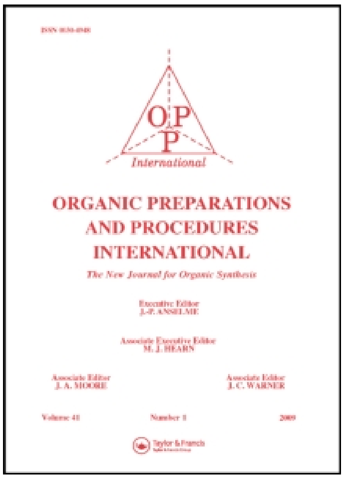

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N,N'-DIALKYLATION OF SULFONYLAMIDES OF p-PHENYLENEDIAMINES

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N,N'-DIALKYLATION OF SULFONYLAMIDES OF p-PHENYLENEDIAMINES

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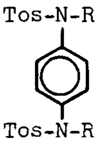
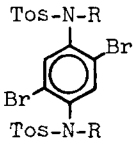
N,N'-Dialkyl-N,N'-ditosyl p-phenylenediamines (I and II) were prepared.



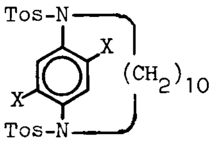
I

a: R=C_2H_5
b: R=$(CH_2)_{10}Br$
c: R=$(CH_2)_{10}O-C_6H_4OCH_3(p)$



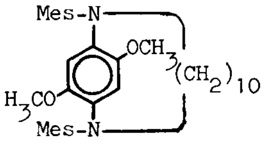
II

a: R=C_2H_5
b: R=$(CH_2)_{10}Br$

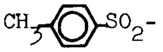


III

a: X=H
b: X=Br
c: X=OCH_3



IV

Tos = 

Mes = CH_3SO_2-

The ansacompounds III-IV were required as starting materials which could be used for the preparation of catenanes. The method used was that of Stetter et al.[2-9] However several minor but essential modifications were necessary in our cases to obtain reasonable yields. Several of the sulfonamides showed dimorphism, a phenomenon often encountered with this type of compound.[10]

EXPERIMENTAL*

Starting materials.

1,10-Decanediol was prepared analogously to 1,6-hexanediol[12] in 74-85% yield, bp. 144-145°/1.5 mm, mp. 70.5-71.5°, lit.,[13] bp. 150-151°/3 mm, mp. 70.8-71.8°.

1,10-Dibromodecane[14] was obtained from 1,10-decanediol and hydrogen bromide in 90% yield, bp. 105.5-106°/0.4 mm, n_D^{30} 1.4908, lit.,[14] bp. 139-142°/2 mm.

1-Bromo-10-(p-methoxyphenoxy)-decane was synthesized from p-methoxyphenol and 1,10-dibromodecane according to a procedure of Ziegler and Weber.[15] The product was purified by crystallization from absolute ethanol. Yield 65%, mp. 62.5-63.5°, lit.,[15] mp. 61-62°.

N,N'-Ditosyl-p-diaminobenzene prepared according to the procedure of Stetter and Roos[5] was impure. The crude product was purified in the following way: 91 g (mp. 269-272°) was dissolved in a mixture of 625 ml of 1N potassium hydroxide and 200 ml of methanol. This solution was stirred

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[*] All melting points are corrected and were determined in an oil bath; boiling points are uncorrected. UV spectra were obtained using a Zeiss spectrophotometer, model PMQ II. Infrared spectra were recorded with a Perkin-Elmer, Model 125, grating spectrophotometer. PMR spectra were determined on a Varian A-60 instrument with tetramethylsilane as an internal standard (τ=10.00); concentration of solutions in w/v. Unless otherwise stated signal integration ratios were in fair agreement with the theoretical values. Elemental analyses were performed under the supervision of Mr. W.M. Hazenberg in our Microanalytical Department.

