tallization from the partially evaporated reaction mixture and purified by recrystallization from ethanol. A yield of 15 g. (65%) of diaminonitromesitylene was obtained, m. p. 186–187°. The melting point recorded for this compound is 184°.[9]

N,N'-Dimethyltriaminomesitylene.—To a suspension of 10 g. of diaminonitromesitylene in 60 ml. of water was added 20 g. of dimethyl sulfate and the mixture warmed gently for two hours. A vigorous reaction took place and the diaminonitromesitylene went into solution. After standing overnight, the solution was made alkaline with sodium hydroxide and extracted with ether. The ether solution was dried over potassium hydroxide, filtered, and the ether removed by distillation. The crude mixture of methylated amines was dissolved in 17 ml. of concentrated hydrochloric acid and a solution containing 6.9 g. of sodium nitrite dissolved in 20 ml. of water was added dropwise. The solution was aged for fifteen minutes and the nitroso derivative extracted successively with ether and benzene. The extracts were combined and dried over potassium hydroxide and the solvents removed by distillation. The residue was dissolved in hydrochloric acid and treated with stannous chloride as previously described. The reaction mixture was made alkaline with sodium hydroxide and extracted with ether. After drying over solid potassium hydroxide, the ether was evaporated and the product distilled under reduced pressure, b. p. 139–141° (3 mm.). The yield was 2 g. (20%).

Anal. Calcd. for $C_{11}H_{19}N_3$: C, 68.36; H, 9.89; N, 21.75. Found: C, 68.09; H, 10.07; N, 21.47.

Summary

1. N,N'-Diacetyl-N,N'-dimethyldiaminomesitylene was prepared by methylation of N,N'-diacetyldiaminomesitylene and by acetylation of N,N'-dimethyldiaminomesitylene. Only a single isomer was obtained.

2. It is obvious in these molecules either that the methyl and acetyl groups do not cause adequate restriction between the nitrogen and the ring or that one isomer is formed exclusively in the reactions.

URBANA, ILLINOIS RECEIVED AUGUST 5, 1948

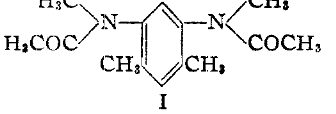
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Substituted Aromatic Amines. VI. Stereoisomers of N,N'-Dialkyl-N,N'-dibenzenesulfonyldiaminomesitylene[1]

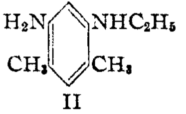
BY ROGER ADAMS AND J. J. TJEPKEMA

cis and *trans* isomers of N,N'-dimethyl-N,N'-diacetyldiaminomesitylene (I) could not be obtained.[1] This failure may have been due to lack of restricted rotation because of the inadequate size of the methyl and acetyl groups. In this investigation, the influence of larger substituents on the nitrogen atoms was studied. The methyl groups were replaced by larger alkyl radicals and instead of the acetyl groups benzenesulfonyl groups were introduced.

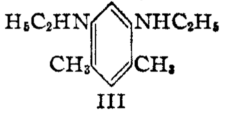
By ethylation of diaminomesitylene, it was possible to obtain either a monoethyl derivative with a single amino group ethylated (II) or a diethyl derivative in which an ethyl group was substituted on each amino group (III). The hindrance to tri- and tetra-alkylation induced by the adjacent ring methyl groups makes possible the isolation of these mono- and dialkyl derivatives in a form essentially free from more highly alkylated products. For the preparation of the dialkyl derivative, one mole excess of ethyl bromide was used and this did not lead to the formation of by-products in appreciable amounts. Upon treatment of either the N-monoethyl (II) or the N,N'-diethyl derivative (III) with excess of benzenesulfonyl chloride in pyridine solution under mild conditions, the same monoethyldibenzenesulfonyl derivative (IV) was formed. An ethyl group from the diethyl derivative (III) is lost and replaced by a benzenesulfonyl group (IV). This unexpected replacement is probably the result of the crowded condition of the atoms. When the reaction of the diethyl derivative (III) with benzenesulfonyl chloride was carried out at more elevated temperatures, a small amount of the N,N'-dibenzenesulfonyldiaminomesitylene (VI) was also isolated. In this case both the ethyl groups were lost. On the other hand, the monoethyldibenzenesulfonyldiaminomesitylene (IV) could be alkylated in alkaline solution with ethyl bromide to the N,N'-diethyl-N,N'-dibenzenesulfonyldiaminomesitylene (V), m. p. 212–212.5°. Only one product was isolated. When N,N'-dibenzenesulfonyldiaminomesitylene (VI) was dialkylated with ethyl bromide under similar conditions, the main reaction product was V but an isomeric by-product was also formed, m. p. 168–169°. Because of the non-identity but great similarity of the infrared spectrum of this compound with that of V it is considered to be the stereoisomer of V. On the basis of the lower melting point and greater solubility it has been assigned the *cis*-form (VII).



I



II



III

The N,N'-dibenzenesulfonyldiaminomesitylene (VI) was also treated in alkaline solution with *n*-

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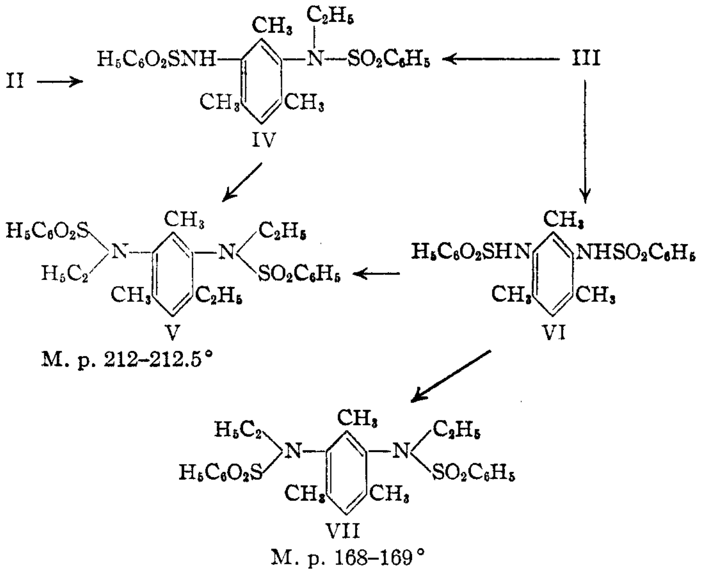
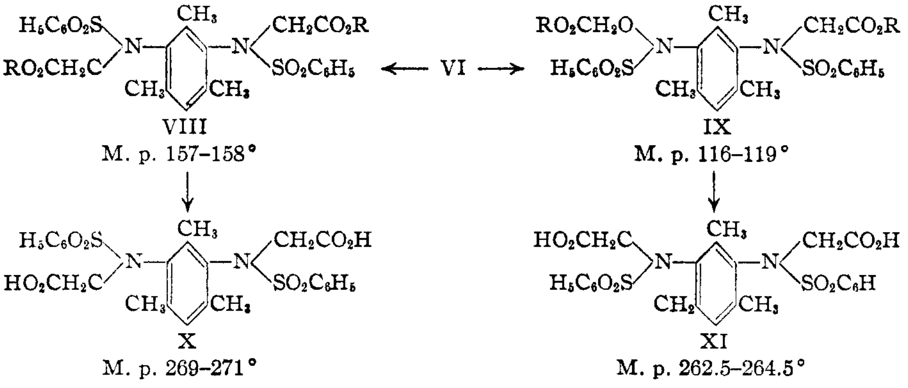
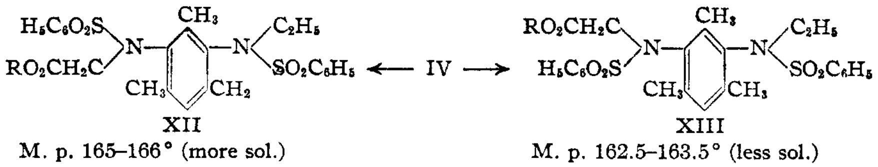
(1) For previous paper in this series, see (a) Adams and Chase, THIS JOURNAL, **70**, 2667 (1948); (b) Adams and Sundholm, *ibid.*, **70**, 2667 (1948).



butyl bromide, *n*-dodecyl bromide and benzyl chloride. In each case two isomers were obtained in approximately the same amounts. *t*-Butyl groups could not be introduced by this reaction. The steric hindrance is presumably too great. With *s*-butyl bromide a reaction took place but because of the many isomers (four racemic mixtures and two *meso* forms) the isolation of the individual compounds from the reaction mixture was not attempted. Under similar experimental conditions, cyclohexyl bromide failed to react.



