INVESTIGATION OF 2,1,3-THIA- AND 2,1,3-SELENADIAZOLES

LXVII.* NITRATION OF NAPHTHO[1,2-d][2,1,3]THIADIAZOLE

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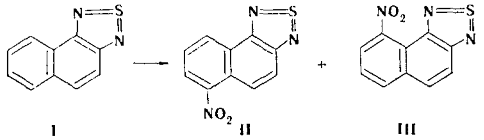
The nitration of naphtho[1,2-d][2,1,3]thiadiazole under the conditions that are normally used for aromatic compounds gives a mixture of 6- and 9-nitronaphthothiadiazoles, which can be reduced to 6- and 9-amino derivatives, respectively. 6-Hydroxynaphthothiadiazole is obtained from 6-aminonaphthothiadiazole by the Sandmeyer reaction, while 8-hydroxynaphthothiadiazole is converted to the 8-amino derivative under the conditions of the Bucherer reaction. 4-Carboxy-5-(o-carboxyphenyl)-2,1,3-thiadiazole was obtained by the oxidation of naphtho[1,2-d][2,1,3]-thiadiazole with a potassium dichromate–dilute sulfuric acid mixture.

In developing our research on the reactivity of condensed 2,1,3-thiadiazole systems, we turned to a study of the substitution reactions of naphtho[1,2-d][2,1,3]-thiadiazole (I) [2].

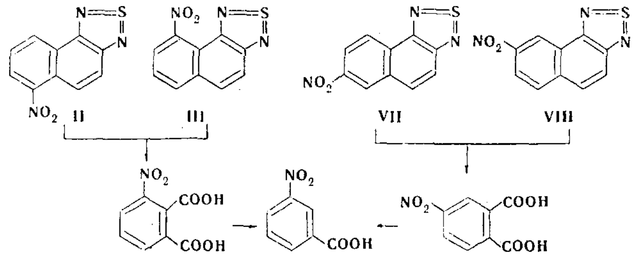
In the present paper we report the results of a study of the nitration of I.

A mixture of two isomeric nitro derivatives – 6-nitro- (II) and 9-nitronaphthothiadiazole (III) – is formed in high yield when I is nitrated with a nitrating mixture. Isomer II is the chief reaction product, and a small amount of III can be isolated only by chromatography.



The 6-amino (IV) and 9-aminonaphthothiadiazoles (V) obtained from nitro derivatives II and III can be separated by fractional crystallization; we used this method to establish the structure of nitro compounds II and III. Amines IV and V were converted to the corresponding chlorides and bromides† by means of the Sandmeyer reaction, while amine IV was converted to the corresponding hydroxy derivative (VI).

The position of the nitro group in II was determined by means of its oxidation products and by data from a study of amine IV.



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*See [1] for communication LXVI.

†See the following communication for information regarding the chloro-and bromonaphthothiadiazoles.

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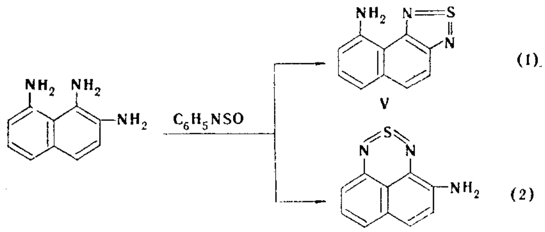
m-Nitrobenzoic acid was isolated from the oxidation of nitro compound II with potassium permanganate in the presence of alkali; this result corresponds to four possible positions for the nitro group (isomeric structures II, III, VII, and VIII). 3-Nitrophthalic acid was isolated when the reaction was carried out without alkali; the formation of this acid shows that the nitro group occupies either the 6 or 9 positions. To solve this problem, we synthesized amine IV by the reaction of thionylaniline with 1,2,5-triaminonaphthalene (IX) [3]. In view of the fact that triamine IX is formed in very low yield, the aminonaphthothiadiazole (IV) obtained from it was not isolated in pure form. Spots with identical R_f values were detected when the latter was chromatographed in the presence of amine IV, obtained from nitro compound II.