For the preparation of compound IV we used for the slow addition of the reactants to the condensing agent (K_2CO_3 suspension) a "Dauerinfusionsgerät", supplied by B. Braun, Melsingen, Western Germany; with this apparatus the rate of the addition can be kept constant. Dimethylformamide (DMF) was dried with CaO and distilled at 15 mm from CaO; bp. 47-47.5°/15 mm, n_D^{20} 1.4305, lit.,[11] bp. 153°/760 mm, n_D^{25} 1.4269.

for ½ hr with decolorizing charcoal and then filtered. The filtrate was stirred and acidified with 4N hydrochloric acid. The precipitate was collected, washed with water and with methanol and then crystallized from 2 l. of a 1:3 mixture of DMF and methanol. Yield 79 g (63%), mp. 274-275° (lit.,[5] mp. 275-276°).

IR spectrum (KBr): 3220 cm^{-1} (N-H), 1315 and 1155 cm^{-1} (SO_2).

UV spectrum (96% ethanol), λ_{max}: 225 mμ (log ε 4.42) and about 245 mμ (sh).

N,N'-Ditosyl-1,4-diamino-2,5-dibromobenzene was prepared from 1,4-diamino-2,5-dibromobenzene.[16]

N,N'-Ditosyl-1,4-diamino-2,5-dimethoxybenzene was obtained in a yield of 79% in the same way as the above mentioned compound. It melted at about 313° (dec.).

IR spectrum (KBr): 3240 cm^{-1} (N-H), 1333 and 1155 cm^{-1} (SO_2).

UV spectrum (dichloromethane), λ_{max}: 308 mμ (log ε 3.96).

Anal. Calc'd for $C_{22}H_{24}N_2O_6S_2$ (476.58): C 55.4; H 5.1; N 5.9; S 13.5.
Found: C 55.6; H 5.0; N 5.9; S 13.5.

N,N'-Dimesyl-1,4-diamino-2,5-dimethoxybenzene was prepared according to the procedure described.[16]

The di-alkylated compounds I-IV.

N,N'-Diethyl-N,N'-ditosyl-p-diaminobenzene (Ia).

This compound was obtained according to the procedure for the preparation of the corresponding dimethyl derivative.[17]

N,N'-Diethyl-N,N'-ditosyl-p-diaminobenzene is a white crystalline substance, mp. 203.5-205°. The compound can be recrystallized from acetone.

IR spectrum (0.1 molar, in dichloromethane): 1343 and 1167 cm^{-1} (SO_2).

UV spectrum (96% ethanol), λ_{max}: 229 mμ (log ε 4.35).

PMR spectrum ($CDCl_3$): τ 2.67 (A_2B_2 system), aromatic protons of the tosyl groups, τ 3.03 (s), protons of the "central" benzene nucleus, τ 6.42 (q), $NC\underline{H}_2$, τ 7.59 (s) $C\underline{H}_3$, τ 8.93 (t), $N\text{-}CH_2\text{-}C\underline{H}_3$, J = 7 cps.

Anal. Calc'd for $C_{24}H_{28}N_2O_4S_2$ (472.63): C 61.0; H 6.0; N 5.9; S 13.6.
Found: C 60.9; H 6.1; N 5.9; S 13.6.

N,N'-bis(10-Bromodecyl)-N,N'-ditosyl-p-diaminobenzene (Ib).

