

most striking is that referred to by D. Deutsch.<sup>2</sup> He dissolved certain dyes in water and produced a color change by shaking this solution with equal volumes of benzene or another immiscible liquid. Deutsch explained the color change, which is reversible and can be repeated at will, by assuming that the dissociation of the dyestuff molecule changes according to the dielectric constant of the medium, *i. e.*, dissociation increases in a medium of high dielectric constant (water), and decreases in a medium of low dielectric constant (benzene). This theory has been opposed by Thiel,<sup>3</sup> who is of the opinion that this explanation does not hold for the cases of *thymolsulfonephthalein* and *tropaeoline OO*.

The purpose of my experiments was to repeat Deutsch's findings and to offer, if possible, a more general explanation of the phenomenon.

Various concentrations of every dyestuff were tried at a given *pH*, to determine the conditions of most pronounced color change. The following concentrations have been found to be the most effective ones.<sup>4</sup>

Malachite green base (C. I. 657) in 0.4 <i>N</i> HCl.....	0.0025%
Brilliant green base (C. I. 662) in 0.25 <i>N</i> HCl.....	.025-0.01%
Brom thymol blue in tap water.....	.001-0.0005%
Thymolsulfonephthalein (C. I. 764) in 0.0016 <i>N</i> HCl.....	.01-0.025%
Rhodamine O (C. I. 749) in benzene...	.0005%

It should be mentioned here that the color changes do not reach their maximum stability in the first twelve hours, because the dissolution of the dye is not instantaneous. Since the color of the solution becomes increasingly deeper, final observations were made with specimens which had been stored for at least twelve hours. This change is particularly pronounced in the case of *thymolsulfonephthalein*.

It was also found that methyl violet (C. I. 680),<sup>5</sup> which so far has not been reported in connection with these experiments, gives a color change in 0.1 *N* hydrochloric acid. The color changes on shaking from blue to purple. I was unable to reproduce the color change of *tropaeoline OO* (C. I. 143), under the conditions given by

(2) D. Deutsch, *Ber.*, **60**, 1036 (1927); D. Deutsch, *Z. physik. Chem.*, **136** 353 (1928).

(3) Thiel, *Z. Elektrochem.*, **35**, 266 (1929).

(4) Deutsch used in all cases 0.01% solutions.

(5) The *methyl violet* used and reported by Deutsch is actually *crystal violet* (C. I. 681).

Deutsch. However I did obtain a distinct color change in the foam at a *pH* of 2.28.

A general explanation of the entire phenomenon, on basis of the Hardy-Harkins rule of least abrupt change in the interfacial layer, seemed promising. However since the color changes of the sulfonephthaleins did not yield to explanation on this basis, a general explanation is still missing.

CINCINNATI, OHIO

RECEIVED APRIL 15, 1940

#### 4,4'-Diaminodiphenyl Sulfone

BY A. M. VANARENONK AND E. C. KLEIDERER

4,4'-Diaminodiphenyl sulfone has recently<sup>1</sup> become of interest because of its potency in combating experimental streptococcal infections in mice.

In our work we have been employing a method which differs from the published procedures.<sup>2,3,4</sup>

Thioaniline in an impure form may be obtained commercially and purified by means of its relatively insoluble disulfate. Subsequent acetylation with acetic anhydride and oxidation with hydrogen peroxide yields the 4,4'-diacetylaminodiphenyl sulfone, which may then be hydrolyzed to produce the free 4,4'-diaminodiphenylsulfone.

**Purification of Thioaniline.**—300 g. of crude thioaniline is dissolved in a solution of 300 g. of concentrated sulfuric acid in 6 liters of water, boiled for a few minutes and filtered. The filtrate is treated with 50 g. of decolorizing carbon, boiled, filtered, and concentrated without heat under vacuum until cold and filtered. The filtrate is then concentrated under vacuum to about 2 liters, cooled, and filtered. The two lots of precipitate are dissolved in 8 liters of boiling water, treated with Norit and filtered. While the filtrate is still warm, it is made alkaline with ammonia and cooled in the chill room overnight. The purified thioaniline weighs 95–105 g. and melts at 105–107° (uncor.). The product is a light tan in color.

**4,4'-Diacetylaminodiphenyl Sulfone.**—To 30 g. of thioaniline in a beaker is added a solution of 60 cc. of acetic anhydride in 120 cc. of glacial acetic acid. The solution is boiled gently for one hour on a hot plate, allowed to cool to room temperature, and 500 cc. of glacial acetic acid added; 50 cc. of superoxol is added with stirring, and the solution is allowed to stand without stirring for three hours. The temperature of the solution rises to about 40° during the first hour. At the end of the three hours, it is warmed to 50° and allowed to stand for two hours and then heated to boiling when practically all of the precipitate dissolves. The solution is allowed to cool until ebullition ceases and 30 cc. of superoxol added. The solution is allowed to come

(1) Buttle, Stephenson, Smith, Dewing and Foster, *Lancet*, **I**, 1331–1334 (1937).

(2) Fromm and Wittmann, *Ber.*, **41**, 2264–2273 (1908).

(3) British Patent 510,127.

(4) Sugawara and Sakurai, *J. Pharm. Soc. Japan*, **60**, 22–24 (1940); *C. A.*, **34**, 3704 (1940).

to room temperature and placed in the refrigerator overnight. The precipitate is filtered off, and the filtrate treated with twice its volume of water and placed in the refrigerator for several hours.

The precipitate of 4,4'-diacetylaminodiphenyl sulfone weighs about 30 g. The melting point should be between 275–278° (uncor.), and the material in the melting point tube should not become very dark on melting. In case the material is not very pure, it is dissolved in boiling acetic acid, and 10 cc. of superoxol added. It is then placed in the refrigerator and cooled overnight.