Additional proof was obtained in a comparison of amine IV (the product of the reduction of nitro derivative II) with the three other isomeric 7- (X), 8- (XI), and 9-aminonaphthothiadiazoles (V), obtained by alternative synthesis by the reaction of thionylaniline with 1,2,6- [4], 1,2,7- [5], and 1,2,8-triaminonaphthalenes [6], respectively. Amine IV had properties (melting point and UV and IR spectra) that differed from those of amines X, XI, and V. Amine XI was also obtained by the Bucherer reaction [7] by heating the 8-hydroxy derivative of I (XII) with a mixture of ammonium bisulfite and 25% ammonium hydroxide. Hydroxynaphthothiadiazole XII was obtained by the reaction of thionylaniline with 1,2-diamino-7-hydroxynaphthalene [8].

The position of the nitro group in III was proved by comparison of the amine (V) obtained from it with the analogous amine obtained from 1,2,8-triaminonaphthalene and also by comparison of the spectra of amine V (obtained from III) and of the same amine obtained by the reaction of 1,8-naphthalenediamine with sulfur nitride [9].

The preparation of amine V by the reaction of 1,2,8-triaminonaphthalene with thionylaniline is worthy of attention. In this reaction, one might have expected the formation of 2-aminonaphtho[1,8-c,d][1,2,6]-thiadiazine [10-12].



The predominant occurrence of the reaction via direction 1 shows that the formation of the thiadiazole ring is preferred over the formation of the thiadiazine ring.

The results of the nitration of I can be explained when the latter is considered as an α,β-disubstituted naphthalene. As a structural element of the benzo-2,1,3-thiadiazole system, the thiadiazole ring has an electron-withdrawing effect in electrophilic and nucleophilic substitution reactions [13-15]. It is therefore natural when likening I to a disubstituted naphthalene to turn for comparison to α,β-disubstituted naphthalenes that contain electron-withdrawing substituents. It is known [16] that in the electrophilic substitution reactions of β-halo and (partially) α-halo-, α- and β-sulfo-, and α- and β-nitronaphthalenes, the next substituent enters primarily the ring that is not bonded to the substituent; in this case the substituent enters primarily the 5 and 8 positions and, less frequently, the 5 and 7 positions. This is explained by deactivation of the ring attached to the electron-acceptor substituent.

Thus the nitration of I, which leads to a mixture of isomeric 6- and 9-nitro derivatives, proceeds in the same way as the nitration of naphthalene derivatives with electron-acceptor substituents. Naphth[1,2-d]-[2,1,3]oxadiazole [17] is similarly nitrated.

Above it was pointed out that 3-nitrophthalic and m-nitrobenzoic acids are formed by the action of potassium permanganate on nitro compound II; i.e., the benzene ring bonded to the thiadiazole ring and the heteroring itself primarily undergo attack. When benzothiadiazole is oxidized under these conditions, the benzene ring attached to the thiadiazole ring is oxidatively cleaved to give 4,5-dicarboxy-2,1,3-thiadiazole [13-15]. The lower resistance to oxidizing agents of polycyclic heteroaromatic systems as compared with the stability of one- and two-ring systems is an expression of their weakened aromaticity.

No appreciable changes are observed when a potassium dichromate–dilute sulfuric acid mixture or chromic anhydride in concentrated sulfuric acid act on II. Under similar conditions (with the dichromate

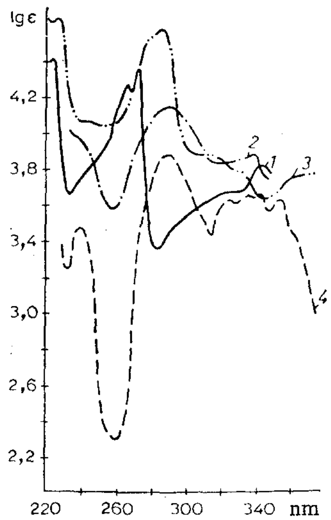


Fig. 1. UV spectra (in ethanol): 1) naphtho-[1,2-d][2,1,3]thiadiazole (I); 2) 6-nitronaphtho-[1,2-d][2,1,3]thiadiazole (II); 3) 8-hydroxy-naphtho[1,2-d][2,1,3]thiadiazole (XII); 4) 9-nitronaphtho[1,2-d][2,1,3]thiadiazole (III).