A mixture of N,N'-ditosyl-p-diaminobenzene (5.83 g; 14 mmole), DMF (50 ml) and sodium methoxide solution [from 646 mg (28.1 mg-at.) of sodium and 15 ml of methanol] was heated at 90° for 1 hr. The methanol was removed in vacuo and the temperature of the residue maintained at 80-90° for 1 hr. After the addition of DMF (50 ml), the suspension was cooled to 0°; then a mixture of 1,10-dibromodecane (33.6 g; 0.112 mole) and DMF (25 ml) was added quickly. The temperature of the mixture was maintained for 5.5 hr between 80 and 83°. The greater part of the solvent was then distilled at 15 mm and the remaining DMF removed by keeping the residue for 1.5 hr at 60°/0.5 mm. This was treated with ether (125 ml); the undissolved material (mainly sodium bromide) was filtered and washed with a little ether. The ether was removed in vacuo and the residue treated with petroleum ether (bp. 40-60°; 150 ml). This mixture was cooled to -10°, the solid material filtered and washed with petroleum ether (75 ml). Yield 8.9 g of nearly white material melting from 58-61° (turbid melt). The crude product was chromatographed on alumina (330 g, Merck, neutral, Brockmann activity II-III). Elution with benzene gave 5.43 g (45%) of N,N'-bis(10-bromodecyl)-N,N'-ditosyl-p-diaminobenzene (Ib) as a white crystalline substance, mp. 68-69°. It can be recrystallized from a 1:3 mixture of benzene and petroleum ether (bp. 60-80°). The mp. remains unchanged. TLC (silica gel, eluent ether) gave one spot.

IR spectrum (0.06 molar, in CH_2Cl_2): 1344 and 1162 cm^{-1} (SO_2).

UV spectrum (96% ethanol), λ_{max}: 229 mμ (log ε 4.35), sh at about 255 mμ.

PMR spectrum (6%, $CDCl_3$): τ 2.68 (A_2B_2 system), arom. protons of the tosyl groups, τ 3.03 (s), protons of the "central" benzene nucleus, τ 6.35-6.75 (m) NCH_2, $BrCH_2$, τ 7.58 (s), CH_3, τ 8.0-8.9 (broad band with a sharp signal at τ 8.72), rest of the protons.

Anal. Calc'd for $C_{40}H_{58}Br_2N_2O_4S_2$ (854.88): C 56.2; H 6.8; N 3.3; S 7.5.
Found: C 56.3; H 6.8; N 3.6; S 7.8.

N,N'-bis[10-(p-Methoxyphenoxy)-decyl]-N,N'-ditosyl-p-diaminobenzene (Ic).

A mixture of sodium methoxide solution (from 1.20 g; 52 mg-at. of sodium and 100 ml of methanol) and a solution of 10.41 g (25.0 mmole) of N,N'-ditosyl-p-diaminobenzene in DMF (65 ml) was refluxed for ½ hr. To the white suspension was added (stirring) a warm (30°) solution of 1-bromo-10-(p-methoxyphenoxy)-decane (17.10 g; 49.8 mmole) in a mixture of DMF (130 ml) and dioxan (15 ml). The reaction mixture was heated for 9 hr on a steam-bath and concentrated in vacuo to about 150 ml. The precipitate which formed upon addition of 200 ml of water in small portions was collected and washed with water, methanol (275 ml), ethanol (50 ml) and petroleum ether (bp. 60-80°; 50 ml). In order to remove any incompletely alkylated product the solid was suspended in a solution of potassium hydroxide (4 g) in a mixture of water (200 ml) and methanol (300 ml). The product was filtered, washed with water once then twice with boiling methanol (250 ml). Yield of N,N'-bis[10-(p-methoxyphenoxy)-decyl]-N,N'-ditosyl-p-diaminobenzene (Ic) was 10.2 g (43%), mp. of 104.5-105.5°. The mp. did not rise after two crystallizations from mixtures of DMF and methanol. Absolute ethanol (50 ml for 1 g) can also be used for recrystallization.

IR spectrum (0.1 molar, in CH_2Cl_2): 1342 and 1158 cm^{-1} (SO_2).

UV spectrum (96% ethanol), λ_{max}: 227 mμ (log ε 4.63) and shoulders at about 250 and 290 mμ.

