3. Bis-(N-trimethylenesulfonamido)-mesitylene was also synthesized. No *cis–trans* isomers were obtained. This is in contrast to N,N′-dimethyl-N,N′-di-(methanesulfonyl)-diaminomesitylene from which *cis–trans* isomers resulted.

4. The lack of *cis–trans* isomerism in bis-(N-trimethylenesulfonamido)-mesitylene has been attributed to bond angle distortions in the molecule due to the five-membered nitrogen ring systems.

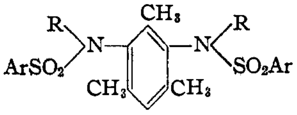
URBANA, ILLINOIS RECEIVED JULY 5, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

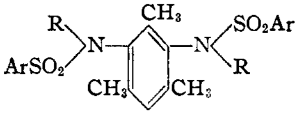
Restricted Rotation in Aryl Amines. IX. Diaminodurene Derivatives

BY ROGER ADAMS* AND NILS K. NELSON[1]

Pairs of isomers (I and II) due to two points of restricted rotation in the molecules have been reported among derivatives of diaminomesitylene.[2]

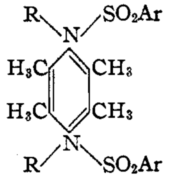


I

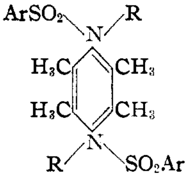


II

In this communication are described similar pairs of isomers obtained from diaminodurene as shown by structures III and IV. In this series the isomers correspond to *cis* and *trans*, each of which has a plane of symmetry. It was assumed that the higher-melting form had the more symmetrical structure, IV. A remarkable difference in physical properties of the members of each pair was noted, much greater than in the mesitylene series. Solubility differences were exemplified by the facile isolation of the less-soluble, higher-melting forms from the mixtures since they were essentially insoluble in hot methanol while the more-soluble lower-melting forms were quite soluble. The differences in melting points of the members of a pair ranged from 75 to 100°. When the lower-melting forms were heated above their melting points, they resolidified. By this treatment they were isomerized to the higher-melting forms.



III



IV

The compounds were made by alkylating N,N′-dibenzenesulfonyldiaminodurene in aqueous methanolic potassium hydroxide with methyl iodide, ethyl bromide and benzyl chloride. The pair of ethyl isomers was also formed by treatment of N,N′-diethyldiaminodurene with benzenesulfonyl chloride. No replacement of one ethyl group as was found in the mesitylene series[2] was observed.

N,N′-Dibenzenesulfonyldiaminodurene was also subjected to cyanoethylation in dioxane solution in presence of Triton B. The product was primarily a monocyanoethylation derivative which upon repetition of the procedure gave essentially a single, high-melting, dicyanoethylated compound. In one experiment which would not be duplicated, dicyanoethylation was obtained in one step and two isomers were formed, the higher-melting corresponding to that resulting from cyanoethylation of the monocyanoethylated derivative and the other melting much lower. The lower-melting was converted to the higher-melting by heating above its melting point. Both isomers were hydrolyzed to the corresponding isomeric acids.

Experimental

Diaminodurene.—A suspension of 44.5 g. of dinitrodurene in 150 ml. of ethanol was reduced under a pressure of 150 atm. of hydrogen with one teaspoonful of Raney nickel catalyst. The temperature rose from 25 to 70° during the course of the reduction. The reaction was complete after four hours.

After addition of 800 ml. of boiling water (which had been boiled for several minutes to liberate any dissolved oxygen) the solution was filtered to remove the catalyst. Small white needles crystallized rapidly when the solution cooled, and after standing thirty minutes, the first crop was removed by filtration, using a rubber dam to exclude air. A second crop, having the same melting point, was obtained when the mother liquor was allowed to stand overnight in an ice box. The yield was 28.7 g. (89%). The melting point was 149–150° (cor.) and was unchanged by crystallization from water.[3] Cain reports m. p. 149°.

N,N′-Dibenzenesulfonyldiaminodurene.—A solution of 17.4 g. of diaminodurene in 50 ml. of pyridine was added slowly to a solution of 47 g. of benzenesulfonyl chloride and 25 ml. of pyridine in a 300-ml. Erlenmeyer flask, while the flask was swirled in an ice–water-bath. After approximately three-fourths of the amine had been added, the reaction product became quite viscous, and it was necessary to add 25 ml. of pyridine. After the addition was completed, the flask was allowed to stand overnight at room temperature. Finely divided yellow crystals precipitated upon standing. The reaction product was poured into 1500 ml. of ice-water, and after standing at room temperature for several hours, the yellow precipitate was removed by filtration.

