Tetrahedron Vol. 36, pp. 1445 to 1450
Pergamon Press Ltd., 1980. Printed in Great Britain

SYNTHESIS AND STUDIES OF TRIS-INDOLOBENZENES AND RELATED COMPOUNDS†

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(*Received in UK 20 August 1979*)

Abstract—The unsymmetrical N,N,N-trimethyl tris-indolobenzene **3** has been synthesized by several routes, including cyclotrimerization of the O-acetate of indoxyl. This condensation involves a 3→2 rearrangement of the precursor formed *in situ*. Similar Wagner–Meerwein rearrangements were also prevalent in LAH reductions of some 3,3-diindolyl oxindoles.

Treatment of the 3,3-diindolyl indolines with strong acid resulted in a cleavage yielding 3,3'-biindolyls.

In connection with the Ullmann coupling of 2-iodo-N-methylindole it was found[1] that the trimeric compound **1** and N-methylindole were the main products rather than N,N'-dimethyl-2,2'-biindolyl (**2**), if activated copper bronze was used. Compound **1** was found to be identical with a product, obtained by Müller[2] in low yield by heating 3-chloro-N-methylindole with aqueous sodium hydroxide in an autoclave at 180–200°. The less likely, unsymmetrical structure **3** can not, however, as pointed out by Hoffmann,[3] be ruled out as an alternative structure for the trimer.

The unsymmetrical cyclo-trimer **3** has now been unambiguously synthesized *via* the routes given in Scheme 1.‡ Compound **3** (m.p. 186–187°) differ considerably from compound **1** (m.p. 265–267°). The ^{1}H-NMR spectrum of **3** shows two somewhat broadened signals for the Me protons in the ratio 2:1, whereas the symmetrical trimer exhibits the expected sharp singlet for the Me groups.

The condensation product **6** is probably formed *via* **9a** (isolable) and **10a**. Clearly the addition of the second molecule of N-methylindole could give either **6** or **11a** (including possible tautomers). Spectroscopic data excluded structure **11a** and gave strong evidence for **6**. This result is intriguing as Zhungietu and Sinyavskaya[4] recently have claimed that isatin and indole yielded **11b** rather than **12a**.

However, analysis by ^{13}C-NMR reveals that the structure **12a** for the isatin-indole 1:2 condensation product originally given by Seidel[5] is correct.§ Furthermore, methylation of **12a** yielded **6**, and the isomer **11b** could be independently synthesized by condensation of 2,3'-biindolyl with 3-hydroxyoxindole in refluxing acetic acid. In a model experiment 2-methylindole and 3-hydroxyoxindole similarly gave **13**, which could be converted to compound **14**. Reduction of **11b** with lithium aluminium hydride furnished the known[6,7] compound **15**.

Compound **12a** could also readily be obtained by alkaline hydrolysis of **12b**, which was conveniently prepared in high yield by heating N-acetylisatin with indole to 210° for 5 min. N-Methylindole similarly gave **12c**. Methylation of the anion of its hydrolysis product, **12d**, with methyl iodide in N,N-dimethylformamide gave **6**.

The reductive rearrangement (**6**→**8**) probably proceeds *via* **16** and **17** (*cf* Ref 8). Witkop[6] has reported a similar rearrangement starting with **18** (yielding **15**). The yield of the indoline (**7**) increased with increasing amounts of LAH. Reduction of **6** with diborane in hot (90°) diglyme exclusively gave **7**. Reduction of **12a** (or better **12b**) with LAH was analogous with the transformation (**6**→**7**+**8**) and the expected products **15** and **19** could be isolated after column chromatography.

The DDQ-induced dehydrogenative rearrangement **7**→**8** probably also involves the cation **17** (*cf* Ref 9). Isobe *et al.*[10,11] have recently reported similar rearrangements of several 3,3-diarylindolines using oxidants such as MnO_2, PbO_2 and $(C_6H_5COO)_2$. When **7** was treated with two equivalents of DDQ the desired unsymmetrical trimer (**3**) could, after column chromatography, be obtained in one step. Coupling of the 2,2'-dilithioderivative of **8** with $CoCl_2$ or $CuCl_2$ also afforded **3**.