When N,N'-dibenzenesulfonyldiaminomesitylene (VI) was treated with ethyl bromoacetate in alkaline solution, again two isomers were obtained in approximately equivalent amounts. The structures VIII and IX are assigned on the basis of relative melting points and solubilities. Each of these compounds was hydrolyzed and the acids X and XI were obtained. The correct assignment of the structures to these isomers was established by resolution studies. Molecule X was shown to be asymmetrical and molecule XI to be symmetrical. Compound X was resolved through its diquinine salt into its enantiomorphs. The *d*-form was obtained in maximum rotation, $[\alpha]^{24}\mathrm{D}$ +55°, but the *l*-form only in a less pure condition, $[\alpha]^{24}\mathrm{D}$ −48°. Compound XI gave only a single salt with quinine and by decomposition the original acid was recovered. These pairs of stereoisomers are, therefore, of the *cis-meso* and *trans*-racemic types as a result of two points of restricted rotation in the molecules.



When the compounds X and XI were boiled under reflux in acetyl chloride, the lower melting *cis*-form dissolved, whereas the higher melting *trans*-form did not dissolve. The difference in behavior may be due to the formation of an intramolecular soluble anhydride of the *cis*-form and the fact that the *trans*-form either does not react or gives a dimeric or polymeric intermolecular anhydride of much higher molecular weight. The products of the reactions were not identified.

Treatment of N-ethyl-N,N'-dibenzenesulfonyldiaminomesitylene with ethyl bromoacetate in alkaline solution gave two isomers XII and XIII. In this pair the lower melting form is the less soluble and has been arbitrarily assigned structure XIII. These esters upon hydrolysis yield the corresponding acids. From the higher melting more-soluble ester was obtained a higher-melting acid, from the lower melting less-soluble ester a lower-melting acid. These acids should both be racemic mixtures but initial resolution experiments were unsuccessful.

Each of the two forms of N,N'-dicarboxymethyl-N,N'-dibenzenesulfonyldiaminomesitylene (X and XI) gave upon nitration in the free position in the mesitylene ring the same mononitro derivative. Similarly, when the two corresponding esters (VIII and IX) were nitrated under similar conditions, the same product resulted, which was identical with the single product obtained from

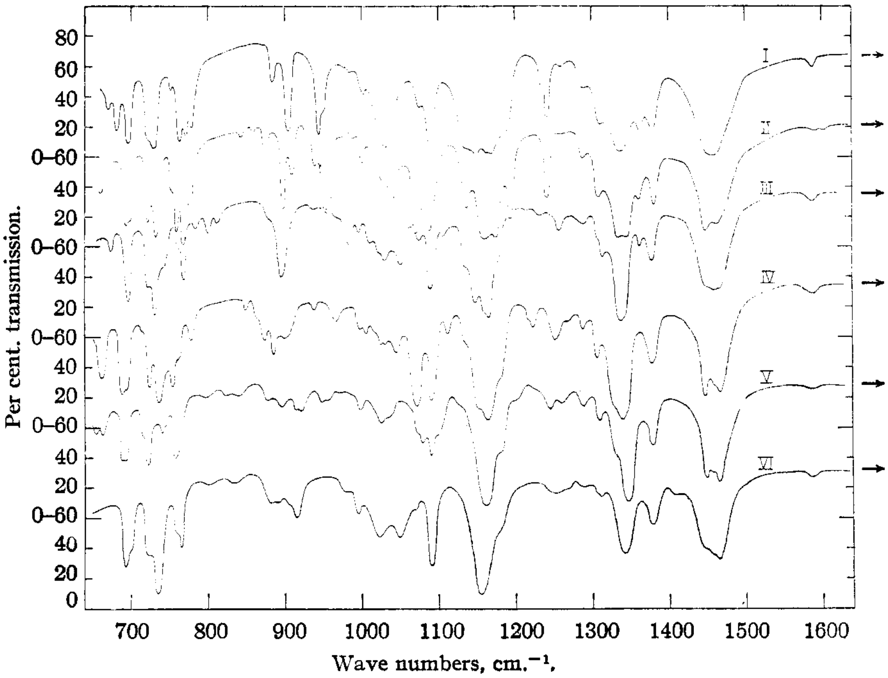


Fig. 1a, b.—Curve I, N,N'-diethyl-N,N'-dibenzenesulfonyldiaminomesitylene, m. p. 212–212.5°; Curve II, isomer of I, m. p. 168–169°; Curve III, N,N'-dibutyl-N,N'-dibenzenesulfonylidiaminomesitylene, m. p. 156.5–157.5°; Curve IV, isomer of III, m. p. 148–149°; Curve V, N,N'-didodecyl-N,N'-dibenzenesulfonyldiaminomesitylene, m. p. 87–88°; Curve VI, isomer of V, m. p. 62.5–64.5°.