The product was dissolved in a solution of 40 g. of

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* Harvard University Ph.D. 1912.

[1] An abstract of a thesis submitted by Nils K. Nelson to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adams and Tjepkema, THIS JOURNAL, **70**, 4204 (1948); Adams and Rothstein, *ibid.*, **71**, 1620 (1949); Adams and Campbell, *ibid.*, **72**, 128 (1950).

[3] Cain, *Ber.*, **28**, 968 (1895).

potassium hydroxide in 200 ml. of water and 200 ml. of methanol. After filtration, it was precipitated by slowly adding concentrated hydrochloric acid until the solution was slightly acidic. The precipitate was filtered and washed twice with water. It gave a finely divided, cream-colored product, melting with decomposition between 330 and 340°. The yield was 46 g. (99%). It was purified by dissolving in base and reprecipitating by acid. No satisfactory organic solvent for this compound was found.

Anal. Calcd. for $C_{22}H_{24}N_2O_4S_2$: C, 59.43; H, 5.44. Found: C, 59.39; H, 5.64.

Isomers of N,N'-Dimethyl-N,N'-dibenzenesulfonyldiaminodurene.—To a solution of 2.5 g. of potassium hydroxide in 100 ml. of water and 100 ml. of methanol in a 500-ml. round-bottomed flask was added 5 g. of N,N'-dibenzenesulfonyldiaminodurene. After the sulfonamide dissolved, 15 ml. of methyl iodide was added, and the mixture was stirred with a mechanical stirrer for twelve hours. During the course of the reaction, finely divided white crystals formed. The mixture was filtered, and the precipitate was extracted with 400 ml. of boiling methanol.

The insoluble product was recrystallized three times from a mixture of chloroform and methanol. Approximately 1 g. of small white crystals was obtained, m. p. 325–326° (cor.).

Anal. Calcd. for $C_{24}H_{28}N_2O_4S_2$: C, 60.99; H, 5.97. Found: C, 60.93; H, 5.79.

Upon cooling, long white needles crystallized from the methanol extract. A second crop of crystals was obtained from the mother liquor when it was concentrated to a volume of 200 ml. and allowed to stand in an ice-box overnight. The two crops were combined and recrystallized three times from ethanol. The yield was 0.2 g. of white needles which melted at 231.5–232° (cor.), but resolidified at 233° to form the high-melting isomer, m. p. 325–326° (cor.).

Anal. Calcd. for $C_{24}H_{28}N_2O_4S_2$: C, 60.99; H, 5.97. Found: C, 60.94; H, 6.05.

Isomers of N,N'-Diethyl-N,N'-dibenzenesulfonyldiaminodurene.—(A) In a solution of 4.24 g. of potassium hydroxide in 190 ml. of methanol and 150 ml. of water was dissolved 8 g. of N,N'-dibenzenesulfonyldiaminodurene. To this solution was added 21 g. of ethyl bromide, and the mixture was boiled under reflux for four hours. A cream-colored precipitate formed slowly as the reaction proceeded. The mixture was filtered while warm, and the precipitate was washed once with 50 ml. of methanol, and twice with 100 ml. of distilled water.

The precipitate was extracted with 300 ml. of boiling ethanol and recrystallized three times from a mixture of chloroform and methanol. The yield was 2 g. of small white prisms, m. p. 299–300° (cor.).

Anal. Calcd. for $C_{26}H_{32}N_2O_4S_2$: C, 62.37; H, 6.44. Found: C, 62.59; H, 6.55.

Concentrating the methanol mother liquors yielded a product melting at 195–205°. Recrystallization three times from methanol produced 0.5 g. of long white needles, m. p. 209.5–210° (cor.).

Anal. Calcd. for $C_{26}H_{32}N_2O_4S_2$: C, 62.37; H, 6.44. Found: C, 62.12; H, 6.47.