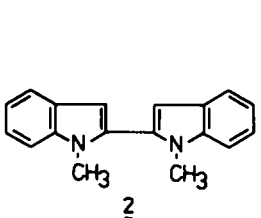
Compound **7** was readily cleaved to N-methylindole, (which in secondary reactions was transformed to a mixture of the known dimer and trimer) and N,N'-dimethyl-3,3'-biindolyl by treatment with strong acid (e.g. HClaq). A transient violet-blue colouration observed during the reaction might indicate the formation of **21**, as indicated in Scheme 2. This cleavage reaction might be of interest for the preparation of unsymmetrical 3,3'-biindolyls. This aspect has, however, not been explored. It was also noted that the related indoline derivative (**20a**) failed to cleave off N,N-dimethylaniline by treatment with strong acid. The precursor of **20a**, **20b**, was conveniently prepared by refluxing isatin and N,N-dimethylaniline in acetic acid. The parent compound of **7**, **19**, also underwent acid-induced cleavage yielding 3,3'-biindolyl. Interestingly similar cleavages are prevalent in the mass spectra of **7** and **19**.

In view of the known[12] oligomerization of 3(2H)-benzofuranone (to a symmetrical cyclotetramer) and 3(2H)-benzothiophenone[13,14] (to the symmetrical cyclotrimer **27**) we have also studied the acid-catalyzed (trifluoroacetic acid) condensation of N-methylindoxyl (**22**) using the O-acetate as a precursor. After chromatography and gradient sublimation the unsymmetrical trimer **3** as well as cyclotetramer and cyclopentamer fractions were obtained. A rationalization is given in Scheme 3. The N-methylindoxyl-group in the suggested intermediate (**23**), should by virtue of the electron-donating N atom show considerable

†Presented in part at the 13th Nordiske Kemikermøde, Copenhagen, 1968 p. 74.

‡After the completion of this work the parent compound of **3**, diindolo [2,3-*a*:2',3'-*c*]carbazole, has been reported[26] as a product from reactions of indole with a $TiCl_3$-H_2O_2-system.

§The Russian workers seemed to be unaware of Seidel's paper.



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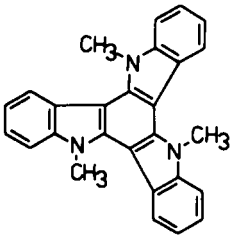

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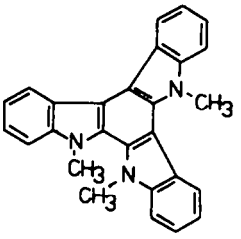

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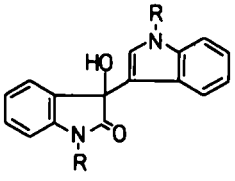

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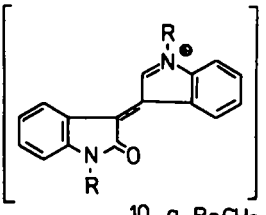
b R=H



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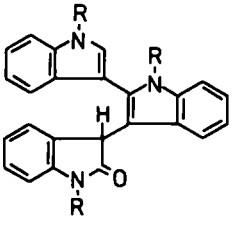
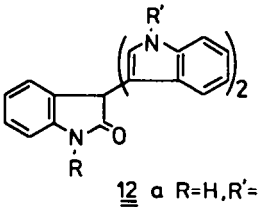
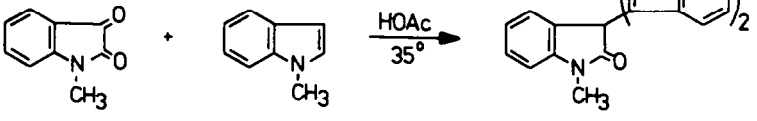
b R=H