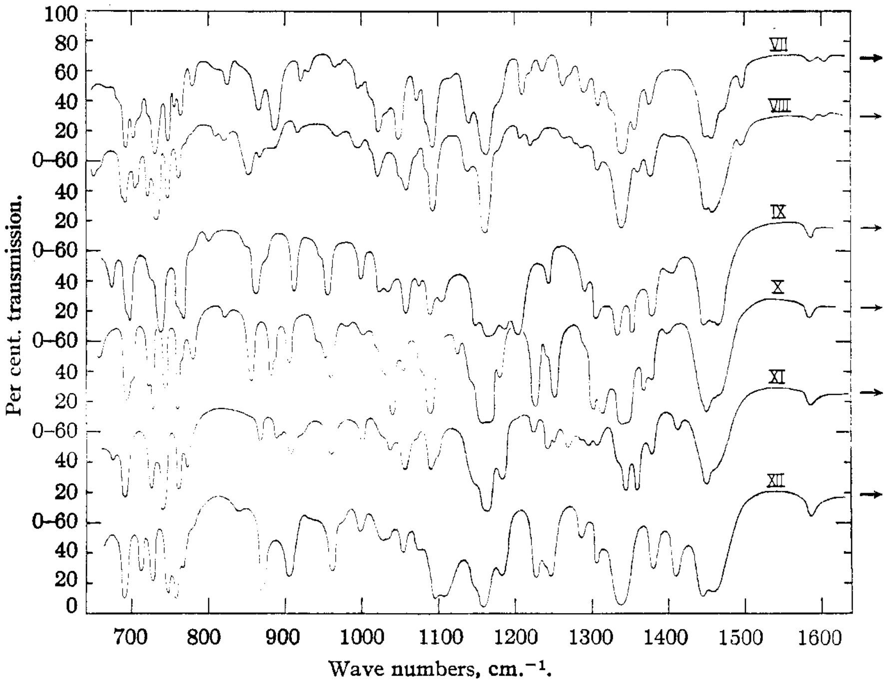
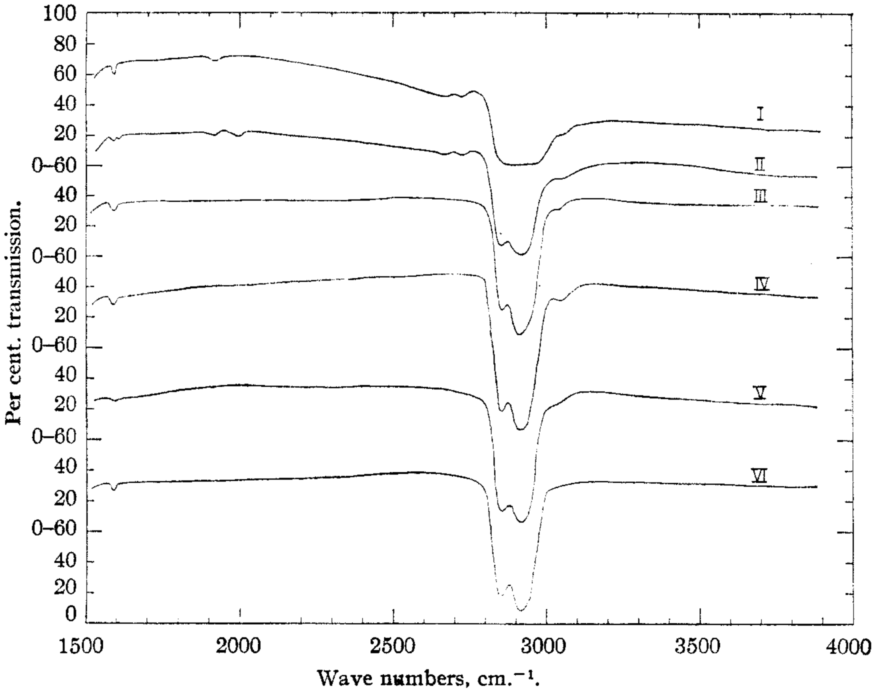
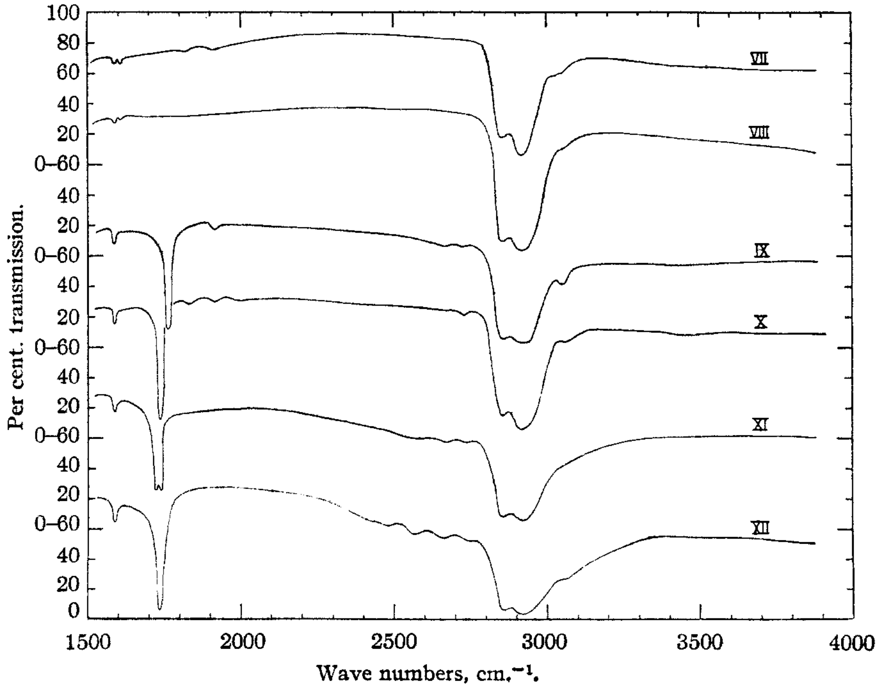


Fig. 2a, b.—Curve VII, N,N'-dibenzyl-N,N'-dibenzenesulfonyldiaminomesitylene, m. p. 228–229°; Curve VIII, isomer of VII, m. p. 198–199°; Curve IX, N-ethyl-N'-carbethoxymethyl-N,N'-dibenzenesulfonyldiaminomesitylene, m. p. 165–166°; Curve X, isomer of IX, m. p. 162.5–163.5°; Curve XI, N-ethyl-N'-carboxymethyl-N,N'-dibenzenesulfonyldiaminomesitylene, m. p. 221–222°; Curve XII, isomer of XI, m. p. 203.5–204.5°.



Each crystalline compound was ground with mineral oil between two rock salt plates to form a homogeneous paste. Samples prepared in this manner scatter much less light than do dry powdered crystals. Only in the regions of the C–H stretching frequencies (2850 and 2920 cm.$^{-1}$) and C–H deformational frequencies (1378 and 1460 cm.$^{-1}$) does the mineral oil mask the absorption bands of the sample. No suitable solvent was found for the products which would permit determination of the spectra in solution.



nitro-N,N'-dibenzenesulfonyldiaminomesitylene and ethyl bromoacetate. It is apparent that the presence of the nitro group modifies the normal restricted rotation in such a way that only one form may exist.[1b]

The ethylation of nitro-N,N'-dibenzenesulfonyl-

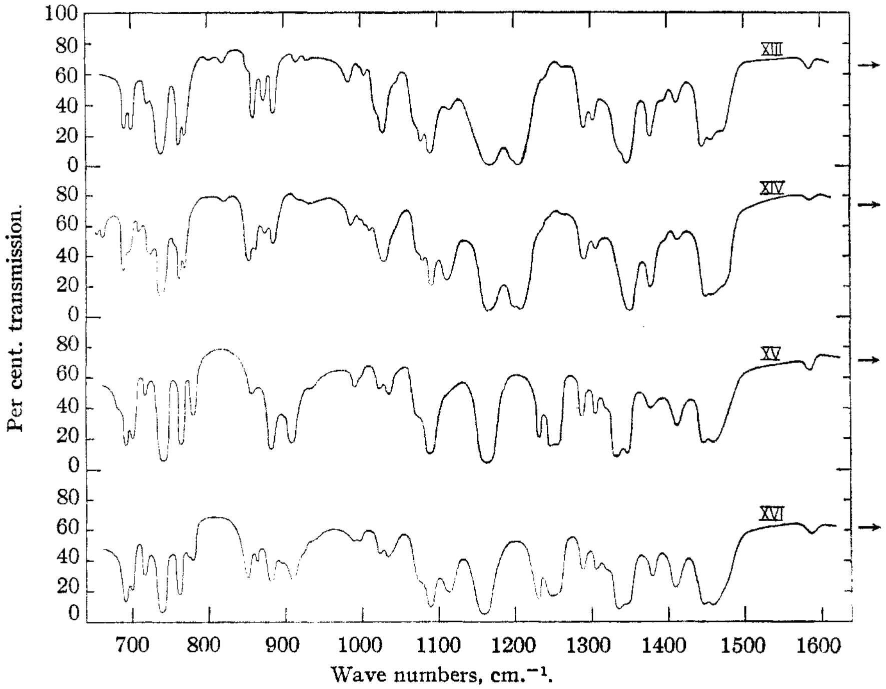


Fig. 3a, b.—Curve XIII, N,N′-dicarbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene, m. p. 157–158°; Curve XIV, isomer of XIII, m. p. 116–119°; Curve XV, N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene, m. p. 269–271°; Curve XVI, isomer of XV, m. p. 262.5–264.5°.

diaminomesitylene gave only one diethyl derivative forming plates, m. p. 167–169.5°, when the crystallization took place from a warm solution but crystallizing in needles, m. p. 189–190°, when the solution was cooled rapidly. The higher melting product was always obtained when N,N′-diethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 212–212.5°) was nitrated. Experiments to transform the higher melting form to the lower melting form were unsuccessful. Whether these two different melting products are isomorphs or two diastereoisomers, one of which very readily changes to the other, was not determined. The infrared spectra of the chloroform solutions of the two forms were identical.