(B) To a solution of 2 g. of benzenesulfonyl chloride in 5 ml. of pyridine was added 0.2 g. of N,N'-diethyldiaminodurene (prepared as described below) in 10 ml. of pyridine. The mixture was warmed on a steam-cone for fifteen minutes and poured into 100 ml. of ice water. A light brown gum formed which stuck to the sides of the beaker. The water was removed by decantation and the gum was triturated with 100 ml. of a 5% aqueous methanolic potassium hydroxide solution and filtered. To determine if any monoethyl N,N'-dibenzenesulfonyldiaminodurene was present, the filtrate was acidified with hydrochloric acid. The solution remained clear indicating its absence.

The gum was then washed once with water and extracted with 50 ml. of boiling methanol. The insoluble product was recrystallized twice from chloroform. It yielded small white prisms, m. p. 299–300° (cor.). A melting point of the product mixed with the high-melting isomer from (A) showed no depression.

The methanol extract was concentrated to a volume of 15 ml., treated with Norit and allowed to cool. Long yellow needles formed on standing which were purified by two recrystallizations from methanol. The product melted at 209–210° (cor.) and gave no melting point depression with the low-melting product from (A).

When the compound melting at 209–210° was heated above its melting point for several minutes and allowed to cool, it resolidified. Upon recrystallization this product melted at 299–300° (cor.) and was identical with the higher-melting isomer.

N,N'-Diethyldiaminodurene.—To a solution of 13 ml. of glacial acetic acid and 26 ml. of concentrated sulfuric acid was added 4.3 g. of a mixture of isomeric N,N'-diethyl-N,N'-dibenzenesulfonyldiaminodurene. The suspension was boiled under reflux for forty-eight hours. The sulfonamide slowly dissolved, and the reaction mixture turned dark brown. The product was poured into 100 ml. of ice-water, and the mixture was made alkaline with aqueous ammonia. This dark mixture was extracted three times with 150 ml. of ether. Little of the decomposition product dissolved in the ether. The ether extract was evaporated to dryness. The product was an oil which was converted to the crystalline dihydrochloride as described below. In one experiment, the product crystallized and was purified from a mixture of methanol and water, giving long silky needles, m. p. 66–67° (cor.). The yield was about 0.5 g. (26%).

Dihydrochloride of N,N'-Diethyldiaminodurene.—To a solution of 0.2 g. of N,N'-diethyldiaminodurene in 10 ml. of acetone was slowly added concentrated hydrochloric acid until the solution was slightly acidic. A green precipitate formed, which turned white as more acid was added. The white amine hydrochloride was removed by filtration. It was dissolved in methanol, a drop of very dilute hydrochloric acid was added, and the product was precipitated by adding acetone. This was repeated several times, yielding white crystals which sublime slowly between 310 and 320°.

Anal. Calcd. for $C_{12}H_{24}N_2 \cdot 2HCl$: C, 57.33; H, 8.94. Found: C, 57.03; H, 9.24.

Isomers of N,N'-Dibenzyl-N,N'-dibenzenesulfonyldiaminodurene.—To a solution of 3 g. of potassium hydroxide in 200 ml. of water and 500 ml. of methanol was added 10 g. of N,N'-dibenzenesulfonyldiaminodurene. After the sulfonamide had dissolved, 10 g. of benzyl chloride was added, and the solution was boiled under reflux for two hours. The small cream-colored crystals which formed during the course of the reaction were removed by filtration and extracted with 300 ml. of boiling methanol.

The product which was insoluble in methanol was recrystallized four times from a mixture of chloroform and methanol. A white powder was obtained, m. p. 272–273° (cor.).

Anal. Calcd. for $C_{36}H_{36}N_2S_2O_4$: C, 69.20; H, 5.81. Found: C, 69.03; H, 5.96.

Upon cooling, small white crystals precipitated from the methanol extract. Three recrystallizations from methanol gave a product, m. p. 200–201° (cor.).

Anal. Calcd. for $C_{36}H_{36}N_2S_2O_4$: C, 69.20; H, 5.81. Found: C, 69.26; H, 5.71.

When the low-melting isomer was heated above its melting point for several minutes and allowed to cool, it solidified. The product, after recrystallization, proved to be the high-melting isomer.