PMR spectrum (10%, in $CDCl_3$): τ 2.70 (A_2B_2 system), arom. protons of the tosyl group, τ 3.05 (s), protons of the "central" benzene nucleus, τ 3.23 (s) arom. protons of the groups $OC_6H_4OCH_3$, τ 6.0-6.65 (m), $NC\underline{H}_2$, $OC\underline{H}_2$, $OC\underline{H}_3$, τ 7.61 (s), $C\underline{H}_3$ of the tosyl groups, τ 8.1-8.85, broad band with a sharp signal at τ 8.72, remaining protons.

Anal. Calc'd for $C_{54}H_{72}N_2O_8S_2$ (941.32): C 68.9; H 7.7; N 3.0; S 6.8.

Found: C 68.7; H 7.8; N 2.9; S 6.6.

N,N'-Diethyl-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene (IIa).

To a stirred sodium methoxide solution [from 3.24 g (0.141 g-at.) of sodium and methanol (235 ml)] was added 40.0 g (69.6 mmole) of N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene. After the suspension had refluxed for 2 hr, DMF (350 ml) was added and the mixture maintained 1 hr at 80°. Methanol was removed at about 20 mm and the temperature brought to 50°. To this stirred mixture was added in 10 min. a solution of ethyl iodide (27.3 g; 0.175 mole) in DMF (100 ml). The temperature rose to 80° and the mixture was stirred for another 3 hr at the same temperature. After one night at room temperature, the nearly white substance which had crystallized was collected and subsequently washed with DMF (100 ml), methanol (50 ml) and water (500 ml). Recrystallization from a mixture of DMF (400 ml) and methanol (500 ml) gave 35.8 g (82%) of N,N'-diethyl-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene, mp. 218-219.5°; if the melt is cooled or maintained for a short time at 220°, the compound solidifies and the mp. is 228-228.5°. The compound can also be purified by crystallization from acetic acid or a mixture of acetone and water. Sometimes the high melting modification or a mixture of both was obtained. By heating the high melting modification for 2 hr at 150° it was transformed in the lower melting one.

IR spectra were taken for both modifications. The spectra of 0.05 molar solutions in CH_2Cl_2 were identical and those of KBr discs of the two forms showed only minor differences. The solutions showed in the range of the SO_2 vibrations strong absorptions at 1352, 1168 cm^{-1} and a shoulder at 1150 cm^{-1}; the KBr discs had in that region three, nearly equally strong, absorption peaks, *viz*. at 1352, 1167 and 1150 cm^{-1}.

For UV and PMR spectrum the low melting modification was used.

UV spectrum (96% ethanol), λ_{max}: 229 mμ (log ε 4.49), a shoulder at about 295 mμ (log ε 3.07).

PMR spectrum (10%, in $CDCl_3$): τ 2.52 (A_2B_2 system), aromatic protons of the tosyl groups, τ 2.69 (s), protons of the "central" benzene nucleus, τ 6.40 (q), $NC\underline{H_2}CH_3$, τ 7.54 (s), $C\underline{H_3}$, τ 8.87 (t), $NCH_2C\underline{H_3}$, J = 7 cps.

Anal. Calc'd for $C_{24}H_{26}Br_2N_2O_4S_2$ (630.45): C 45.7; H 4.2; N 4.5; S 10.2.

Found: C 45.7; H 4.2; N 4.6; S 10.2.

N,N'-bis(10-Bromodecyl)-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene (IIb).

A suspension formed from a solution of sodium methoxide (prepared from 1.398 g or 60.8 mg-at. of sodium and 100 ml of methanol) and N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene (17.22 g; 30.0 mmole), was refluxed for 2 hr. Then DMF (150 ml) was added and the mixture heated for 2 hr at 80°. By distillation *in vacuo* solvent was removed until pure DMF distilled. To the residue which was cooled to 0° was quickly added 1,10-dibromodecane (130 g; 0.43 mole) and DMF (50 ml). This mixture was heated at 85-87° for 3 hr. The greater part of the DMF was distilled from the mixture (to remove all of it the residue was heated for ½ hr at 80°/1 mm). To the remaining mixture was added 500 ml of ether and the undissolved material was collected, powdered and washed with 700 ml of ether. The undissolved material was washed with water (800 ml) and dried. It melted at 109-115.5°.