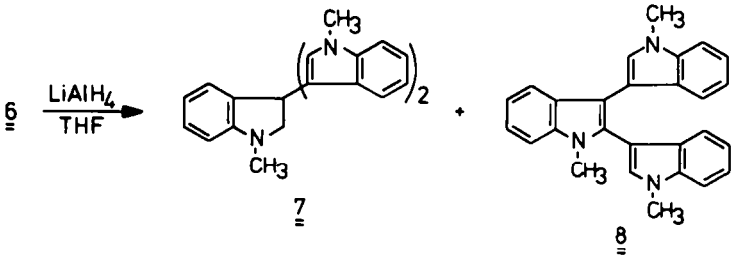
11 a R=CH3
b R=H



12 a R=H, R'=H
b R=COCH3, R'=H
c R=COCH3, R'=CH3
d R=H, R'=CH3
e R=CH3, R'=H



4 + 5 → (HOAc, 35°) 6

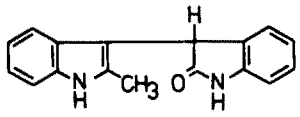


6 → (LiAlH4, THF) 7 + 8

7 → (DDQ, dioxane) 8 → (DDQ, dioxane) 3

8 → (1. BuLi, 2. CuCl2) 3

Scheme 1.



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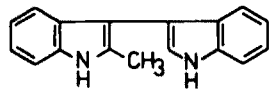

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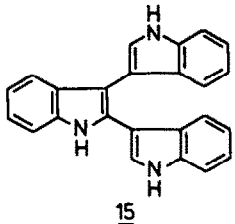

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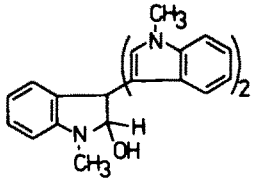

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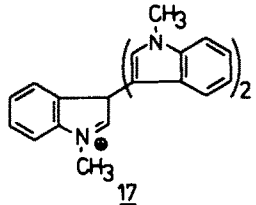

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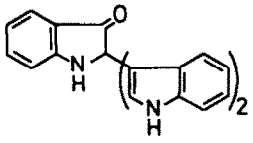

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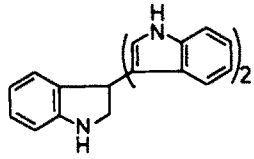

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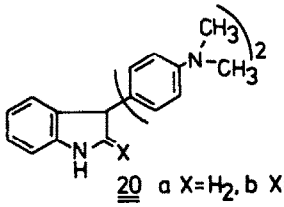
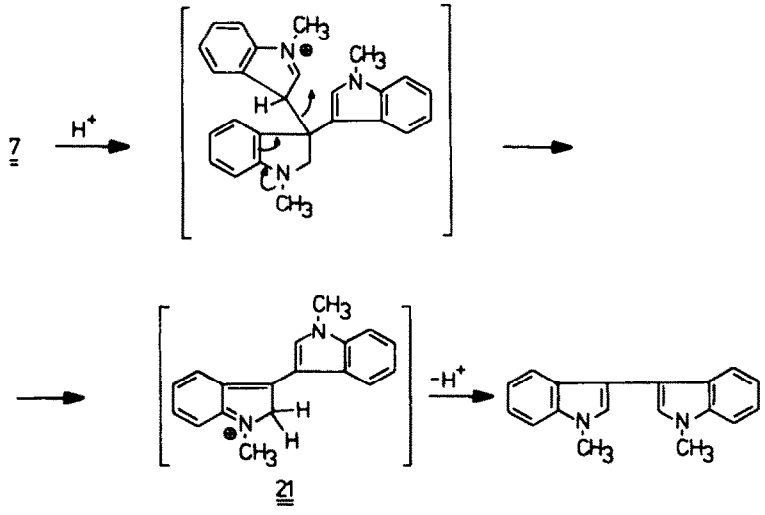