N-Cyanoethyl-N,N'-dibenzenesulfonyldiaminodurene.—To 275 ml. of dioxane in a 500-ml., three-necked, round-bottomed flask, which was equipped with a mechanical stirrer and was resting in a Glas-col mantle, was added 10 g. of N,N'-dibenzenesulfonyldiaminodurene. The mixture was warmed to 55° and 20 g. of a 40% aqueous solution of benzyltrimethylammonium hydroxide (Triton B) was added dropwise. The sulfonamide partially dissolved. After the mixture had been stirred for five minutes, a solution of 10 ml. of acrylonitrile in 25 ml. of dioxane was added dropwise. The addition was completed in ten minutes. It was stirred for ninety-six hours while the temperature was kept between 50 and 60°. To this reaction mixture was added 10 ml. of acrylonitrile (dropwise and with stirring) and the mixture was stirred at 58° for one hour.

To the reaction product was added an equal volume of ethylene dichloride. The mixture was neutralized with concentrated hydrochloric acid, and washed twice with 300 ml. of water. The yellow-orange solution was evaporated to dryness under reduced pressure, and the residue was washed from the flask with 50 ml. of methanol and filtered. Two recrystallizations from methanol gave a white powder, m. p. 262–263° (cor.). The yield was 7.8 g. (69.5%).

Anal. Calcd. for $C_{25}H_{27}N_3O_4S_2$: C, 60.34; H, 5.47. Found: C, 60.12; H, 5.71.

N,N'-Dicyanoethyl-N,N'-dibenzenesulfonyldiaminodurene from Monocyanoethyl Analog.—By a similar cyanoethylation experiment, a mixture of 80 ml. of dioxane, 5 g. of N-cyanoethyl-N,N'-dibenzenesulfonyldiaminodurene, 4.4 g. of a 40% solution of Triton B was stirred at 50 to 60° for twenty-four hours. A solution of 5 ml. of acrylonitrile in 10 ml. of dioxane was added, and the mixture was again stirred for twenty-four hours at temperatures between 50 and 60°. Another 6 ml. of acrylonitrile was introduced and the reaction was allowed to proceed for another hour.

To the product was added 100 ml. of ethylene dichloride. The mixture was acidified with concentrated hydrochloric acid and the solid present was filtered. The filtrate was washed with three 100-ml. portions of water. It was then evaporated to dryness and the residue washed with 50 ml. of methanol. The methanol-insoluble material was collected on a filter. The solid from filtration of the ethylene dichloride and the solid left after the methanol extraction were combined and purified from a mixture of chloroform and methanol. It proved to be the dicyanoethylated product, m. p. 283–284° (cor.). The yield was 3.3 g. (58%). A melting point of this material with the high-melting isomer described in the next experiment showed no depression.

When the methanol extracts were evaporated to dryness only a trace of residue resulted.

N,N'-Dicyanoethyl-N,N'-dibenzenesulfonyldiaminodurene by Direct Cyanoethylation.—(Two isomers.) In a manner similar to that for preparing the monocyanoethyl derivative, 10 g. of N,N'-dibenzenesulfonyldiaminodurene was cyanoethylated in presence of 20 g. of 40% aqueous Triton B, and the mixture was stirred for a week with the temperature held between 55 and 60°. In this experiment, after standing several hours in an ice box, fine white crystals precipitated from the ethylene dichloride solution. The crystals were separated by filtration, the filtrate was evaporated to dryness, and the residue was extracted with 200 ml. of hot chloroform. Upon cooling the chloroform, crystals were obtained, m. p. 280–281° (cor.). The material from the ethylene dichloride, that insoluble in the chloroform and that separating from the chloroform, were combined and recrystallized once from a mixture of chloroform and methanol, once from a mixture of chloroform and ethanol, twice from dioxane, and three times from nitromethane. A white crystalline product was obtained, m. p. 284–285.5° (cor.). The yield was 2.5 g. (20%).

Anal. Calcd. for $C_{28}H_{30}N_4O_4S_2$: C, 61.06; H, 5.49. Found: C, 61.35; H, 5.63.

The chloroform filtrate was concentrated to 50 ml. and filtered. The precipitate was N-cyanoethyl-N,N'-dibenzenesulfonyldiaminodurene. Upon cooling, the filtrate yielded the lower-melting isomer, a white crystalline product which after three recrystallizations from ethyl acetate melted at 209–210° (cor.). The yield was 0.25 g. Upon heating in a metal-bath at 215° for five minutes, then allowing to cool, the material solidified. It was recrystallized from a mixture of chloroform and methanol and then had a m. p. 284–285° (cor.). It proved to be the high-melting isomer.