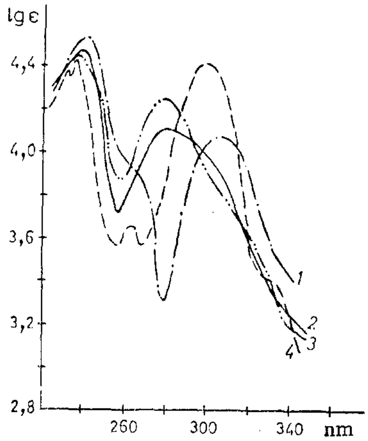
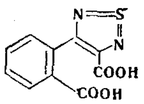


Fig. 2. UV spectra (in ethanol): 1) 7-amino-naphtho[1,2-d][2,1,3]thiadiazole (XV); 2) 9-aminonaphtho[1,2-d][2,1,3]thiadiazole (XVII); 3) 6-aminonaphtho[1,2-d][2,1,3]thiadiazole (XIV); 4) 8-aminonaphtho[1,2-d][2,1,3]thiadiazole (XVI).

TABLE 1. Shift of the Maximum of the Absorption Band as a Function of the Type and Position of the Substituent

Substituent and compound number		Substituent position	λ_1, nm	λ_2, nm	λ_{av} nm	$\Delta\lambda_{av}=\lambda_{av}-\lambda_{av_0}$, nm
	I		268	274	271	
NO_2	II	6	290			+19
	III	9	290			+19
	IV	6	278			+ 7
NH_2	X	7	305			+34
	XI	8	298			+27
	V	9	280			+ 9
OH	XII	8	280	286	283	+12

mixture), 4-carboxy-5-(o-carboxyphenyl)-2,1,3-thiadiazole (XIII) is obtained from I, judging from the results of elementary analysis and potentiometric titration.



XIII

Thus the introduction of an electronegative group into the naphthodiazole molecule increases the stability of the system with respect to the action of the dichromate mixture or chromic acid. This makes it possible to assume that oxidation proceeds hydrolytically under these conditions.

Electronic Spectra

The electronic spectrum of I has three absorption bands. The first band is situated at 210-225 nm and has two maxima; the second band is observed at 265-275 nm, and it also has two maxima. Finally, the third band, which has a rather distinctly expressed structure, is found at 290-360 nm. Similar groups of bands are present in the spectra of derivatives of I. As seen from Figs. 1 and 2, all three groups of bands in the spectra of the naphthothiadiazoles are quite characteristic. In general, the spectrum of I recalls the spectra of hydrocarbons with condensed aromatic rings, such as naphthalene and phenanthrene [18, 19]. This similarity is evidence that naphthothiadiazoles are aromatic systems with a common π-electron cloud.

The introduction of such substituents as an amino group converts the structured band to a smooth curve with one maximum. This is caused by participation of the unshared electron pairs in the resonance of the aromatic system. Nitro groups have an identical effect in the 6 and 9 positions. In the case of amino groups, however, the maximum shift is observed in the 7 position. The amino groups can be arranged in the following order with respect to the degree of decrease in the bathochromic shift: 7-NH_2 > 8-NH_2 > 9-NH_2 > 6-NH_2. Like other positions of the nitro group, the 6 and 9 positions of the amino group are identical. This can be used to identify the type of substitution from data on the bands in this region.

Replacement of a hydrogen by a hydroxyl group also induces a bathochromic shift.

