p. 200—201° (decomp.), which became yellow on brief exposure to sunlight; the colour disappeared when the sample was kept in the dark (Found : C, 49·0; H, 3·3. $C_{14}H_{12}O_3NClS_2$ requires C, 49·1; H, 3·5%).

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