Anal. Calcd. for $C_{28}H_{30}N_4O_4S_2$: C, 61.06; H, 5.49. Found: C, 61.36; H, 5.61.

This experiment in which low-melting isomer was isolated could not be repeated.

N,N-Dicarboxyethyl-N,N'-dibenzenesulfonyldiaminodurene.—(A) (High-melting isomer.) To a mixture of 20 ml. of glacial acetic acid and 20 ml. of hydrochloric acid was added 0.5 g. of N,N'-dicyanoethyl-N,N'-dibenzenesulfonyldiaminodurene (m. p. 284–285.5° (cor.)). The slurry was allowed to boil under reflux for twenty hours. Upon cooling, the mixture was filtered, and the fine white precipitate was recrystallized twice from dioxane, m. p. 310–311° (cor.).

Anal. Calcd. for $C_{28}H_{32}N_2O_8S_2$: C, 57.12; H, 5.48. Found: C, 57.31; H, 5.72.

(B) (**Low-melting isomer.**)—In a similar manner 0.2 g. of N,N'-dicyanoethyl-N,N'-dibenzenesulfonyldiaminodurene (m. p. 209–210° (cor.)) in 10 ml. of hydrochloric acid and 10 ml. of glacial acetic acid was hydrolyzed. The clear reaction product was poured into 200 ml. of ice water, and the mixture was heated to boiling to cause it to coagulate. After standing for several hours, the mixture was filtered and the precipitate was recrystallized six times from a mixture of methanol and water. The acid crystallized in long white needles, m. p. 210–211.5° (cor.). The analysis of the product indicated it was a hydrate which was not dehydrated by heating for four days in an Abderhalden at 100°.

Anal. Calcd. for $C_{28}H_{32}N_2O_8S_2 \cdot H_2O$: C, 55.43; H, 5.64. Found: C, 55.99; H, 5.86.

When the compound was heated above its melting point for several minutes, it resolidified to form the isomer, m. p. 310–311° (cor.).

Reaction of Higher-Melting N,N'-Dicarboxyethyl-N,N'-dibenzenesulfonyldiaminodurene with Acetic Anhydride.—To 500 ml. of acetic anhydride was added 0.5 g. of N,N'-dicarboxyethyl-N,N'-dibenzenesulfonyldiaminodurene (m. p. 310–311° (cor.)) and the mixture was allowed to boil under reflux for twenty-two hours. At the end of the reaction, 450 ml. of acetic anhydride was removed by distillation under reduced pressure, and the remaining mixture was filtered. The fine white precipitate was recrystallized three times from acetic anhydride. The shiny white crystals softened around 200° and melted with decomposition at 208–210° (cor.). The compound appears to be a mixed anhydride, N,N'-diacetylcarboxyethyl - N,N' - dibenzenesulfonyldiaminodurene.

Anal. Calcd. for $C_{32}H_{36}N_2O_{10}S_2$: C, 57.13; H, 5.39; acetyl, 12.80. Found: C, 57.33; H, 5.50; acetyl, 12.75.

The original acid (m. p. 310–311° (cor.)) was recovered when this compound was hydrolyzed with 20 ml. of a dilute solution of acetic acid and hydrochloric acid.

Summary

1. N,N'-Dimethyl-, N,N'-diethyl- and N,N'-dibenzyl - N,N' - dibenzenesulfonyldiaminodurene were prepared by alkylating N,N'-dibenzenesulfonyldiaminodurene. Pairs of *cis–trans* isomers were obtained in each case.

2. The *cis-* and *trans*-N,N'diethyl-N,N'-dibenzenesulfonyldiaminodurenes were also prepared by benzenesulfonation of N,N'-diethyldiaminodurene.

3. N,N'-Dibenzenesulfonyldiaminodurene reacted stepwise with acrylonitrile in the presence

of Triton B to form first N-cyanoethyl-N,N′-dibenzenesulfonyldiaminodurene, then a single N,N′ - dicyanoethyl - N,N′ - dibenzenesulfonyldiaminodurene. In one reaction when dicyanoethylation was accomplished in one step, *cis* and *trans* isomers were formed. The two N,N′-dicyanoethyl - N,N′ - dibenzenesulfonyldiaminodurenes hydrolyzed to the corresponding isomeric N,N - dicarboxyethyl - N,N - dibenzenesulfonyldiaminodurenes.

