Photochemical Studies

II. The Structure of the Photodimers of Carbostyril and N-Methylcarbostyril

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On irradiation with ultraviolet light, carbostyril and some of its derivatives dimerize. Dimers of carbostyril and N-methylcarbostyril are shown to have the trans-head-head-cyclobutane structures IIa and IIb. The two photodimers are shown to be interrelated.

Photodimerization of α,β-unsaturated lactams have only been observed in a few cases. 2-Pyridone and some of its derivatives were found to form cyclooctadiene rings on irradiation, resulting from 3,6-addition. The photodimerization of carbostyril and N-methylcarbostyril has been described, but no detailed structural evidence was forwarded. Taylor and Paudler suggested a cyclobutane structure for dimers of both pyridones and N-methylcarbostyril, but with no definite proof.

The present paper describes the investigation of the structure of the photodimers of carbostyril and N-methylcarbostyril. The assignment of a trans-head-head-cyclobutane structure to both dimers has been made on the basis of spectroscopic as well as chemical evidence.

SPECTROSCOPIC EVIDENCE

The amide carbonyl absorption band in the infrared spectra (Table 1) showed a shift to higher frequencies on dimerization of the carbostyrils, thus indicating the disappearance of the α,β-double bond.

The absence of the conjugated carbonyl group was confirmed by, (a) the hypsochromic shift in the ultraviolet spectra of the dimers, compared with the spectra of the monomers, and (b) the similarity of the spectra of the dimers with those of the 3,4-dihydrocarbostyrils (Table 2).

The nuclear magnetic resonance spectra of the dimers showed the presence of typical aromatic protons (Table 3). This eliminated the possibility of struc-
Table 1. Observed carbonyl absorption frequencies in the infrared.

<table>
<thead>
<tr>
<th></th>
<th>In KBr cm⁻¹</th>
<th>In dimethylsulfoxide cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbostyril</td>
<td>1665</td>
<td>1660</td>
</tr>
<tr>
<td>Dimer of carbostyril</td>
<td>1715</td>
<td>1680</td>
</tr>
<tr>
<td>N-Methylcarbostyril</td>
<td>1655</td>
<td>1660</td>
</tr>
<tr>
<td>Dimer of N-methylcarbostyril</td>
<td>1672</td>
<td>1663</td>
</tr>
</tbody>
</table>

It is observed that the unusually high carbonyl frequency of the carbostyril dimer (compared to the carbonyl frequency of the N-methylcarbostyril dimer) in the solid state, disappears in solution. The high carbonyl frequency of the compound containing the \(-CO-NH\) group is supposed to be due to intermolecular hydrogen bonding, which may also explain the insolubility in many solvents.

Table 2. Ultraviolet spectra. Solvent: ethanol

<table>
<thead>
<tr>
<th></th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbostyril</td>
<td>229</td>
<td>4.54</td>
<td>268</td>
<td>3.85</td>
<td>328</td>
<td>3.80</td>
</tr>
<tr>
<td>Dimer of carbostyril</td>
<td>229</td>
<td>4.59</td>
<td>270</td>
<td>3.87</td>
<td>329</td>
<td>3.79</td>
</tr>
<tr>
<td>N-Methylcarbostyril</td>
<td>211</td>
<td>4.62</td>
<td>260</td>
<td>4.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimer of N-methylcarbostyril</td>
<td>210</td>
<td>4.33</td>
<td>248</td>
<td>4.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4-Dihydrocarbostyril</td>
<td>210</td>
<td>4.32</td>
<td>250</td>
<td>4.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solvent: dioxane

<table>
<thead>
<tr>
<th></th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
<th>(m\mu)</th>
<th>log (\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbostyril</td>
<td>232</td>
<td>3.92</td>
<td>276</td>
<td>3.28</td>
<td>331</td>
<td>3.77</td>
</tr>
<tr>
<td>Dimer of carbostyril</td>
<td>224</td>
<td>4.33</td>
<td>259</td>
<td>4.23</td>
<td>290</td>
<td>3.66</td>
</tr>
<tr>
<td>N-Methylcarbostyril</td>
<td>254</td>
<td>4.24</td>
<td>278</td>
<td>3.76</td>
<td>334</td>
<td>3.79</td>
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<tr>
<td>Dimer of N-methylcarbostyril</td>
<td>259</td>
<td>4.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4-Dihydrocarbostyril</td>
<td>252</td>
<td>4.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Methyl-3,4-dihydrocarbostyril</td>
<td>253</td>
<td>4.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Structures analogous to those of the pyridone dimers and others where the aromatic character of the benzene nucleus is affected. The aliphatic protons in the carbostyril dimer gave rise to a sharp singlet \((\tau = 5.88)\) in trifluoroacetic acid. No other suitable solvent could be found for this compound.