The lower melting form of N,N′-didodecyl-N,N′-dibenzenesulfonyldiaminomesitylene was nitrated to a crystalline nitro derivative but from the nitration of the higher melting form only an oil was obtained.

The infrared spectra of several pairs of isomers were compared and are shown in Chart I. The isomers of each pair show a close resemblance. No regularity could be detected which would permit any general conclusions about the *cis*- and *trans*-forms. It is to be noted in reading the chart that all the higher or all the lower melting members of the pairs are not necessarily of the same geometric configuration.

Absence of absorption bands above 3100 cm.$^{-1}$ shows that no N–H is present in any of the compounds. The weak absorption found between 3000–3100 cm.$^{-1}$ in all samples is due to the C–H stretching frequencies on the benzene rings. The strongly H-bonded OH of the acids also shows up in this region as a series of weak bands between 2500 and 3200 cm.$^{-1}$.

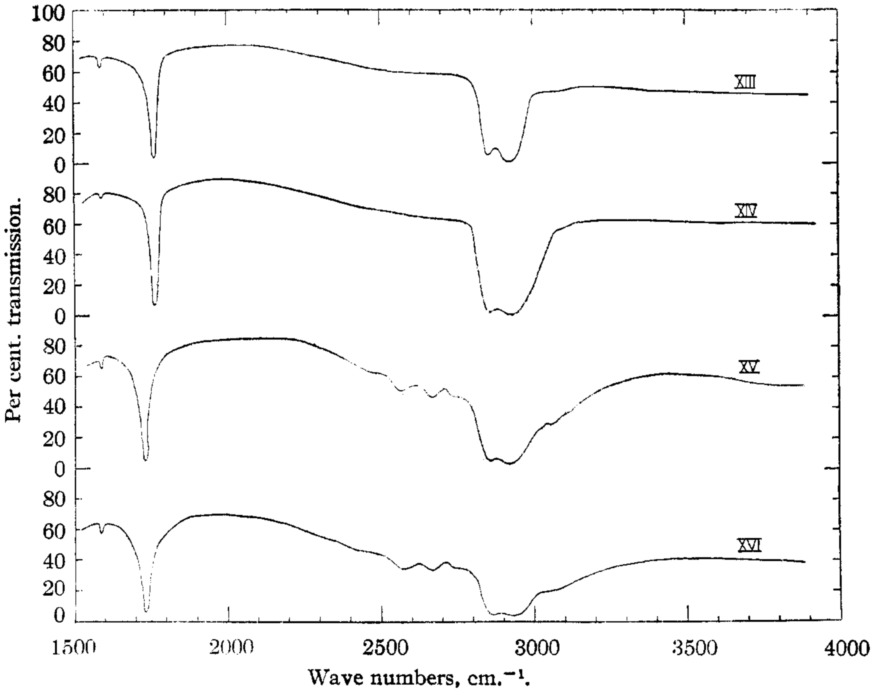
The C=O stretching frequencies of the acids and esters give rise to strong absorption bands between 1720 and 1765 cm.$^{-1}$. The anomalous doublet appearing at 1721 and 1740 cm.$^{-1}$ in the high melting mono acid (Chart I, Curve XI) is probably due to its crystalline structure. This type doublet has been found in certain crystalline forms of several keto steroids.

The weak band between 1580 and 1600 cm.$^{-1}$ in all spectra arises from the stretching of the carbon-carbon bonds in the phenyl rings. The vibration in which the six carbon atoms of the phenyl rings move in a rigid plane perpendicular to the five hydrogen atoms gives rise to fairly characteristic strong bands between 690 and 700 cm.$^{-1}$ and between 740 and 760 cm.$^{-1}$ in all the compounds.

The consistent strong absorption between 1160 and 1180 cm.$^{-1}$ is associated with the $-SO_2-$ group.

In such complex molecules it is impossible to assign the C–O and C–N stretching frequencies to certain bands. These are usually strong bands and lie between 1000 and 1280 cm.$^{-1}$. The C–C valency vibrations are found over a wider range, about 810–1150 cm.$^{-1}$. Like the C–O and C–N vibrations, the frequencies of these are also too much influenced by slight changes in molecular configuration to be identified.

So it is the difference in the absorption bands



arising from these single bonds and from vibrations of extensive parts of the molecule that indicate the non-identity of a pair of diastereoisomers and the similarities in the characteristic absorptions of groups like C=O, $-SO_2-$, C_6H_5, N–H, etc., indicate that each pair of isomers contains the same functional groups.

The infrared spectra were made and interpreted by Mrs. Agatha L. Johnson to whom the authors are very grateful.

Experimental

N-Ethyldiaminomesitylene.—A mixture of 30 g. of diaminomesitylene[1] and 25 g. of ethyl bromide was shaken with 150 ml. of water for eighteen hours in a stoppered flask. The diaminomesitylene went into solution and only a few drops of ethyl bromide remained. The solution was made alkaline with 10% aqueous sodium hydroxide and was then extracted three times with 75 ml. of ether. The ethereal solution was dried with potassium hydroxide pellets. The product was distilled *in vacuo* to give a light yellow oil, b. p. 101–106° (0.5 mm.), $n^{20}D$ 1.5592, $n^{25}D$ 1.5561. The yield was 24 g. (67.5%).

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18. Found: C, 74.51; H, 10.44.

N,N'-Diethyldiaminomesitylene.—(A). A mixture of 31 g. of N-ethyldiaminomesitylene and 20 g. of ethyl bromide was shaken for forty-eight hours in a stoppered flask with 100 ml. of water. Complete solution took place. After making alkaline with 10% aqueous sodium hydroxide it was extracted three times with 75 ml. of ether and the ethereal solution was dried with potassium hydroxide pellets. The product was purified by distillation *in vacuo*, b. p. 116–117° (1 mm.), $n^{20}D$ 1.5460. The yield was 29.5 g. (84%).

Anal. Calcd. for $C_{13}H_{22}N_2$: C, 75.67; H, 10.76. Found: C, 75.75; H, 10.78.

(B). To a solution of 45 g. of diaminomesitylene in 150 ml. of ethanol was added 100 g. of ethyl bromide and the solution was boiled under reflux for twelve hours. The excess ethyl bromide and most of the ethanol was removed from the solution by distillation from a steamcone and the product isolated as described in (A). The yield was 65%.

N,N'-Dibenzenesulfonyldiaminomesitylene.—To a solution of 35 g. of diaminomesitylene in 75 ml. of pyridine was added dropwise with stirring a mixture of 100 g. of benzenesulfonyl chloride and 50 ml. of pyridine at such a rate that the temperature was kept below 10°. External cooling in an ice–salt-bath was required. The stirring was continued for two hours at room temperature when the reaction was complete. The solution was then poured with stirring into 800 ml. of water and 300 g. of cracked ice. The yellow precipitate was collected on a filter and was recrystallized from acetone in white prisms, m. p. 253–254° (cor.). The mother liquor gave a second crop with the same melting point. The yield was 83 g. (83%).

Anal. Calcd. for $C_{21}H_{22}O_4N_2S_2$: C, 58.58; H, 5.15; N, 6.51. Found: C, 58.55; H, 4.98; N, 6.62.