20 a X=H_2, b X=O



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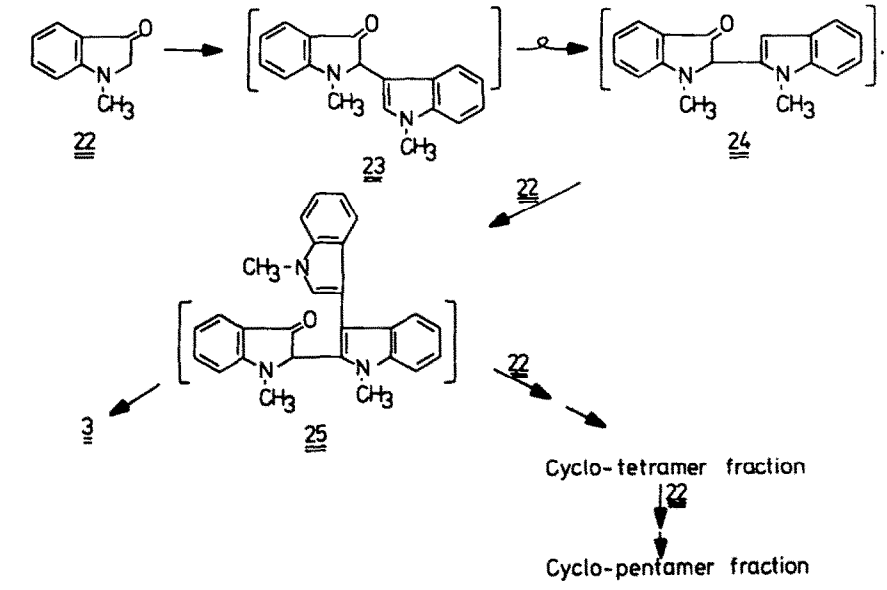
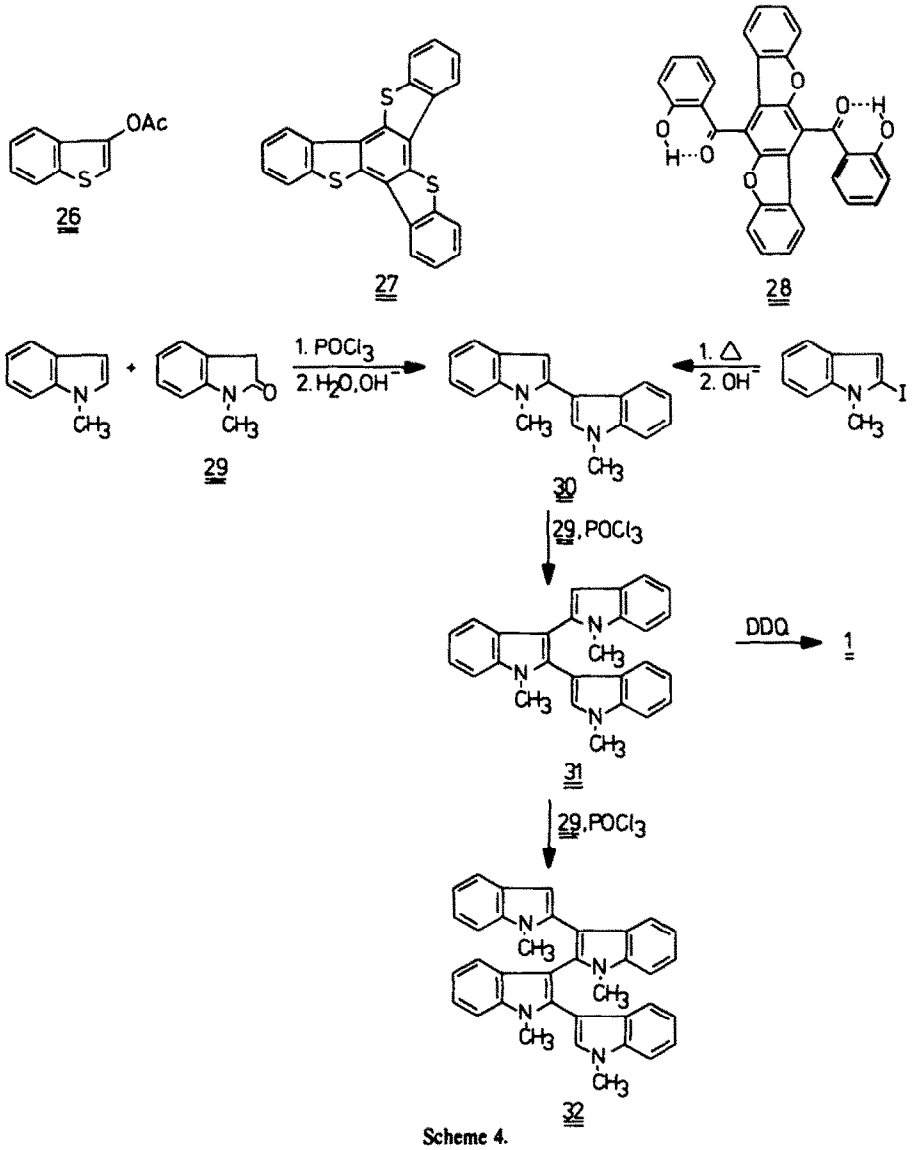
Scheme 2.