The spectrum of the N-methylcarbostyril dimer could be recorded in both trifluoroacetic acid and deuteriochloroform. In deuteriochloroform the aliphatic protons gave rise to a degenerate doublet \((\tau = 6.27)\), \((N-\text{CH}_3, \tau = 6.56)\). In trifluoroacetic acid this absorption shifted a little downfield and was observed as a narrow pair of doublets \((\tau_1 = 6.00, \tau_2 = 5.74, j_1 = j_2 = 5 \text{ cps}) (N-\text{CH}_3, \tau = 6.33)\).

At first, this seemed to exclude a cyclobutane structure, and a search was made for compounds with isolated protons such as V-VI (a and b). However, the ultraviolet spectra ruled out structures of that kind, and interest was
focused on cyclobutane structures like I—IV (a and b). These are very much like the coumarin dimers. Two such compounds were prepared, and their nuclear magnetic resonance spectra recorded (Table 3). The trans-head-head-isomer (IIc) showed the presence of aliphatic protons as a sharp singlet \((\tau = 6.15)\) when recorded in deuteriochloroform. This singlet was split into a doublet \((\tau_1 = 5.87, \tau_2 = 5.97)\) in trifluoroacetic acid. The cis-head-head-dimer (Ic), when recorded in trifluoroacetic acid, presented the cyclobutane protons as a singlet \((\tau = 5.69)\). The almost identical chemical shifts of the aliphatic protons of the two carbostyril dimers with the cyclobutane protons of the coumarin dimers strongly suggested structures I—IV (a and b) for the two carbostyrils. The chemical shifts of some other cyclobutane methine protons are also recorded (Table 3).

\[
\begin{align*}
I & \quad \text{a. } X = \text{NH} \\
II & \quad \text{b. } X = \text{N-CH}_3 \\
III & \quad \text{c. } X = \text{O} \\
IV & \quad \text{V} & \quad \text{VI} \\
& \quad \text{a. } X = \text{NH} \\
& \quad \text{b. } X = \text{N-CH}_3 \\
& \quad \text{c. } X = \text{O}
\end{align*}
\]

**CHEMICAL EVIDENCE**

Many attempts were made to hydrolyze the dimers, but all were unsuccessful.

When treated with trifluoroacetic acid for some time, the carbostyril dimer monomerized. This was shown to be common for dimers containing the NH-group.\(^4\)

In order to examine how substitution affected dimerization, a number of methyl substituted carbostyrils were irradiated, and it was found that while carbostyrils substituted in the benzene nucleus easily dimerized, 3- and 4-substitution seemed to hinder dimerization.\(^4\)

The cyclobutane structure was demonstrated in the following manner:

The carbostyril dimer was ozonized, oxidized with hydrogen peroxide, and the product hydrolyzed with dilute hydrochloric acid. Without purification the hydrolyzate was methylated with diazomethane. The methylation yielded a crystalline compound. Infrared and nuclear magnetic resonance spectroscopy, and mixed melting point analysis showed the purified sample to be identi-
Table 3. Nuclear magnetic resonance spectra.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Cyclobutane protons $\tau$ (p.p.m.)</th>
<th>Aromatic protons $\tau$ (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>8</td>
<td>CDCl₃  CF₃COOH 6.10</td>
<td>CDCl₃  CF₃COOH</td>
</tr>
<tr>
<td>CH₃O₂C CO₂CH₃</td>
<td>9</td>
<td>6.15  6.23 (Found)</td>
<td></td>
</tr>
<tr>
<td>CH₃O₂C CO₂CH₃</td>
<td>9</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>CH₃O₂C CO₂CH₃</td>
<td>9</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>XH₂C CH₂X</td>
<td>9</td>
<td>a. 7.42  b. 7.10</td>
<td></td>
</tr>
<tr>
<td>XH₂C CH₂X</td>
<td>9</td>
<td>a. 7.42  b. 7.10</td>
<td></td>
</tr>
<tr>
<td>a. $X = O₂CCH₃$  b. $X = O₂CC₆H₅$</td>
<td>9</td>
<td>a. 7.42  b. 7.10</td>
<td></td>
</tr>
<tr>
<td>Io</td>
<td></td>
<td>5.69</td>
<td>3.00</td>
</tr>
<tr>
<td>IIc</td>
<td></td>
<td>6.15  5.92*</td>
<td>2.82  2.72</td>
</tr>
<tr>
<td>Dimer of carbostyril</td>
<td></td>
<td>5.88</td>
<td>2.75</td>
</tr>
<tr>
<td>Dimer of N-methylcarbostyril</td>
<td></td>
<td>6.27  5.87**</td>
<td>3.00  2.62</td>
</tr>
</tbody>
</table>

* Doublet: $\tau_1 = 5.87$; $\tau_2 = 5.97$
** Narrow doublet of doublets: $\tau_1 = 6.00$; $\tau_2 = 5.74$

...cal with a sample of tetramethyl cis-trans-cis-cyclobutanetetracarboxylate prepared from trans-head-head-coumarin dimer. By chromatography a further amount of the main product could be obtained together with a small amount of a compound VII, m.p. 152—154°C. This result limits the possible structures for the carbostyril dimer to IIa or IVa. By treating the N-methylcarbostyril dimer in a similar manner, the tetramethyl cis-trans-cis-cyclobutanetetracarboxylate was obtained, together with small amounts of two other compounds, VIII, m.p. ca. 320°C and IX, m.p. 145—147°C. Thus the N-methylcarbostyril dimer must have structures IIIb or IVb.

Attempts to synthesize the N-methylcarbostyril dimer from the carbostyril dimer by methylation with methyl iodide or dimethyl sulfate were unsuccessful. However, it was possible to correlate the dimers in the following manner.

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N-Methylcarbostyril dimer on reduction with lithium aluminium hydride in diethyl ether yielded X. This compound could be converted to its monomethiodide (XI) on treatment with methyl iodide in benzene at room temperature. Both the monomethiodide (XI) and X on treatment with boiling methyl iodide yielded the dimethiodide (XII). On treatment with strong aqueous potassium hydroxide both XI and XII reverted to X.

The carbostyril dimer was transformed to X in the following manner. Reduction with lithium aluminium hydride in dioxane yielded an oil which crystallized after some time to give XIII. When XIII was treated with methyl iodide followed by strong aqueous potassium hydroxide, it gave a crystalline product which was identified as X by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy, and mixed melting point.

![Chemical structures](image)

This shows that the two dimers have the same orientation with respect to the cyclobutane ring i.e. that they are both either trans-head-head IIa-IIb or trans-head-tail IVa-IVb compounds. The dipole moment of the trans-head-tail-form must be zero, while that of the trans-head-head-dimer should be rather large (the dipole moment of the trans-head-head-coumarin dimer has been found to be 5.7 D). The dipole moment of the carbostyril dimer could not be measured because of the poor solubility of this compound. However, the dipole moment of the corresponding amine XIII was found to be 2.53 D (in benzene), and the dipole moment of the N-methylcarbostyril dimer was found to be 5.28 D (in benzene). Lit. gives 4.62 D (in chloroform). This, together with the reported spectroscopic and chemical evidence, establish the two dimers as IIa and IIb.

**EXPERIMENTAL**

Microanalysis were carried out in the microanalysis department of this laboratory by Preben Hansen.

Melting points (uncorrected) were determined on a Reichert melting point microscope, mixed melting points on a Büchi melting point apparatus.

Infrared spectra were recorded either on a Perkin Elmer "Infraord", or on its model 21 double beam spectrophotometer. Ultraviolet spectra were recorded on a Perkin Elmer model 137 UV spectrophotometer, and nuclear magnetic resonance spectra were recorded on a Varian A60 with tetramethylsilane as internal reference.