To prove that both benzenesulfonyl groups are attached to different amino groups, the compound was dissolved in concentrated sulfuric acid, cooled in ice and salt, carefully diluted with twice its volume of water and treated with a cold sodium nitrite solution. An alkaline solution of β-naphthol was then added drop by drop. No dye was formed.

N-Ethyl-N,N'-dibenzenesulfonyldiaminomesitylene.—(A). To a solution of 32 g. of N-ethyldiaminomesitylene in 100 ml. of pyridine cooled in an ice–salt-bath a solution of 70.5 g. of benzenesulfonyl chloride in 50 ml. of pyridine was added dropwise with stirring at such a rate that the temperature stayed below 10°. The stirring was continued at room temperature for another two hours when the reaction was complete. The solution was poured into 700 ml. of water and 300 g. of cracked ice. The water layer was decanted from the oily precipitate after a half hour. The product was dissolved in 100 ml. of ethanol and poured into 1 l. of ice water. The product precipitated again as an oil. It was dissolved in 200 ml. of ethanol and boiled with decolorizing charcoal for twenty minutes. After removal of the charcoal the brown solution was placed in an ice-box. Crystallization started after five days and a thin crust of yellow crystals was formed in two weeks. When this was broken, crystallization started throughout the solution. Three days later the crystals were collected on a filter and washed with cold ethanol. After recrystallization twice from ethanol, twice from benzene and once again from ethanol, pure white needles were obtained, m. p. 176–177° (cor.). The yield was 22 g. (25%).

Anal. Calcd. for $C_{23}H_{26}O_4N_2S_2$: C, 60.24; H, 5.72. Found: C, 60.23; H, 5.74.

(B). A solution of 10.3 g. of N,N′-diethyldiaminomesitylene in 30 ml. of pyridine and 18.1 g. of benzenesulfonyl chloride was heated on a steamcone for fifteen minutes. The pyridine was then almost completely removed by distillation *in vacuo* and the warm residue was poured into water. A brown tar precipitated. The water was decanted and the residue was dissolved in ethanol. This solution was again poured into water with stirring. The resulting precipitate was dissolved in 250 ml. of boiling ethanol and to this solution was added 125 ml. of warm water. An oily semicrystalline product separated from the solution on standing in an ice-box overnight. Recrystallizations successively from carbon tetrachloride, ethanol, twice from carbon tetrachloride and finally from 75% ethanol gave a product, m. p. 176–177° (cor.). The mother liquor of the first recrystallization was poured into 250 ml. of water. The precipitate consisted mainly of the same product. The yield was 3.5 g. (15%). When the reaction mixture was worked up as under (A) the yield of N - ethyl - N,N′ - dibenzenesulfonyldiaminomesitylene was 29%.

Anal. Calcd. for $C_{23}H_{26}O_4N_2S_2$: C, 60.24; H, 5.72; N, 6.11. Found: C, 60.44; H, 5.81; N, 6.16.

A small fraction separated from the first mother liquor which was less soluble in carbon tetrachloride and ethanol. After crystallization from acetone it melted at 248–250° (cor.); yield 30 mg. It proved by analysis and infrared spectrum to be N,N′-dibenzenesulfonyldiaminomesitylene.

Anal. Calcd. for $C_{21}H_{22}O_4N_2S_2$: C, 58.58; H, 5.15; N, 6.51. Found: C, 58.61; H, 5.15; N, 6.97.

N,N′-Diethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—(A). To a solution of 1 g. of N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene in 10 ml. of ethanol containing 0.25 g. of potassium hydroxide was added 0.55 g. of ethyl bromide. The mixture was boiled under reflux for two hours. Crystallization started during the reaction. The reaction mixture was cooled in an ice-box for twelve hours. The crystals were collected on a filter and then heated with 20 ml. of water on a steamcone for fifteen minutes to dissolve potassium bromide. The product was recrystallized three times from ethanol in white needles, m. p. 212–212.5° (cor.). The yield was 150 mg. (30%) on the basis of unrecovered starting material. About 500 mg. of starting material was recovered from the mother liquor of the reaction mixture.

Anal. Calcd. for $C_{25}H_{30}O_4N_2S_2$: C, 61.70; H, 6.21. Found: C, 61.83; H, 6.29.

(B) (Two Isomers).—To 75 ml. of absolute ethanol was added gradually 0.48 g. of sodium hydride then 20 ml. of dry acetone. After addition of 8.4 g. of N,N′-dibenzenesulfonyldiaminomesitylene, the mixture was boiled under reflux for ten hours during which time 4.5 g. of ethyl bromide in four portions was introduced. The solvent was then evaporated until approximately 50 ml. was left and the solution was placed in an ice-box for twenty hours. The crystals were washed with cold ethanol and warm water to remove the sodium bromide. Three recrystallizations from ethanol raised the melting point to 210–211° (cor.). The yield was 2.7 g. (30%). The product was identical with that prepared in (A).

The mother liquors from the initial reaction product and from the first crystallization were combined and diluted with water. The white precipitate was four times recrystallized from a water–ethanol mixture, yielding 250 mg. of hard white crystals in clusters, m. p. 168–169° (cor.).

Anal. Calcd. for $C_{25}H_{30}O_4N_2S_2$: C, 61.70; H, 6.21. Found: C, 61.78; H, 6.41.

Isomers of N,N′-Di-*n*-butyl-N,N′-dibenzenesulfonyldiaminomesitylene.—To a solution of 8.6 g. of N,N′-dibenzenesulfonyldiaminomesitylene in 100 ml. of absolute ethanol containing 0.96 g. of sodium hydride was added 6 g. of *n*-butyl bromide. The solution was boiled under reflux for four hours. After cooling in an ice-box crystals appeared which were collected on a filter after twenty-four hours. They were washed with ethanol and then with water to remove the sodium bromide. Two recrystallizations from ethanol raised the melting point to 156.5–157.5° (cor.). The yield was 4 g. (37%).

Anal. Calcd. for $C_{29}H_{38}O_4N_2S_2$: C, 64.17; H, 7.06. Found: C, 64.10; H, 7.02.

The mother liquor of the reaction mixture was combined with the wash ethanol and concentrated to half its volume. Crystallization took place upon cooling. The crystals were collected on a filter, washed with ethanol and three times recrystallized from absolute ethanol, m. p. 148–149° (cor.). The yield was 2.5 g. (23%). A melting point of a mixture with the product melting at 156.5–157.5° was 127–136°.

Anal. Calcd. for $C_{29}H_{38}O_4N_2S_2$: C, 64.17; H, 7.06. Found: C, 64.36; H, 7.07.

Another 3 g. of impure material was also obtained from the mother liquors.

Isomers of N,N′-Didodecyl-N,N′-dibenzenesulfonyldiaminomesitylene.—To a solution of 8.6 g. of N,N′-dibenzenesulfonyldiaminomesitylene in 75 ml. of ethanol containing 0.96 g. of sodium hydride was added 15 g. of dodecyl bromide. The solution was boiled under reflux for three and one-half hours. When cooled in an ice-box an oil separated which on standing at room temperature for twenty-four hours crystallized. It was collected on a filter and washed with ethanol and water to remove the sodium bromide. After a recrystallization from an ethanol–acetone mixture (5:1) followed by a recrystallization from ethanol, the product formed fine white needles, m. p. 87–88° (cor.). The yield was 5 g. (32.5%).

Anal. Calcd. for $C_{45}H_{70}O_4N_2S_2$: C, 70.45; H, 9.20. Found: C, 70.60; H, 9.47.