Recrystallization (<55°) from a mixture of DMF (300 ml) and methanol (625 ml) gave, after washing of the crystals with 200 ml of methanol (0°), 17.12 g of the desired compound as a white substance melting at 112-114.5°. The above mentioned ethereal solutions were combined and evaporated to dryness *in vacuo* and the residue treated with petroleum ether (bp. 40-60°). After one night at room temperature the undissolved material was filtered and washed with 500 ml of petroleum ether. Recrystallization from a mixture of DMF (150 ml) and methanol (450 ml) gave another 7.18 g of the same product melting at 114.5-116°. The total yield of slightly impure N,N'-bis(10-bromodecyl)-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene (IIb) was 24.3 g (80%).

Pure IIb was obtained as follows. Chromatography of 3.57 g over 82 g of alumina ("aktiv, standardisiert", Merck) gave by elution with benzene 1.87 g of a white substance with mp. 93.5-94.2°. The product solidified slowly at about 95° and melted again at 117-117.5°. Long storage of the low melting modification caused change to the higher melting form.

IR spectrum (0.1 molar, in CH_2Cl_2) of both modifications are identical: 1352 and 1162 cm^{-1} (SO_2 vibrations).

UV spectrum (96% ethanol), λ_{max}: 228 mμ (log ε 4.58) and shoulders at about 265 and 295 mμ.

PMR spectrum (10% in $CDCl_3$): τ 2.56 (A_2B_2 system), arom. protons of tosyl groups, τ 2.75 (s), protons of the "central" benzene nucleus, τ 6.3-6.8 (m), $BrC\underline{H_2}$, $NC\underline{H_2}$, τ 7.57 (s), $C\underline{H_3}$, τ 8.0-8.9, broad band with a sharp signal at τ 8.74, rest of the protons.

Anal. Calc'd for $C_{40}H_{56}Br_4N_2O_4S_2$ (1012.70): C 47.4; H 5.6; N 2.8; S 6.3.
Found: C 47.9; H 5.7; N 3.1; S 6.4.

N,N'-Ditosyl-N,N'-decamethylene-*p*-diaminobenzene (IIIa).

With a Hershberg[18] dropping funnel a solution of 8.33 g (20.0 mmole) of N,N'-ditosyl-*p*-diaminobenzene and 6.00 g (20.0 mmole) of 1,10-dibromodecane in 350 ml of DMF was added gradually in 21 hr to a vigorously stirred suspension of 41 g (0.30 mole) of potassium carbonate in 350 ml of DMF (nitrogen atmosphere). During the addition the temperature of the reaction mixture was maintained between 130 and 135°. Stirring and heating at the same temperature was continued for another 2½ hr after the addition had finished. The solid material was filtered at room temperature and washed with DMF (150 ml). The solution in DMF was concentrated *in vacuo* to 400 ml. Cooling to 0° caused crystallization; the crystals were filtered and washed with DMF (20 ml). The filtrate was evaporated to dryness *in vacuo*; the residue (brown, mainly oily product) was treated with 100 ml of methanol. The undissolved solid material was collected, subsequently washed with 50 ml of DMF-methanol mixture (1:8), methanol (30 ml) and petroleum ether (20 ml). The yellowish material (6.87 g) was stirred with a mixture of methanol (25 ml) and 0.3 N potassium hydroxide solution (60 ml). The undissolved product was filtered and subsequently washed with 75 ml of the same mixture, water, methanol (50 ml) and ether (50 ml). Nearly white product (6.21 g) melting from 170-189° was obtained. Treatment of the substance with benzene (275 ml) resulted in a turbid solution. Addition of Norit (3 g) and filtration afforded a clear solution, which was diluted with 400 ml of petroleum ether. After a few days the solid which had formed, was filtered and washed with benzene-petroleum ether (2:3). The product consisted of large colorless crystals and a white powder; these were manually separated and weighed respectively 5.41 g (mp. 187.5-189.5°) and 0.20 g (mp. 115-187°).