The residue obtained by precipitating the filtrate with water is filtered off and saved until a sufficiently large number of residues is obtained. These are combined and dissolved in boiling glacial acetic acid, and 5 cc. of superoxol for each 10 g. of residue added. The solution is cooled overnight in the refrigerator and the precipitate filtered off. The residue from each run amounts to about 10–20% of the weight of thioaniline used.

**4,4'-Diaminodiphenyl Sulfone.**—To 10 g. of 4,4'-diacetylaminodiphenyl sulfone is added a solution of 25 cc. of concentrated hydrochloric acid (sp. gr. 1.2) in 75 cc. of water. The mixture is refluxed for one and one-half to two hours when all of the solid is dissolved. Decolorizing carbon is then added and refluxing continued for one hour. It is filtered while hot, the filtrate cooled, ammonium hydroxide added until the solution is almost neutral and then cooled again. When the solution is cold, an excess of ammonia is added. The precipitate is filtered off, dissolved in water with just enough hydrochloric acid added to dissolve the amine, and decolorizing carbon added. It is allowed to stand for fifteen minutes or more and then filtered. The filtrate is made alkaline with ammonia, cooled, and filtered. The product weighs about 7 g., and melts at 172–174° (uncor.). It may be recrystallized from methyl alcohol if a purer product is desired, the pure 4,4'-diaminodiphenyl sulfone melting at 175–176° (uncor.).

THE LILLY RESEARCH LABORATORIES  
INDIANAPOLIS, INDIANA RECEIVED SEPTEMBER 9, 1940

## NEW COMPOUNDS

### ADDITION COMPOUNDS OF ZINC, CADMIUM, COBALT AND NICKEL HALIDES WITH 1,4-DIOXANE

1,4-Dioxane was dehydrated by refluxing with sodium metal for two hours, allowing to remain in contact with anhydrous magnesium sulfate for twenty-four hours, and distilling. Dioxane thus purified gave no color reaction with anhydrous copper sulfate. The anhydrous halides were commercial preparations.

Two procedures for the preparation of the compounds were employed. If the halide is appreciably soluble in dioxane at room temperature, a 25-ml. portion of the solvent was saturated by adding an excess of finely powdered halide. After standing for several days the solution was decanted, and then evaporated in a desiccator over concentrated sulfuric acid until crystals separated out. The compounds were separated from the mother liquor by

decantation and pressing between layers of filter paper. This is designated in the Table as procedure I.

When the halide is slightly soluble, it was allowed to remain in contact with the dioxane for several days before removing and separating from the solvent as described above, procedure II.

Formulas were determined by analysis for halide content by Mohr's method. The experimental percentages given are the mean of two or more determinations.

TABLE I

Formula	Halide content, %		Color	Pro- cedure
	Calcd.	Found		
ZnCl <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	31.6	31.4	White	I
ZnCl <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	22.7	21.9	White	a
ZnBr <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	39.8	40.0	White	I
ZnI <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	51.2	51.1	White	I
CdCl <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	26.1	25.7	White	II
CdCl <sub>2</sub> ·1/2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	31.2	31.6	White	b
CdBr <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	44.3	44.3	White	II
CdI <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	55.8	55.9	White	II
CoCl <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	32.6	32.7	Pale lavender	II
CoBr <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	40.5	40.3	Dark blue	II
CoI <sub>2</sub> ·3(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> ) <sup>c</sup>	44.0	44.2	Greenish-blue	I
CoI <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	51.9	51.9	Greenish-blue	II
CoI <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )·2H <sub>2</sub> O	58.1	57.7	Bright green	c
CoI <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )·4H <sub>2</sub> O	53.6	53.8	Pink	d
NiCl <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	32.6	32.5	Pale yellow	II
NiBr <sub>2</sub> ·(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	52.1	52.0	Bright orange	II
NiI <sub>2</sub> ·2(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	51.9	51.8	Yellow	I

<sup>a</sup> Separated on cooling solution to 0°C. <sup>b</sup> Formed when the mono-1,4-dioxane compound stands over sulfuric acid. <sup>c</sup> Formed by exposing the anhydrous to atmospheric moisture for 2 hours. <sup>d</sup> Formed by exposing the anhydrous compound to atmospheric moisture for 2–3 days. <sup>e</sup> Very hygroscopic and unstable.

ST. LOUIS UNIVERSITY SR. RODERICK JUHASZ, S.C.N.  
ST. LOUIS, MISSOURI L. F. YNTEMA

RECEIVED OCTOBER 30, 1940

### 2,4-DIHYDROXYBENZAL 2,4-DINITROPHENYL-HYDRAZONE

Immediately upon the addition of 1.4 g. of 2,4-dihydroxybenzaldehyde, dissolved in 10 cc. of 95% alcohol to 2 g. of 2,4-dinitrophenylhydrazine, dissolved in the least possible amount of dilute sulfuric acid, a bright red crystalline precipitate began to form. It was recrystallized from hot amyl alcohol: m. p. 286° decomn., yield 87%; insoluble in water, methanol, ligroin, benzene, chloroform, ether, and acetone; slightly soluble in hot higher alcohols; soluble in ethylene glycol, hot nitrobenzene, and dilute alkalies. It decomposed upon continued heating in most solvents. *Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>O<sub>8</sub>N<sub>4</sub>: N, 17.61. Found: N, 17.90.

CHEMICAL LABORATORY  
UNIVERSITY OF GEORGIA  
ATHENS, GEORGIA

ALFRED W. SCOTT  
JOHN M. BURNS

RECEIVED OCTOBER 3, 1940

### SUBSTITUTED AMIDES

In the course of a comprehensive study of the insecticidal value of substituted amides, it was necessary to prepare cer-