On standing the mother liquor of the reaction mixture combined with the wash ethanol deposited crystals, which after cooling in an ice-box were collected on a filter and washed with ethanol. After two recrystallizations from ethanol the product formed waxy white needles, m. p. 62.5–64.5° (cor.). The yield was 4 g. (25%).

Anal. Calcd. for $C_{45}H_{70}O_4N_2S_2$: C, 70.45; H, 9.20. Found: C, 70.45; H, 9.32.

A considerable amount of non-crystalline material was found in the combined mother liquors.

Isomers of N,N′-Dibenzyl-N,N′-dibenzenesulfonyldiaminomesitylene.—To a solution of 8.6 g. of N,N′-dibenzenesulfonyldiaminomesitylene in 100 ml. of absolute ethanol containing 0.96 g. of sodium hydride, was added 6.5 g. of benzyl chloride. The mixture was boiled under reflux for three hours during which time the solution turned light red and later colorless. After cooling in an ice-box, the crystals which appeared were collected on a filter and washed with ethanol and then with warm water to remove the sodium chloride. The crystals were extracted with 100 ml. of an ethanol–acetone mixture (3:1) and the product was obtained by cooling. It was purified by recrystallization from ethanol–acetone (5:1). The product formed white needles, m. p. 198–199° (cor.). The yield was 3.5 g. (28.5%).

Anal. Calcd. for $C_{35}H_{34}O_4N_2S_2$: C, 68.83; H, 5.61. Found: C, 69.11; H, 5.74.

The residue from the extraction was twice recrystallized from acetone giving hard prisms, m. p. 228–229° (cor.). The yield was 4.5 g. (37%).

Anal. Calcd. for $C_{35}H_{34}O_4N_2S_2$: C, 68.83; H, 5.61. Found: C, 68.96; H, 5.79.

From the mother liquors of the reaction and the recrystallizations another 3 g. of impure crystalline material was obtained.

Isomers of N,N′-Dicarbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—In a solution of 2.88 g. of sodium hydride in a mixture of 200 ml. of absolute ethanol and 50 ml. of dry acetone was dissolved 25.8 g. of N,N′-dibenzenesulfonyldiaminomesitylene. A solution of 21 g. of ethyl bromoacetate in 100 ml. of absolute ethanol was added and the mixture was boiled under reflux for three hours. After cooling, the crystalline mass was collected on a filter, washed with cold ethanol and then with warm water to dissolve the sodium bromide. After one recrystallization from acetone, 9 g. of product, m. p. 157–158° (cor.), was obtained. A second crop from the mother liquors gave after recrystallization 1.5 g. of pure product. The yield was 10.5 g. (28.5%).

Anal. Calcd. for $C_{29}H_{34}O_8N_2S_2$: C, 57.79; H, 5.69; N, 4.65; S, 10.64. Found: C, 58.01; H, 5.91; N, 4.67; S, 10.82.

The filtrate of the initial reaction mixture and the wash ethanol were combined and about one-third of the solvent was distilled. After cooling overnight in an ice-box, a product separated which was collected on a filter, washed with ethanol, then with water and twice recrystallized from ethanol; m. p. 116–119° (cor.). The yield was 9.5 g. (26.5%).

Anal. Calcd. for $C_{29}H_{34}O_8N_2S_2$: C, 57.79; H, 5.69; N, 4.65; S, 10.64. Found: C, 57.95; H, 5.83; N, 4.59; S, 10.44.

Another 5 g. of impure material could be obtained from the mother liquors.

Isomers of N,N′-Dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—A solution of 13.5 g. of N,N′-dicarbethoxymethyl - N,N′ - dibenzenesulfonyldiaminomesitylene (m. p. 157–158°) in 150 ml. of glacial acetic acid and 50 ml. of 4 *N* sulfuric acid was boiled under reflux for seven hours. Crystallization started in the boiling mixture after two hours. After standing in an ice-box for four hours the crystals were collected on a filter. More material could be recovered from the filtrate by adding 250 ml. of water. This and the original crystals were mixed and twice recrystallized from an acetone–water mixture; m. p. 269–271° (cor.) with decomposition. The yield was 10.5 g. (86%).

Anal. Calcd. for $C_{25}H_{26}O_8N_2S_2$: C, 54.93; H, 4.80; N, 5.13; S, 11.73. Found: C, 55.08; H, 4.85; N, 5.00; S, 11.80.

The same procedure was followed for the hydrolysis of N,N′ - dicarbethoxymethyl - N,N′ - dibenzenesulfonyldiaminomesitylene (m. p. 116–119°). From 9.5 g. of ester 6.9 g. (76%) of acid resulted; m. p. 262.5–264.5° (cor.) with decomposition.

Anal. Calcd. for $C_{25}H_{26}O_8N_2S_2$: C, 54.93; H, 4.80; N, 5.13; S, 11.73. Found: C, 55.23; H, 4.86; N, 5.03; S, 11.52.

By refluxing this product, m. p. 262.5–264.5°, with acetyl chloride for four hours, a solution resulted whereas the higher melting form did not dissolve.

Resolution of N,N′-Dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 269–271°).—A solution of 6.49 g. of quinine in 100 ml. of acetone was added to a suspension of 5.47 g. of N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene in 200 ml. of boiling acetone. The mixture was boiled and filtered. Crystallization started upon cooling in an ice-box. After thirty-six hours the crystals were collected on a filter. The yield of less-soluble salt, m. p. 194.5–195° (cor.), fraction I, was 5 g.

The filtrate was evaporated to half its volume and when cooled an oily semi-crystalline product precipitated. This, fraction II, weighed 2.5 g.

Fraction I was recrystallized from absolute ethanol, m. p. 195.5–196.5° (cor.). Fraction II was recrystallized from the mother liquor of the recrystallization of fraction I. The product also had an m. p. of 195.5–196° (cor.). The total yield was 5.5 g. The melting point rose to 203–204° (cor.) when dried for four hours *in vacuo* at 110° and the indication is that water was retained in the product as obtained directly from the solvent.

Anal. (undried salt). Calcd. for $C_{25}H_{26}O_8N_2S_2 \cdot 2C_{20}H_{24}O_2N \cdot H_2O$: C, 64.33; H, 6.32. Found: C, 64.68; H, 6.51.

Anal. (dried salt). Calcd. for $C_{25}H_{26}O_8N_2S_2 \cdot 2C_{20}H_{24}O_2N_2$: C, 65.30; H, 6.24. Found: C, 64.95; H, 6.44.

Rotation (dried less-soluble salt). 100 mg. made up to 10 ml. with methanol at 24° gave α_D −8.25; *l*, 1; $[\alpha]^{24}_D$ −82.5°.

The mother liquors from fractions I and II were evaporated to about half the volume, cooled and the precipitate collected on a filter. This procedure was repeated once more. These two crops were discarded. The resulting solution of about 50 ml. volume was then evaporated to dryness giving a white powder weighing 4.0 g., m. p. 147–168° (cor.). This salt was not further purified.

Decomposition of the Less-soluble Salt (m. p. 195.5–196.5°); **Preparation of *d*-N,N′-Dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.**—A suspension of 1 g. of the salt in 60 ml. of water and 10 ml. of methanol was stirred and treated with a solution of 1 g. of potassium hydroxide in 15 ml. of water. The mixture was heated for a few minutes to 75°. The solution was cooled and the quinine removed by filtration. The filtrate was acidified with hydrochloric acid and a precipitate was formed. The solution was heated and acetone added until the precipitate dissolved. The acid crystallized upon cooling. It was recrystallized from a methanol–water mixture, m. p. 209–211° (cor.); the compound melted, crystallized and melted again at 252–253° (cor.). The yield was 275 mg.

Anal. Calcd. for $C_{25}H_{26}O_8N_2S_2$: C, 54.92; H, 4.80. Found: C, 54.51; H, 5.05.