The first mentioned substance was again recrystallized from a benzene-petroleum ether mixture. Yield of N,N'-ditosyl-N,N'-decamethylene-p-diaminobenzene (IIIa) was 5.02 g (45%), mp. 189.5-190.5°.
IR spectrum (0.1 molar, in CH_2Cl_2): 1342 and 1160 cm^{-1} (SO_2).
UV spectrum (96% ethanol), λ_{max}: 231 mμ (log ε 4.29), 255 mμ (sh).

PMR spectrum (10%, in $CDCl_3$): τ 2.61 (A_2B_2 system), arom. protons of the tosyl groups, τ 2.98 (s), protons of the "central" benzene nucleus, τ 6.48 (t), NCH_2, τ 7.56 (s), CH_3, τ 8.3-9.5 broad band with a maximum at τ 9.28.

Anal. Calc'd for $C_{30}H_{38}N_2O_4S_2$ (554.78): C 65.0; H 6.9; N 5.1; S 11.6.
Found: C 65.1; H 6.8; N 5.0; S 11.3.

MW, determined with a Mechrolab osmometer, Model 301 A, in benzene: 568, 561.

N,N'-Ditosyl-N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene (IIIb).

A solution of N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene (22.97 g; 40.0 mmole) and 1,10-dibromodecane (12.00 g; 40.0 mmole) in DMF (675 ml) was added in a nitrogen atmosphere with the aid of a Hershberg[18] dropping funnel in 15 hr in an as constant a rate as possible to a vigorously stirred suspension of 100 g (0.72 mole) of potassium carbonate in DMF (500 ml). The temperature of the mixture was maintained between 132 and 137°. When the addition was finished, stirring at the same temperature was continued for an additional 2 hr. After one night at room temperature the solid was filtered and washed with DMF (100 ml). The filtrate was evaporated to dryness in vacuo; to the residue (a brown syrupy mass) was added 200 ml of methanol and then 20 ml of water. After one night at 0° the crystalline product was filtered and washed with 50 ml of a methanol-water mixture (9:1). A white solid (4.87 g) and a tough gray mass were obtained. The latter was removed manually and crystallized from 220 ml of methanol (Norit) to give, after 4 days at 0°, a crystalline solid which was collected and washed with 70 ml of methanol. In this way 6.74 g of a yellowish solid was isolated. It was combined with the above 4.87 g, boiled with 300 ml of benzene, cooled to 40° (3.5 g of a syrupy mass did not dissolve) and filtered. The filtrate was concentrated to 80 ml and then 200 ml of petroleum ether was added. After 2 hr the solution was decanted

(1.2 g of precipitated oil was left) and crystals appeared immediately. After 2 days at -5°, the solid was filtered, washed with 20 ml of benzene-petroleum ether (2:5) and 10 ml of methanol. The crystals (6.83 g, mp. 151-153°) were recrystallized from 400 ml of methanol. Yield 6.20 g (23%) of N,N'-ditosyl-N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene (IIIb), mp. 152.5-153.5°. IIIb is probably dimorphic since one recrystallization gave a product with a mp. 163-164°.

<u>IR spectrum</u> (0.1 molar, in CH_2Cl_2): 1353 and 1164 cm^{-1} (SO_2).

<u>UV spectrum</u> (96% ethanol), λ_{max}: 227 mμ (log ε 4.57), 264 mμ (sh, log ε 3.99).