EXPERIMENTAL

6-Aminonaphtho[1,2-d][2,1,3]thiadiazole (IV) and 9-Aminonaphtho[1,2-d][2,1,3]thiadiazole (V). A. A mixture of 30 ml of nitric acid (sp. gr. 1.4) and 50 ml of sulfuric acid (sp. gr. 1.84) was added slowly with stirring at 0-2° to 18.6 g (0.1 mole) of I [20] in 50 ml of concentrated sulfuric acid, after which the mixture was stirred at 20° for 30 min and poured over 2 kg of ice. The precipitate was removed by filtration, washed with water until it was neutral, and air dried to constant weight to give 22.6 g (98%) of a mixture of nitro compounds II and III with mp 115-155°. Glacial acetic acid (4 ml) was poured into a mixture of 50 g of iron filings and 200 ml of boiling water, after which 16 g of the mixture of II and III was added in small portions with stirring. The mixture was then refluxed for 15 min, cooled to 5°, and filtered. The solid material was washed with ice water, and it and the filtrate were extracted with ether. The ether was evaporated to give 9.6 g (70%) of a substance with mp 80-85°. Successive fractional crystallization from 4% hydrochloric acid, treatment of the filtrates with 25% ammonium hydroxide, and subsequent fractional crystallization from alcohol gave amine IV with mp 149-150° and amine V with mp 127-128°. These products did not depress the melting points of amines obtained by alternative synthesis (see below). The hydrochloride of amine IV with mp 264-265° (from 4% hydrochloric acid) was also isolated in the process of separating the mixture; it did not depress the melting point of the hydrochloride of amine IV (mp 182°) obtained by reduction of nitronaphthothiadiazole. Found, %: N 17.8, 17.6; Cl 14.3, 14.4. $C_{10}H_7N_3S \cdot HCl$. Calculated: N 17.7; Cl 14.9%. In addition, a substance with mp 112-114°, which, according to the results of analysis, corresponds to aminonaphtho[1,2-d][2,1,3]thiadiazole, was also isolated. This substance is possibly a mixture of amines IV and V, since only two nitro derivatives (II and III) were detected during the chromatographic investigation of the mixture of nitration products with mp 115-155°.

B. A mixture of 1,2,5-triaminonaphthalene hydrochloride (the product of the reduction of 1,5-dinitro-2-aminonaphthalene), 1 ml of thionylaniline, and 15 ml of pyridine was heated on a boiling-water bath for 1 h, cooled, and acidified with 4% hydrochloric acid until it gave an acid reaction to Congo. The resulting precipitate was dried and crystallized from alcohol (with activated charcoal). The reaction product was chromatographed in a loose layer of activity II (Brockmann classification) aluminum oxide and on paper in the presence of a reference spot – amine IV with mp 149-150°, obtained by reduction of nitro derivative II; both substances had R_f 0.78 (in ether). The paper chromatography was carried out in butanol–ethanol–water (3 : 1 : 4) with development with UV light and iodine vapors.

6-Nitronaphtho[1,2-d][2,1,3]thiadiazole (II). A mixture of nitric acid (sp. gr. 1.4) and 5 ml of sulfuric acid (sp. gr. 1.84) was added slowly with stirring at 0-2° to 1.86 g (0.01 mole) of I in 7 ml of concentrated sulfuric acid, after which the mixture was stirred at 20° for 30 min and poured over 200 g of ice. The resulting precipitate was removed by filtration, washed with water until it was neutral, and recrystallized from ethanol or isopropyl alcohol to give 0.94 g (41%) of colorless crystals with mp 182-183°. Found, %: N 17.4, 17.5; S 14.0, 13.8. $C_{10}H_5N_3O_2S$. Calculated, %: N 18.2; S 13.9.

6-Aminonaphtho[1,2-d][2,1,3]thiadiazole (IV). A total of 0.8 ml of 98% acetic acid was added to a mixture of 3.5 g of iron filings and 20 ml of boiling water, after which 1 g (0.0045 mole) of II was added in portions with stirring. The mixture was refluxed for 20 min, cooled to 5°, and filtered. The solid material was washed with ice water, and it and the filtrate were extracted with ether. The ether was evaporated and the residue was crystallized from aqueous alcohol to give 0.78 g (90%) of a substance with mp 149-150° that was soluble in alcohol and ethyl acetate. The product did not depress the melting point of amine IV, isolated from a mixture of amines IV and V with mp 80-85°. Chromatography of the substance in a thin layer of aluminum oxide and on paper in the presence of amine IV, obtained from 1,2,5-triaminonaphthalene, gave identical R_f values (0.78 in a thin layer and 0.73 on paper). Found, %: N 20.9; 20.8; S 15.9, 15.8. $C_{10}H_7N_3S$. Calculated, %: N 20.9; S 15.9. The hydrochloride was obtained by saturation of an ether solution of amine IV with hydrogen chloride (while cooling); it had mp 264-265° and was insoluble in ether. The acetyl derivative was obtained as follows. A mixture of 1 g (0.005 mole) of amine IV, 0.6 ml of acetic anhydride, and 10 ml of acetic acid was heated on a boiling-water bath for 40 min. It was then cooled, diluted with water, and heated to the boiling point. This mixture was then cooled and the precipitate was removed by filtration, washed with water, and crystallized from alcohol to give 0.95 g (78%) of colorless needles with mp 230-232°. Found, %: N 16.8, 17.0. $C_{12}H_9N_3OS$. Calculated, %: N 17.3. The benzoyl derivative [1.25 g (83%)] was obtained as colorless needles with mp 212° (from alcohol) from 1 g (5 mmole) of amine IV, 0.7 g of benzoyl chloride, and 10 ml of pyridine by heating at 100° for 1 h. The product was insoluble in water. Found, %: N 14.2, 13.9; S 10.64. $C_{17}H_{11}N_3OS$. Calculated, %: N 13.8; S 10.5.