4. The lower-melting isomers of the N,N′-dialkyl - N,N′ - dibenzenesulfonyldiaminodurenes and of the N,N′-dicyanoethyl derivative were converted to the corresponding higher-melting isomers when heated above their melting points.

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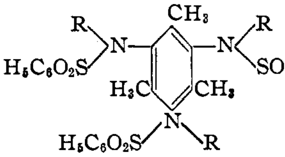
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

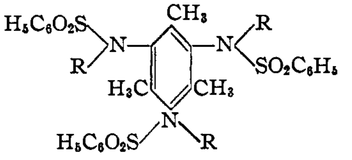
Restricted Rotation in Aryl Amines. X. Stereoisomers of N,N′N″-Trialkyl-N,N′,N″-tribenzenesulfonyltriaminomesitylenes

BY ROGER ADAMS* AND BRUCE ENGLUND[1]

Preceding papers in this series[2a,b] have reported the stereoisomerism of N,N′-dialkyl-N,N′-diarylsulfonyldiaminomesitylenes which arises from two points of restricted rotation in the molecule. The present paper describes the synthesis, separation and isomerization of pairs of isomeric N,N′,N″-trialkyl-N,N′,N″-tribenzenesulfonyltriaminomesitylenes (I and II). Although these molecules possess three points of restricted rotation, the other elements of symmetry present in them limit the number of possible stereoisomers to two, one *cis* and one *trans*.



I



II

$R = CH_3, C_2H_5, C_6H_5CH_2, H_5C_2O_2CCH_2, HO_2CCH_2$

These pairs of isomers were prepared following the general methods of synthesis of N,N′-dialkyl-N,N′-diarylsulfonyldiaminomesitylenes reported previously. Triaminomesitylene was obtained by catalytic reduction of trinitromesitylene. This was converted into the N,N′,N″-tribenzenesulfonyltriaminomesitylene by means of benzenesulfonyl chloride in pyridine at room temperature with a long reaction time. When N,N′,N″-tribenzenesulfonyltriaminomesitylene was treated in aqueous alkaline solutions with methyl iodide, ethyl iodide or benzyl chloride, two isomers of the corresponding N,N′,N″-trialkyl-N,N′,N″-tribenzenesulfonyltriaminomesitylene were formed. Two isomers of N,N′,N″-tricarbethoxymethyl-N,N′,N″ - tribenzenesulfonyltriaminomesitylene were also obtained when ethyl bromoacetate was added to an anhydrous ethanol–acetone solution of N,N′,N″-tribenzenesulfonyltriaminomesitylene, made alkaline with sodium hydride. In this case a marked preponderance (9:1) of the less soluble, high-melting isomer was formed. Each of the isomeric esters gave a single acid upon hydrolysis and the two acids so obtained were isomeric.

The low-melting N,N′,N″-trimethyl-N,N′,N″-tribenzenesulfonyltriaminomesitylene isomer when melted, resolidified and melted again at the same point as the high-melting isomer with which it proved to be identical. Thermal isomerization of the *cis* form to the more stable *trans* form had apparently resulted. Parallel isomerizations were effected by fusing the low-melting forms of N,N′,-N″-triethyl- and N,N′,N″-tricarbethoxymethyl-N,N′,N″ - tribenzenesulfonyltriaminomesitylenes. The tribenzyl and tricarboxymethyl analogs decomposed under the conditions required for isomerization.

The infrared spectra of the pairs of isomers were determined and in each case served to establish the *cis–trans* isomerism. The spectra also established the purity of each of a pair of isomers with respect to the other.

In the benzenesulfonation of triaminomesitylene, difficulties were encountered. The procedure with benzenesulfonyl chloride and pyridine at 5° and short reaction time as followed for diaminomesitylenes gave very small amounts of mono- and di-benzenesulfonyl derivatives and a large amount of red oil. Under more vigorous conditions, the same products resulted with even larger quantities of undesirable by-products. Heating benzenesulfonyl chloride and triamino-

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* Harvard University Ph.D. 1912.

[1] An abstract of a thesis submitted by Bruce Englund to the Graduate College of the University of Illinois, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. He held the Standard Oil Company of Indiana Fellowship, 1948–1949.

[2] (a) Adams and Tjepkema, THIS JOURNAL, **70** 4204 (1948); (b) Adams and Rothstein, *ibid.*, **71**, 1620 (1949).