<u>PMR spectrum</u> (20%, in $CDCl_3$): τ 2.51 (A_2B_2 system), arom. protons of the tosyl groups, τ 2.65 (s), protons of the "central" benzene nucleus, τ 6.1-7.0 (m), $NC\underline{H_2}$, τ 7.55 (s), $C\underline{H_3}$, τ 8.3-9.3 broad signal with a maximum at τ 9.08 and a shoulder at τ 9.18 (remaining protons).

<u>Anal</u>. Calc'd for $C_{30}H_{36}Br_2N_2O_4S_2$ (712.60): C 50.6; H 5.1; Br 22.4; N 3.9; S 9.0.

Found: C 50.5; H 5.1; Br 22.3; N 4.1; S 9.2.

MW: calc'd 712.6; found 730 (ebullioscopic in benzene).

<u>N,N'-Ditosyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene (IIIc)</u>.

To a solution of sodium methoxide prepared from 460 mg (20.0 mg-at.) of sodium and methanol (1200 ml) was added 4.77 g (10.0 mmole) of N,N'-ditosyl-1,4-diamino-2,5-dimethoxybenzene and 500 ml of DMF. The suspension was refluxed until the solid had disappeared. The solution was cooled at 0°, a solution of 3.00 g (10.0 mmole) of 1,10-dibromodecane in 100 ml of DMF was added and the cooled solution was added dropwise to vigorously stirred DMF (500 ml) the temperature of which was kept between 108 and 118° (N_2 atmosphere). The addition was completed after 4½ hr; during the reaction methanol was distilled off and 450 ml of DMF added.

The reaction mixture was then stirred for another 2 hr at 118-123°. The solvent was distilled at a pressure of 15 mm and to the residue (10 g of a brown syrupy mass) was added 50 ml of methanol and then 75 ml of water. After 2 days at -5° the precipitate was filtered and washed with water. This material was refluxed with 100 ml of methanol for 1 hr, the mixture was kept for one night at -5° and the precipitate again filtered and washed with methanol (35 ml). The resulting slightly brown substance (3.85 g) melted from 155->200°. It was stirred with a mixture of methanol (40 ml) and 0.7 N potassium hydroxide solution (60 ml). The undissolved product was filtered and again treated in a similar manner; the undissolved material was washed with water and dried to give a slightly brown substance (2.81 g melting from 145-163°; turbid melt). The solid was treated with 50 ml of benzene, Norit added and the mixture filtered. The filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in 115 ml of boiling methanol, treated with 2 g of Norit, filtered and the solution concentrated to 60 ml. After one night at 0° the crystals were collected, washed with methanol (10 ml), with petroleum ether (10 ml) and dried for 2 hr at 65°. The white product (1.59 g, mp. 162-164.5°) was recrystallized from methanol (50 ml) and dried for 5 hr at 80°/0.2 mm. Yield 1.57 g (26%) of N,N'-ditosyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene (IIIc), mp. 163.5-164.5°. TLC [silica gel; eluent: petroleum ether (bp. 40-60°)-ether 1:3] gave one spot.

IR spectrum (0.1 molar, in CH_2Cl_2): 1333 and 1152 cm^{-1} (SO_2).

UV spectrum (96% ethanol), λ_{max}: 227 mμ (log ε 4.52), 309 mμ (log ε 3.84).

PMR spectrum (20%, in $CDCl_3$): τ 2.58 (A_2B_2 system), arom. protons of the tosyl groups, τ 3.19 (s), protons of the "central" benzene nucleus, τ 6.46 (m), $NC\underline{H_2}$, τ 6.66 (s), $OC\underline{H_3}$, τ 7.59 (s), $SO_2C_6H_4C\underline{H_3}$, τ 8.4-9.3 with a maximum at τ 9.22 (remaining protons).

Anal. Calc'd for $C_{32}H_{42}N_2O_6S_2$ (614.84): C 62.5; H 6.9; N 4.6; S 10.4.
Found: C 62.5; H 7.0; N 4.6; S 10.4.

MW: calc'd 614.8; found 607 (ebullioscopic in benzene).