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Electric dipole moments were determined by measuring the dielectric constants of solutions of the compounds in benzene at 25°C with the apparatus Dipolometer DM 01 (Wissenschaftlich-Technische Werkstätten, Weilheim). The calculations were made using the equation and method of Hedestrand.

General procedure for photochemical reactions. Method a. This method has been described elsewhere.

Method b. The solution to be irradiated was placed in a glass cylinder equipped with a sintered glass inlet for nitrogen.* A low pressure mercury lamp, NK 6/20 (Hanau) was then immersed into the cylinder.

Method c. The irradiations were carried out in a cylinder shaped reaction chamber with outer cooling, which was again equipped with a sintered glass inlet for nitrogen.* In the reaction chamber was placed a Q81 (Hanau) high pressure mercury lamp with a quartz cooling mantle through which was led deionized water during irradiations.

Carbostyril dimer. Method a. See previous paper. Method b. Carbostyril (10.00 g, 0.069 mole) dissolved in 96% ethanol (100 ml) was irradiated for 6 days at 35°C. The precipitated crystals were isolated (7.00 g, 70%) m.p. ca. 300°C, subl. The IR: Table 1, the UV: Table 2. and the NMR: Table 3, spectra were identical with those given for the carbostyril dimer.

N-Methylcarbostyril dimer. Method c. N-Methylcarbostyril (5.00 g, 0.0315 mole) dissolved in 96% ethanol (60 ml) was irradiated for 12 h at ca. 10°C. Half an hour before the reaction was started deoxygerized nitrogen was led through the solution, and this was continued during the irradiation. The precipitated white crystals were isolated (4.00 g, 80%) m.p. 211–213°C. Recrystallization from ethanol raised the melting point to 215–216°C. (Found: C 75.45; H 5.78; N 8.80. Calc. for C_{15}H_{13}N_{2}O: C 75.48; H 5.70; N 8.80). IR: Table 1. UV: Table 2. NMR: Table 3. (N-CH_{3}, τ = 6.56 in deuteriochloroform; τ = 6.33 in trifluoroacetic acid). Dipole moment 5.28 D (benzene).

Coumarin dimers. These were prepared according to the method described by Schwenk et al.

Hydrocarbostyrils. 3,4-Dihydrocarbostyril was prepared according to the method described by Cavallito et al. The same method was used to prepare N-methyl-3,4-dihydrocarbostyril. (Found: C 74.37; H 6.91. Calc. for C_{15}H_{11}NO: C 74.51; H 6.85). UV: Table 2.

Attempted hydrolysis of the dimers. The carbostyril dimer or the N-methyl carbostyril dimer was boiled with hydrochloric acid in several concentrations, but only the starting material could be isolated. When boiled with 50% aqueous, 50% ethanolic, or 80% ethanolic potassium hydroxide for 24 h only starting material was again isolated.

Monomerization of the carbostyril dimer in trifluoroacetic acid. The carbostyril dimer (100 mg) in trifluoroacetic acid (0.5 ml) was kept at room temperature for ca. 60 h. During this time the nuclear magnetic resonance spectrum of the solution changed pattern from that of the carbostyril dimer to that of the monomer. The solvent was evaporated and it was found that the infrared spectrum and the melting point also corresponded to that of the monomer carbostyril.

Irradiation of substituted carbostyrils. See Ref.

Tetramethyl cis-trans-cis-cyclobutanetetracarboxylate. This was prepared from trans-head-head-coumarin dimer according to the method described by Schwenk et al. M.p. found: 143–144°C. Lit. 144.5°C. (Found: C 50.12; H 5.57. Calc. for C_{15}H_{10}O_{5}: C 50.00; H 5.60). NMR: Table 3. (O-CH_{3}, τ = 6.31 in deuteriochloroform).