6-Hydroxynaphtho[1,2-d][2,1,3]thiadiazole (VI). A solution of 0.3 g (4.2 mmole) of sodium nitrite in 4 ml of water was added at −2 to −8° to a solution of 0.5 g (2.5 mmole) of amine IV in 10 ml of sulfuric acid (sp. gr. 1.84) and 5 ml of water. The solution was stirred for 30 min, after which it was added dropwise to hot 50% sulfuric acid (on a boiling-water bath). The mixture was stirred until the evolution of gas bubbles had ceased, and it was then made alkaline with 30% alkali solution and filtered. The filtrate was acidified with hydrochloric acid to give a substance with mp 198-200° (from aqueous solutions). Found,%: N 13.9, 13.7; S 15.6. $C_{10}H_6N_2OS$. Calculated, %: N 13.9; S 15.8.

9-Nitronaphtho[1,2-d][2,1,3]thiadiazole (III). A mixture of 1.8 ml of nitric acid (sp. gr. 1.4) and 5 ml of sulfuric acid (sp. gr. 1.84) was added slowly with stirring at 0-2° to 1.86 g (0.01 mole) of I in 7 ml of concentrated sulfuric acid, after which the mixture was stirred at 20° for 30 min and poured over 200 g of ice. The precipitate was removed by filtration, washed with water until it was neutral,* and dried. The mixture of nitro isomers was separated by preparative thin-layer chromatography (TLC) on a loose layer of activity II (Brockmann classification) aluminum oxide. A 5.5-mg sample of the mixture (with mp 115-155°) was dissolved in 1 ml of chloroform and chromatographed with a petroleum ether−ether (1 : 1) system. The aluminum oxide layer containing a spot with R_f 0.64 (detection in UV light), which corresponds to III,† was collected and extracted with chloroform. The chloroform extract was filtered, and the residue was crystallized from alcohol to give light-yellow crystals with mp 126-127°. Found,%: N 18.5, 18.6. $C_{10}H_5N_3O_2S$. Calculated, %: N 18.2.

9-Aminonaphtho[1,2-d][2,1,3]thiadiazole (V). A. A mixture of 4 g (0.017 mole) of 1,8-dinitro-2-naphthylamine hydrochloride [7], 32 g (0.14 mole) of hydrated stannous chloride, and 40 ml of alcohol saturated with hydrogen chloride was heated with stirring for 30 min on a water bath (70°). It was then cooled and diluted with a fivefold quantity of water, and the tin was precipitated with hydrogen sulfide. The mixture was filtered, and the filtrate was vacuum evaporated to dryness in a stream of carbon dioxide. Dry pyridine (50 ml) and 6.6 ml of thionylaniline were added to the residue, and the mass was heated for 1 h on a boiling-water bath, cooled, and acidified (with respect to Congo) with 4% hydrochloric acid. The precipitate was removed by filtration and crystallized from aqueous alcohol to give light-yellow needles with mp 127-128° that did not depress the melting point of a sample isolated from a mixture of amines IV and V. Found, %: N 20.9, 20.8; S 15.6, 15.6. $C_{10}H_7N_3S$. Calculated, %: N 20.9, S 15.9. The hydrochloride was obtained as follows: A mixture of 0.2 g of amine V and 20 ml of hydrochloric acid (sp. gr. 1.19) was refluxed for 30 min to give 0.1 g (40%) of a substance with mp 201-203° (from 8% hydrochloric acid) that did not depress the melting point of a sample obtained from amine V, which was isolated from a mixture of amines IV and V (see below).