N,N'-Dimesyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene (IV).

With a Braun-apparatus (see Experimental*) a solution of N,N'-dimesyl-1,4-diamino-2,5-dimethoxybenzene (32.44 g; 0.1000 mole) and 1,10-dibromodecane (30.76 g; 0.1025 mole) in 1.25 l of DMF was introduced at a rate of 67.5 ml/hr directly into a suspension of potassium carbonate (312 g; 2.25 mole) in DMF (2 l). During the addition the mixture was stirred (750 rotations/min) and the temperature kept between 89 and 91°. A slow stream of nitrogen was passed through the suspension to remove traces of dimethylamine formed from DMF by hydrolysis. When the addition was complete stirring was continued for another hour at the same temperature. The suspension was then cooled to room temperature, the solid filtered and washed with DMF (200 ml). The filtrate was evaporated to dryness *in vacuo* and the residue boiled with 225 ml of methanol (1 hr). To the stirred mixture was added dropwise 600 ml of water. After keeping it for one night at room temperature, the solid was filtered with suction, washed with 150 ml of methanol-water (1:5), dried and then washed with ether (300 ml). A yellow product (41.5 g) melting from 161-167° (mp. of the solidified melt 176-180°) was obtained. This substance was purified by chromatography on 460 g of silica gel. Elution with benzene and benzene-ethyl acetate (4:1) yielded first nearly pure fractions, and later less pure ones (determined by TLC). The former (28.2 g) were crystallized from a mixture of chloroform (70 ml) and ether (450 ml); the solution was kept at -5° for one day. The crystals were collected, washed with ether (100 ml) and dried. N,N'-dimesyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene was obtained as a white substance, mp. 168.5-171° (mp. of the solidified melt 185.5-186.5°). The above mentioned less pure fractions (total 6.18 g) were purified by chromatography on 125 g of alumina (Merck, "aktiv, neutral"). Elution with benzene, mixtures of benzene and dichloromethane and finally benzene-ethyl acetate (4:1) gave fractions containing only one component (TLC; silica gel; dichloromethane-ethyl acetate 1:1). These combined residues from the eluates (5.03 g) were recrystallized from a chloroform-ether mixture (1:7) to yield 4.74 g of the higher melting modification as a white substance (mp. 186.0-187.0°). The total yield was 31.24 g (68%). For analysis and spectra the substance was again chromatographed over alumina and crystallized from a mixture of chloroform and ether. A product with a mp. of about 171° was obtained. The melting point of this lower melting material is difficult to determine because during melting, it changes into the higher melting form (mp. 187.5-188.4°). IV can exist in more than one modification as shown by heating the lower melting form for a few minutes at 180°. This caused the formation of the higher melting modification (weight was unchanged). This substance probably was a third modification with a melting point of 191.0-191.4°.

The IR spectrum (0.2 mole, in CH_2Cl_2) of the lower melting (mp. 171°) and the higher melting (187.5-188.4°) modification are identical: 1330 and 1148 cm^{-1} (SO_2). The IR spectra (KBr) show differences in the "fingerprint" region.

UV spectrum (96% ethanol), λ_{max}: 220 mμ (log ε 4.28), 304 mμ (log ε 3.86), about 240 mμ (sh) (log ε 3.90).

PMR spectrum (20%, in $CDCl_3$): τ 3.00 (s), arom. protons, τ 6.14 (s), $OC\underline{H_3}$, τ 6.1-6.8 (m), $NC\underline{H_2}$, τ 7.06 (s), $SO_2C\underline{H_3}$, τ 8.3-9.2 (broad signal), remaining protons.

Anal. Calc'd for $C_{20}H_{34}N_2O_6S_2$ (462.64): C 52.0; H 7.4; N 6.1; S 13.9.

Found: C 52.0; H 7.6; N 6.3; S 13.8.

MW: calc'd 462.6; found 471 (ebullioscopic in benzene).

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