Scheme 3.



Scheme 4.

migratory aptitude. Similar acid-induced 3→2-isomerizations involving groups such as benzyl, Me, and t-Bu are well-established.[8,15,16] The detailed composition of the cyclotetramer fraction and the cyclopentamer fraction has not been established, but from a mechanistic point of view it seems likely that they should contain unsymmetrical isomers.

In connection with these studies, it was noted that **26** when refluxid with trifluoroacetic acid gave the known trimeric compound **27**, whereas 3(2H)-benzofuranon yielded the tetrameric product **28** (*cf* Refs 12 and 17). The symmetrical structure of **27** has been verified[18] by degradation with Raney nickel, which yielded 1,3,5-triphenylbenzene.

As outlined in Scheme 4 the symmetrical cyclotrimer (**1**) has also been prepared by a stepwise procedure. The immediate precursor (**31**) may be obtained in one step if N-methyloxindole (**29**) is used in two equivalents in the first Vilsmeier step. By further reaction even a tetrameric derivative could be characterized and in principle it seems possible to build up even larger oligomers and polymers.

EXPERIMENTAL

M.ps were determined on a micro hot stage m.p. apparatus and are uncorrected. IR spectra were recorded with a Perkin Elmer 421 IR spectrophotometer as KBr discs. ^{1}H-NMR spectra were recorded on a Varian-A60 or a Bruker WP 200 instrument. All chemical shifts are related to TMS ($\delta_H = 0$). Mass spectra were recorded with an LKB 9000 instrument (direct inlet, 70 eV).

3,3-*Bis*(N-*methyl*-3-*indolyl*)-N-*methyloxindole*(**6**)

Method A. N-Methylisatin (16.1 g, 0.1 mol) was added with stirring to a soln of N-methylindole (26.2 g, 0.2 mol) in AcOH (80 ml) at 35°. A clear light soln was obtained within 10 min. After 24 hr EtOH was added to the slurry and the solid collected by filtration and dried, yield 39.3 g (92%) m.p. 223–228° (after recrystallization from EtOAc/EtOH the m.p. was 232–234°). IR: 3058 (w), 2982 (w), 1710, 1616, 1472, 1368, 1339, 748 NMR($CDCl_3$): δ_H 3.22 (3, NCH_3, s), 3.49 (6, NCH_3, s), 6.8–7.5 (14, arom., m). MS[*m/e*(% rel. int.)]: 406(M + 1, 31), 405(M, 100), 377(33), 376(98), 275(29), 248(16), 247(77), 202.5(16). Only peaks higher than 15% are listed.

Method B. 3,3-Bis(3-indolyl)oxindole (3.63 g) in N,N-dimethylformamide (50 ml) was treated with sodium hydride (0.97 g) under N_2 at 35° until the evolution of H_2 ceased, whereupon MeI (4.30 g) was added and the mixture was stirred at 45° for 6 hr. The mixture was then poured into water and the solid formed collected, washed, dried and recrystallized from EtOAc/EtOH, yield 3.20 g (79%) m.p. 232–234°.