Rotation. 100 mg. made up to 10 ml. with methanol at 24° gave α_D +0.55°; *l*, 1; $[\alpha]^{24}_D$ +55°.

Decomposition of the More-soluble Salt (m. p. 147–168°); **Preparation of *l*-N,N′-Dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.**—The impure more-soluble salt was decomposed in a manner similar to the decomposition of the less-soluble salt. The crude acid after crystallization from an acetone–water mixture had a m. p. of 147–163° (cor.).

Rotation. 50 mg. made up to 10 ml. with methanol at 24° gave α_D −0.24; *l*, 1; $[\alpha]^{24}_D$ −48°.

Attempted Resolution of N,N′-Dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 262.5–264.5°).—A solution of 3.25 g. of quinine in 50 ml. of boiling acetone was added to a boiling suspension of 2.73 g. of N,N′ - dicarboxymethyl - N,N′ - dibenzenesulfonyldiaminomesitylene in 100 ml. of acetone. Before all of the acid dissolved a precipitate formed which could not even be dissolved in 600 ml. of acetone. This was removed by filtration (fraction I, m. p. 147–163° (cor.)). During the gradual evaporation of the acetone four separate fractions were obtained with melting points respectively 147–163°, 147–168°, 147–168°, 142–168°. The combined fractions weighed 5.4 g. Upon recrystallization from ethanol-benzene (2:1) and ethanol, the melting point rose to 166–167° (cor.). The analysis of this salt repeatedly gave poor results and it is assumed to have been due to partial hydrolysis of the salt during recrystallization.

Anal. Calcd. for $C_{25}H_{26}O_8N_2S_2 \cdot 2C_{20}H_{24}O_2N_2$: C, 65.30; H, 6.24. Found: C, 64.57; H, 6.44.

Rotation (dried salt). 100 mg. made up to 10 ml. with methanol at 24° gave α_D −1.14°; *l*, 1; $[\alpha]^{24}_D$ −114°.

Decomposition of the salt following the procedure given for the decomposition of the salts of the higher melting acid gave on recrystallization the original acid, m. p. 260.5–262.5° (cor.), which was optically inactive.

Nitro-N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylenes.—To 10 ml. of fuming nitric acid (sp. gr. 1.59) was added gradually under external cooling 500 mg. of N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 269–271°). The reaction mixture was kept below 0° for thirty minutes after the solution was complete and then poured into 100 ml. of water and 50 g. of cracked ice. The white precipitate was collected on a filter, washed with water and twice recrystallized from an acetone–water mixture. The yield was 400 mg. (62%) of m. p. 247–250° (cor.) with decomposition.

Anal. Calcd. for $C_{25}H_{25}O_{10}N_3S_2$: C, 50.57; H, 4.26. Found: C, 50.80; H, 4.37.

Following the same procedure for N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 262.5–264.5°), 500 mg. gave 375 mg. (59%) of the nitro derivative, m. p. 241–243° (cor.) with decomposition. This product proved to be somewhat difficult to purify to maximum melting point but infrared spectra showed it to be identical with the nitration product of the 269–271° melting acid.

Anal. Calcd. for $C_{25}H_{25}O_{10}N_3S_2$: C, 50.57; H, 4.26. Found: C, 50.60; H, 4.41.

Isomers of N-Ethyl-N′-carbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—In a solution of 1.95 g. of sodium hydride in 200 ml. of absolute ethanol, 36.5 g. of N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene was dissolved. After adding 13.5 g. of ethyl bromoacetate the mixture was boiled under reflux for twelve hours. An oil separated from the solution upon cooling but when reheated it started to crystallize. After cooling, the crystals were collected on a filter, washed with cold ethanol and then with warm water to remove sodium bromide. The product was purified by recrystallization twice from acetone followed by two crystallizations from ethanol–acetone mixture (5:1), resulting in white plates, m. p. 162.5–163.5° (cor.). The yield was 8 g. (16%).

Anal. Calcd. for $C_{27}H_{32}O_6N_2S_2$: C, 59.53; H, 5.92; N, 5.14. Found: C, 59.74; H, 6.01; N, 5.01.

The mother liquor of the first recrystallization was evaporated to 200 ml. When cooled, crystallization took place. The crystals were collected on a filter and twice recrystallized from an ethanol–acetone mixture (5:1) followed by a recrystallization from ethanol, resulting in white prisms, m. p. 165–166° (cor.). A melting point of a mixture of this compound and the product melting at 162.5–163.5° was 142–150°. The yield was 11 g. (25%).

Anal. Calcd. for $C_{27}H_{32}O_6N_2S_2$: C, 59.53; H, 5.92; N, 5.14. Found: C, 59.60; H, 6.06; N, 5.25.

From the mother liquors 4 g. of starting material was recovered and 10 g. of a mixture of esters and starting material.

Isomers of N-Ethyl-N′-carboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—A mixture of 7 g. of N-ethyl-N′ - carbethoxymethyl - N,N′ - dibenzenesulfonyldiaminomesitylene (m. p. 162.5–163.5°) in 75 ml. of glacial acetic acid and 30 ml. of 4 *N* sulfuric acid was boiled under reflux for five and a half hours. When cooled to room temperature the reaction product was poured into water. The precipitate was purified by recrystallization from an acetic acid–water mixture (2:1), resulting in white needles, m. p. 203.5–204.5° (cor.). The yield was 6.5 g. (98%). The acid is not soluble in cold dilute alkali.

Anal. Calcd. for $C_{25}H_{28}O_6N_2S_2$: C, 58.12; H, 5.46. Found: C, 58.29; H, 5.70.

By hydrolysis of 11 g. of N-ethyl-N′-carbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 165–166°) in the same manner 9.5 g. (90%) of product resulted. After purification from glacial acetic acid it formed square plates, m. p. 221–222° (cor.). The acid is not soluble in cold dilute alkali.

Anal. Calcd. for $C_{25}H_{28}O_6N_2S_2$: C, 58.12; H, 5.46. Found: C, 57.78; H, 5.69.

Nitrodiaminomesitylene.—To a cooled solution of 3 g. of diaminomesitylene in 20 ml. of concentrated sulfuric acid was slowly added 1.75 ml. of nitric acid (sp. gr. 1.42). The solution first turned green and then yellow. After thirty minutes at room temperature, the solution was poured into 300 g. of cracked ice. The dark red solution thus formed was immediately neutralized with ammonia and the precipitate was collected on a filter. The product was crystallized from ethanol, benzene–petroleum ether (b. p. 90–120°) and ethanol, m. p. 184–185° (cor.). The yield was 1.2 g. (31%). Fittig[2] reports m. p. 184° and Adams and Chase[1] 186–187°.

Nitro-N,N′-dibenzenesulfonyldiaminomesitylene.—(A). To 1 g. of nitrodiaminomesitylene dissolved in 10 ml. of pyridine was added 3.5 g. of benzenesulfonyl chloride. After standing overnight this solution was poured into a mixture of 25 ml. of strong aqueous ammonia and 25 ml. of water. The resulting solution was filtered through a glass filter and was acidified with hydrochloric acid. The precipitate was recrystallized from an ethanol–water mixture (1:1); m. p. 263.5–264.5° (cor.). The yield was 1.75 g. (72%).

Anal. Calcd. for $C_{21}H_{21}O_6N_3S_2$: C, 53.04; H, 4.45. Found: C, 52.84; H, 4.57.