B. The alcohol filtrate obtained after isolation of nitro derivative II from the products of nitration of I (see above) was evaporated to dryness, and the residue was reduced with a mixture of iron filings and 2% acetic acid as described above to give a mixture of amines IV and V with mp 68-75°. A 0.3-g sample of this mixture was refluxed for 1 h with 20 ml of hydrochloric acid (sp. gr. 1.19), and the hot mixture was filtered and allowed to stand overnight to give 0.2 g (57%) of a substance with mp 193-194°. Recrystallization from 8% hydrochloric acid gave colorless crystals with mp 201-202° that did not depress the melting point of the hydrochloride obtained via method A. Found, %: N 18.0, 18.0. $C_{10}H_7N_3S \cdot HCl$. Calculated, %: N 17.7. The acetyl derivative was obtained as follows. a. A mixture of 0.2 g of amine V, 2 ml of glacial acetic acid, and 2 ml of acetic anhydride was refluxed for 1 h to give 0.15 g (75%) of a substance with mp 131-134°; recrystallization from glacial acetic acid gave a product with mp 135-137° that did not depress the melting point of a sample obtained from amine V, which was isolated from a mixture of amines IV and V with mp 68-75° (see below).

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*A substance (0.15 g) with mp 280-281° (from alcohol), which was the dinitro derivative of I, was detected in the wash waters. Found, %: N 20.0, 20.3. $C_{10}H_4N_4SO_4$. Calculated, %: N 20.3.

†Under similar conditions, R_f for II was 0.91.

b. A 0.3-g sample of mixture of amines IV and V with mp 68-75°, 3 ml of acetic anhydride, and 3 ml of glacial acetic acid gave 0.2 g (83%) of a substance with mp 130-133°. Recrystallization from glacial acetic acid gave a product with mp 135-137°. Found, %: N 17.8, 18.0; S 13.8, 14.3. $C_{12}H_9N_3OS$. Calculated, %: N 17.3; S 13.9.

7-Aminonaphtho[1,2-d][2,1,3]thiadiazole (X). A mixture of 12 g (0.5 mole) of 1,6-dinitro-2-aminonaphthalene, 8 g (0.7 mole) of tin, and 50 ml of hydrochloric acid (sp. gr. 1.19) was heated for 1 h on a boiling-water bath. The mixture was then cooled, diluted with a sixfold quantity of water, and filtered. The filtrate was saturated with hydrogen sulfide until the precipitation of tin was complete, and the mixture was filtered. The clear filtrate was evaporated to dryness in vacuo in a stream of carbon dioxide. Thionylaniline (20 g) and 100 ml of pyridine were added to the dry residue, and the mass was heated for 1 h on a boiling-water bath. It was then cooled and treated with 4% hydrochloric acid (until it was acid to Congo). The precipitate was removed by filtration, washed with ice water, and crystallized from aqueous alcohol to give a product with mp 158-159°. Found, %: N 20.1, 21.2; S 16.5, 16.5. $C_{10}H_7N_3S$. Calculated, %: N 20.9; S 15.9.

8-Hydroxynaphtho[1,2-d][2,1,3]thiadiazole (XII). A mixture of 2.5 g of 7-hydroxy-1,2-dioximinonaphthalene [21], 12.5 g of stannous chloride, and 13 ml of hydrochloric acid (sp. gr. 1.19) was heated for 1 h on a boiling-water bath. The mixture was cooled, diluted with a fivefold quantity of water, and saturated with hydrogen sulfide until the precipitation of tin was complete. The mixture was filtered, and the precipitate was washed with water. The filtrate and wash waters were vacuum evaporated to dryness in a stream of carbon dioxide, and 6.6 ml of thionylaniline and 15 ml of dry pyridine were added to the residue. The mass was heated for 1 h on a boiling-water bath, cooled, and acidified (with respect to Congo) with 4% hydrochloric acid. The precipitate was removed by filtration, washed with water, and crystallized from aqueous alcohol to give sparkling light-yellow crystals with mp 178-179°. Found, %: N 14.3, 13.9; S 15.4, 15.6. $C_{10}H_6N_2OS$. Calculated, %: N 13.9; S 15.8.