Degradation of carbostyril dimer. Carbostyril dimer (1.00 g, 3.45 mmole) was suspended in 80% aqueous acetic acid (100 ml), and excess ozone passed into the solution for 7 h at room temperature, with constant stirring. 10% Hydrogen peroxide (36 ml) was then added, and the solution left at room temperature. After 48 h, the solution was diluted to twice its volume with water, and the solvents removed by evaporation in vacuo.* Water (50 ml) was added, and the solution again taken to dryness in vacuo. The oily residue was dissolved in 0.4 N hydrochloric acid (40 ml), and heated on a steam bath for 2 h. The solution was evaporated to dryness, water was added, and the evaporation

* Only when stated nitrogen was led through the solutions during irradiation.
** Lit. warns that explosion may occur if evaporation is made at temperatures higher than 40°C. However, the author performed more than twenty ozonizations in the described way, followed by evaporation at 100°C, without accidents.

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repeated. The residue was dissolved in 96 % ethanol (20 ml), and excess diazomethane in ether added. The solvents were removed by evaporation, and the semicrystalline residue (575 mg) was recrystallized from ethanol (177 mg, 18 %), m.p. 138--141°C. After several recrystallizations from ethanol and benzene the melting point was raised to 143--144°C. (Found: C 50.00; H 5.56. Calc. for C_{4}H_{14}O_{4}; C 50.00; H 5.60.) It was identified by infrared and nuclear magnetic resonance spectroscopy, and by mixed melting point as being tetramethyl cis-trans-cis-cyclobutanetetracarboxylate.

VII. By chromatography on florisor of the mother liquor from the above methylation, some of the main product (50--50 benzene-petrolether) was isolated as well as a second fraction (2--98 ethyl acetate-benzene, 50 mg), which on recrystallization from ethanol had m.p. 152--154°C. (Found: C 48.50; H 5.51; N 5.30). This was not examined further.

Degradation of the N-methylcarboaryl dimer. N-Methylcarboaryl dimer (750 mg, 2.39 mmole) was oxidized and oxidized as described for the carboxyl dimer. The product was dissolved in 0.4 N hydrochloric acid (40 ml), and the solution left at room temperature for 60 h before heating on a steam bath. The raw product was methylated as described for the carboxyl dimer. On crystallization from ethanol the product from the methylation gave a crystalline compound (101 mg, 15 %), m.p. 138--140°C, which after several recrystallizations from ethanol and benzene melted at 143--144°C. (Found: C 50.20; H 5.55. Calc. for C_{11}H_{20}O_{4}; C 50.00; H 5.60.) It was identified as tetramethyl cis-trans-cis-cyclobutanetetracarboxylate by infrared, and nuclear magnetic resonance spectroscopy, and by mixed melting point.

VIII. A small amount of soluble compound (5 mg) which after recrystallization from ethyl acetate had m.p. ca. 320°C, subl., was obtained by recrystallization of the tetrathiomethyl ester from N-methylcarbyosteryl dimer. (Found: C 64.05; H 4.55).

IX. Chromatography on florisor of the mother liquor from the above methylation gave a compound (30 mg) m.p. 145--147°C. (Found: C 52.00; H 5.25; N 5.86). VIII and IX were not further examined.

X. Reduction of the N-methylcarboaryl dimer with lithium aluminium hydride. N-Methylcarboaryl dimer (2.98 g, 9.37 mmole) and lithium aluminium hydride (1.0 g) were suspended in anhydrous ether (750 ml). The mixture was stirred under nitrogen for 4 days after which the excess lithium aluminium hydride was decomposed by addition of a solution of acetone (4 ml) in ether (50 ml), followed by water (6 ml). The precipitated inorganic material was removed by filtration, and the solvent evaporated in vacuo. This gave an oil which crystallized after a short time. Recrystallization from benzene-ether yielded white cubic crystals (2.39 g, 84 %), m.p. 184--185°C. (Found: C 82.40; H 7.68; N 9.52; Mol.wt. 262 (erysosopic in dioxane). Calc. for C_{18}H_{32}N_{2}; C 82.72; H 7.64; N 9.65; Mol.wt. 290). 

\[ \lambda_{\text{max}}^{\text{ethyl}} = 209 \text{ m}_{\mu}, \log \varepsilon = 4.55; 252 \text{ m}_{\mu}, \log \varepsilon = 4.27; 300 \text{ m}_{\mu}, \log 

\varepsilon = 3.77. \] 
Nuclear magnetic resonance spectrum in deuterochloroform: aromatic protons centered at \( \tau = 3.16 \); aliphatic protons as a strong singlet at \( \tau = 7.13 \), and a weak singlet at \( \tau = 6.97 \), in the ratio 4:7. In trifluoroacetic acid: aromatic protons at \( \tau = 2.35 \), aliphatic protons at \( \tau = 5.86 \) (triplet), and \( \tau = 6.62 \) (singlet), in the ratio 4:3:4.