(B). To 100 ml. of nitric acid (sp. gr. 1.59) in a three-necked round-bottom flask fitted with a stirrer and a thermometer and cooled in an ice–salt-bath was added 25 g. of N,N′-dibenzenesulfonyldiaminomesitylene at such a rate that the temperature stayed below 0°. Fifteen minutes after the completion of the addition the reaction mixture was poured with stirring into 1 l. of water and 300 g. of cracked ice. The greenish precipitate was collected on a filter, washed with cold water and added carefully in small amounts of 200 ml. of strong aqueous ammonia. The resulting solution was diluted with 400 ml. of water and filtered. The filtrate was acidified with hydrochloric acid and a white precipitate was formed. It was collected on a filter and recrystallized twice from 75% ethanol, resulting in fine white needles, m. p. 260.5–262.5° (cor.). The yield was 22 g. (80%).

Nitro-N,N′-diethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—(A). To 50 ml. of absolute ethanol containing 0.85 g. of sodium hydride, 7.5 g. of nitro-N,N′-dibenzenesulfonyldiaminomesitylene was added, followed by 5 g. of ethyl bromide. The solution was boiled under reflux for fifteen hours and then cooled in an ice-box for three hours. The crystals were collected on a filter, washed with ethanol and then with warm water to remove the sodium bromide and purified by crystallization first from acetone–ethanol and second from ethanol with slow cooling; white plates, m. p. 167.5–169.5° (cor.). After another recrystallization involving rapid cooling, the product crystallized in needles, m. p. 189–190° (cor.). From the mother liquor of the reaction mixture 1 g. of material was obtained which after one recrystallization melted at 188.5–189.5° (cor.). The infrared spectra of both forms in chloroform solution were identical. The total yield of pure compound was 6.5 g. (81%).

Anal. Calcd. for $C_{25}H_{29}O_6N_3S_2$: C, 56.48; H, 5.50. Found: C, 56.72; H, 5.59.

(B). In 15 ml. of fuming nitric acid (sp. gr. 1.59) cooled in an ice-bath was gradually dissolved 625 mg. of N,N′-diethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 212–212.5°). The solution was kept below 0° for forty-five minutes and was then poured into 100 ml. of water and 50 g. of cracked ice. A white precipitate was formed, which was collected on a filter and washed with water. It was twice recrystallized from ethanol, m. p. 189–190° (cor.). The yield was 450 mg. (85%).

Nitro-N,N′-dicarbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene.—(A). In 200 ml. of absolute ethanol containing 1.95 g. of sodium hydride, 19 g. of nitro-N,N′-dibenzenesulfonyldiaminomesitylene was dissolved. After addition of 14.5 g. of ethyl bromoacetate the solution became cloudy immediately. It was boiled under reflux for twelve hours. Approximately 50 ml. of the ethanol was then distilled and water added adequate to dissolve all of the sodium bromide. When cooled in an ice-box for four hours, crystals were formed throughout the solution. It was purified by two crystallizations from an acetone–petroleum ether (b. p. 30–60°) mixture, resulting in white needles, m. p. 201–202° (cor.). The yield was 8.5 g. (32%).

Anal. Calcd. for $C_{29}H_{33}O_{10}N_3S_2$: C, 53.77; H, 5.14. Found: C, 54.09; H, 5.34.

From the mother liquors of the reaction mixture and the recrystallizations a large amount of non-crystalline material was obtained which could not be purified.

(B). To 10 ml. of fuming nitric acid (sp. gr. 1.59) was added under external cooling 500 mg. of N,N′-dicarbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m.

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(2) Fittig, *Ann.*, **140**, 129 (1867).

p. 157–158°). The reaction mixture was kept below 0° for thirty minutes after the solution was complete and then poured into 100 ml. of water and 50 g. of cracked ice. The white precipitate was collected on a filter and washed with water. It was twice recrystallized from an ethanol–acetone (3:1) mixture. The melting point as well as a melting point of a mixture with the product described under (A) was 201–202° (cor.). The yield was 452 mg. (84%).

(C). Following the same procedure as described under (B), 400 mg. of N,N′-dicarbethoxymethyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 116–119°) gave 305 mg. (70%) of product, m. p. 200–202° (cor.).

Nitration of the Two Forms of N,N′-Didodecyl-N,N′-dibenzenesulfonyldiaminomesitylene.—To 10 ml. of fuming nitric acid (sp. gr. 1.59) was added under external cooling 500 mg. of N,N′-didodecyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 62.5–64.5°). The solution was kept below 0° for thirty minutes, when the reaction was complete, and then poured into 100 ml. of water and 50 g. of cracked ice. An oily precipitate was formed, which was separated by decantation of the water. It was recrystallized from ethanol containing 10% petroleum ether (b. p. 50–80°) and twice from ethanol, forming white plates, m. p. 93–94.5° (cor.). The yield was 375 mg. (71%).

Anal. Calcd. for $C_{45}H_{69}O_6N_3S_2$: C, 66.55; H, 8.56. Found: C, 66.68; H, 8.61.

When the same procedure was followed for the nitration of the other isomer of N,N′-didodecyl-N,N′-dibenzenesulfonyldiaminomesitylene (m. p. 87–88°), only oily products were obtained which could not be purified.

Summary

1. Diaminomesitylene was ethylated with ethyl bromide to N-ethyldiaminomesitylene and to N,N′-diethyldiaminomesitylene. Both compounds upon treatment with benzenesulfonyl chloride in pyridine gave N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene.

2. Ethylation of N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene in alkaline solution with ethyl bromide gave a single product, N,N′-diethyl-N,N′-dibenzenesulfonyldiaminomesitylene. On the other hand, diethylation of N,N′-dibenzenesulfonyldiaminomesitylene resulted in two isomers, the one in larger amounts identical with that obtained by ethylation of the monoethyl derivative and the other a more soluble compound.

3. N,N′-Dibenzenesulfonyldiaminomesitylene was dialkylated with *n*-butyl bromide, dodecyl bromide and benzyl chloride; in each case, pairs of isomers resulted. It was also allowed to react with two moles of ethyl bromoacetate and the two isomers obtained were hydrolyzed to the corresponding acids. The high-melting less-soluble isomer was racemic since it was resolved through its diquinine salt. The low-melting more-soluble isomer was *meso* since it gave a single homogeneous diquinine salt from which the *meso* acid was recovered by decomposition.

4. N-Ethyl-N,N′-dibenzenesulfonyldiaminomesitylene upon treatment with ethyl bromoacetate gave a pair of racemic N-ethyl-N-carbethoxy-N,N′-dibenzenesulfonyldiaminomesitylenes which were hydrolyzed to the corresponding acids. Satisfactory salts for resolution of these substances were not found.

5. Nitration of the isomeric N,N′-dicarboxymethyl-N,N′-dibenzenesulfonyldiaminomesitylenes and the corresponding esters resulted in the formation of a single nitro derivative in each case. Only a single product was isolated from the reaction mixture of ethyl bromoacetate and nitro-N,N′-dibenzenesulfonyldiaminomesitylene and this was identical to that resulting from nitration of the appropriate ester.

6. When nitro-N,N′-dibenzenesulfonyldiaminomesitylene was ethylated, a product in the form of plates, m. p. 167.5–169.5°, was isolated when it crystallized from a slowly cooling solution but in the form of needles, m. p. 189–190°, when the solution was cooled rapidly. Only the higher melting form was isolated from the nitration of the higher melting N,N′-diethyl-N,N′-dibenzenesulfonyldiaminomesitylene was nitrated. Both the higher and lower melting forms in chloroform solution gave the same absorption spectrum. Attempts to convert the higher melting form into the lower melting form were unsuccessful.

7. Nitration of the isomeric N,N′-didodecyl-N,N′-dibenzenesulfonyldiaminomesitylenes resulted in a crystalline mononitro derivative from the lower melting and an uncharacterized oil from the higher melting form.

8. The infrared spectra of each pair of isomers show a close resemblance.

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