8-Aminonaphtho[1,2-d][2,1,3]thiadiazole (XI). A. A sealed tube containing 3 g of ammonium sulfite, 0.5 g of XII, and 20 ml of 25% ammonium hydroxide was heated at 160-170° for 30 h and cooled. The mass was treated with 10% sodium hydroxide solution, and the solid material was removed by filtration, washed with water until it was neutral, and dried to give 0.3 g of yellow crystals with mp 143-145° (from aqueous alcohol). Found: N 20.9; 21.1; S 15.8; 15.6%. $C_{10}H_7N_3S$. Calculated: N 20.9; S 15.9%.

B. A mixture of 0.7 g of 1,7-dinitro-2-aminonaphthalene [6], 42 ml of alcohol, 8.6 ml of hydrochloric acid (sp. gr. 1.19), and 0.7 g of stannous chloride was heated for 2 h on a boiling-water bath. The mixture was then cooled, diluted with a fivefold quantity of water, and saturated with hydrogen sulfide until precipitation of tin was complete. The mixture was filtered, and the precipitate was washed with water. The filtrate and wash waters were vacuum evaporated to dryness in a stream of carbon dioxide. Dry pyridine (15 ml) and 1 ml of thionylaniline were added to the vacuum-dried residue (1,2-diamino-7-hydroxynaphthalene hydrochloride). The mass was then heated for 1 h on a boiling-water bath, cooled, and acidified (with respect to Congo) with 4% hydrochloric acid. The mixture was then concentrated in vacuo, made alkaline (with respect to litmus) with ammonia, and extracted with ether. The solvent was removed, and the residue was crystallized from aqueous alcohol (with charcoal) to give 0.2 g of yellowish-greenish crystals with mp 144-146° that did not depress the melting point of X obtained in experiment A.

Oxidation of 6-Nitronaphtho[1,2-d][2,1,3]thiadiazole (II). A. A solution of 25 g of potassium permanganate in 475 ml of water was added in the course of 1 h to a suspension of 2.5 g of II in 50 ml of hot (90-95°) water. Alcohol (10 ml) was then added and the mixture was cooled. The manganese dioxide was removed by filtration, and the filtrate was acidified (with respect to Congo) with hydrochloric acid and evaporated to dryness to give crystals with mp 205-210° (from water) that did not depress the melting point of 3-nitrophthalic acid [21].

B. A hot solution of 15 g of potassium permanganate in 106 ml of water was added dropwise to a refluxing mixture of 4 g of II, 30 ml of water, and 34.5 ml of 0.5 N sodium hydroxide, and the mixture was refluxed with stirring for another 30 min. It was then cooled and filtered, and the filtrate was acidified (with respect to Congo) with hydrochloric acid and evaporated to dryness to give crystals with mp 133° (from alcohol) that did not depress the melting point of m-nitrobenzoic acid [21].

4-Carboxy-5-(o-carboxyphenyl)-2,1,3-thiadiazole (XIII). A solution of 14 g of potassium dichromate in 90 ml of dilute sulfuric acid (1 :3) was added dropwise in the course of 1.5 h to a solution of 5.5 g of naphthothiadiazole I in 70 ml of dilute sulfuric acid (1 :3). The mass was refluxed for 7 h and poured into a threefold quantity of water. The starting I (2.8 g) was removed by filtration, and the filtrate was evaporated to a volume of 20 ml and cooled. The resulting precipitate was crystallized from water to give colorless crystals with mp 205-207°. Found, %: N 11.1, 10.7; S 13.3, 13.6. mol. wt. 253, 254. $C_{10}H_6N_2O_4S$. Calculated, %: N 11.2; S 12.8; mol. wt. 250.

The UV spectra of alcohol solutions of the compounds were recorded with an SF-4A spectrometer. The IR spectra of mineral oil suspensions were recorded with a UR-10 spectrometer.

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