XI. Monomethiodide of X. The compound X (260 mg, 0.90 mmole) was dissolved in a mixture of benzene (10 ml) and methyl iodide (3 ml) and left in the dark at room temperature for 8 days. The precipitated crystals were isolated and recrystallized from ethanol-water (225 mg, 86 %), m.p. 185--186°C. (Found: N 6.15; I 31.10. Calc. for C_{18}H_{32}N_{2}I_{2}: N 6.69; I 30.54).

XII. Dimethiodide of X. Compound X (318 mg, 1.00 mmole) was boiled with methyl iodide (15 ml) for 5 h. The excess methyl iodide was evaporated, and the residue crystallized from water (480 mg, 84 %), m.p. 260--270°C. (Found: C 46.15; H 5.15; I 44.80. Calc. for C_{18}H_{32}N_{2}I_{2}: C 46.00; H 4.92; I 44.54). The same compound was obtained by boiling XI with methyl iodide, and this was identified by infrared spectroscopy.

Reconversion of monomethiodide (XI) to X. Monomethiodide (XI) (106 mg, 0.25 mmole) and 40 % aqueous potassium hydroxide (10 ml) was heated on a steam bath for 1 h. During this time a precipitate was formed, which was extracted with methylene chloride-ether. The extract was washed with water and then with saturated sodium chloride solution and filtered through anhydrous magnesium sulfate. Evaporation of the solvents left a crystalline residue which after recrystallization was shown to be identical with X, by means of infrared spectroscopy (29 mg, 40 %).

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Reconversion of dimethiodide (XII) to X. Dimethiodide (XII) (230 mg, 0.40 mmole) was treated with aqueous potassium hydroxide in the same way as XI to yield X (58 mg, 50%), which was identified by infrared spectroscopy.

XIII. Reduction of the dimer of carboxylure with lithium aluminium hydride. The carboxylure dimer (2.00 g, 7.90 mmole) and lithium aluminium hydride (2.0 g) were suspended in dioxane (250 ml), and the suspension stirred under nitrogen for 19 h at room temperature. The excess lithium aluminium hydride was decomposed with a solution of water (5 ml) in dioxane (35 ml), ether was added, and the inorganic precipitate removed by filtration. The solvents were evaporated, and the resulting yellow oil left for 2 days, after which crystallization had begun. Treatment with ether-petroether yielded white-yellow crystals (plates), (1.30 g, 63%), m.p. 120°C. Recrystallization from ethanol raised the melting point to 125–126°C. (Found: C 82.20; H 6.89; N 10.72. Calc. for C₁₆H₁₆N₂: C 82.40; H 6.92; N 10.68). λ<sub>max</sub><sup>η-ROH</sup> = 208 μν, log ε = 4.67; 243 μν, log ε = 4.23; 300 μν, log ε = 3.78. Nuclear magnetic resonance spectrum in deuteriochloroform: aromatic protons were centered at τ = 3.17, aliphatic protons as one peak at τ = 6.69, amine protons at τ = 6.35, in the ratio 4:1.

Methylation of XIII with methyl iodide. Compound XIII (525 mg, 2.00 mmole) was boiled with methyl iodide (10 ml) for 5 h. The excess methyl iodide was removed by evaporation and the residue was treated with aqueous potassium hydroxide as described for XI. Crystallization from ethanol yielded a compound (70 mg, 12%), m.p. 184–185°C. (Found: C 82.07; H 7.73; N 9.38. Calc. for C₁₆H₁₆N₂: C 82.72; H 7.64; N 9.65). This compound was shown to be identical with X by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy, and by mixed melting point.

Acknowledgements. The author wishes to thank prof. K. A. Jensen for his encouragement and interest in this work. Thanks are also due to Charles Larsen for measuring the dipole moments, and to J. Rastrup Andersen and K. Schaumburg for their help with the nuclear magnetic resonance spectroscopy.

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