The following compounds were similarly prepared using method A. 3,3-*Bis*(3-*indolyl*)*oxindole* (**12a**), yield 88% m.p. 312–314° (lit,[5] 310°). IR: 3425(NH), 3320(NH), 1710(C = O), 1607, 1470, 755, 735. MS[*m/e* (% rel. int.)]: 364(M + 1, 25), 363(M, 92), 362(19), 335(30), 334(100), 219(50), 117(22). Only peaks higher than 15% are listed. m*: 307.3 (363→334). ^{13}C-NMR: δ_c 109.45, 111.46, 114.30, 118.08, 120.77 (2 peaks, sep. 0.05 ppm), 121.28, 124.18, 124.80, 125.66, 127.70, 134.56, 136.87, 141.30, 178.63. Apparently the signals from two C atoms coincide with a separation less than 0.05 ppm.

3,3-*Bis*(3-*indolyl*)-N-*methyloxindole* (**12e**), yield 92% m.p. 292–293° (lit.[19] 292–293°).

3,3-*Bis*(N-*methyl*-3-*indolyl*)*oxindole* (**12d**), yield 94% m.p. 330–332°. MS[*m/e*(% rel. int.)]: 391(M, 49), 362(100), 346(8), 261(10), 233(21), 232(7), 195½(13). Only main peaks higher than 6% above *m/e* 100 are listed.

Reduction of **6** *with lithium aluminium hydride. Synthesis of* **8**. Compound **6**, (4.05 g) was added in portions to LAH (0.3 g) in refluxing ether (500 ml). After complete addition the mixture was refluxed for 6 hr and then worked up by cautious addition of water (2 ml) followed by filtration after 1 hr. The ether soln was evaporated and the residue crystallized from EtOAc, yield 2.9 g (72%) m.p. 214–215°.

A further crop (0.4 g) as well as a small amount of **7** could be obtained by column chromatography (SiO_2, CH_2Cl_2) of the evaporated mother liquor. *Rf*(**8**) = 0.77, *Rf*(**7**) = 0.57. IR: 3050(w), 1481, 1464, 1340, 1249, 1234, 742. NMR ($CDCl_3$, 200 MHz): δ_H 3.68 (3, NCH_3, s), 3.71 (6, NCH_3, s), 6.8–7.7 (14, arom., m).

The following compound was similarly prepared:

2,3-*Bis*(3-*indolyl*)*indole*, yield 58% m.p. 158–160° (lit.[7] 152–156°).

Reduction of **6** *with diborane—Synthesis of* 3,3-*bis*(N-*methyl*-3-*indolyl*)-N-*methylindoline* (**7**). BF_3-etherate (10.0 g) in diglyme (30 ml) was added dropwise to a stirred mixture of **6** (8.10 g) and $NaBH_4$ (2.5 g) in diglyme (100 ml) at 40° during 1 hr. After complete addition the temp was slowly increased to 80° and kept at this temp for 4 hr. The now clear soln was cooled and mixed with water (300 ml). The solid obtained was dried and recrystallized from MeOAc or EtOAc (with final cooling to −30°),yield 5.2 g (66%) m.p. 236–238°. NMR (pyridine-d_5): δ_H 2.69 (3, NCH_3, s), 3.27 (6, NCH_3, s), 4.13 (2, CH_2, s), 6.5–7.7 (14, arom., m). MS[*m/e*(% rel. int.)]: 392(M + 1, 30), 391(M, 100), 390(26), 377(11), 376(13), 261(28), 260(42), 247(17), 245(13). Only peaks higher than 10% above *m/e* 200 are listed.

The following compound was similarly prepared:

3,3-*Bis*(3-*indolyl*)*indoline* (**19**), yield 62% m.p. 164–166°. IR: 3400(NH) 1601, 1482, 1452, 1337, 1095, 740. MS[*m/e*(% rel. int.)]: 349(M, 2.8), 233(18), 232(100), 231(38), 204(15), 117(73), 116(17), 115(16). Only peaks higher than 10% above *m/e* 100 are listed (except the M^+-peak). m*: 179.4 (232→204).

Synthesis of the cyclotrimer **3**

Method A Dehydrocyclization of **8**. DDQ (227 mg) in dioxane (5 ml) was added to a soln of **8** (389 mg) in dioxane (20 ml). After 20 hr at 25° the DDQ-2H formed was filtered off and the filtrate (after concentration) poured into NaOHaq (15 ml, 1%). The solid formed was collected, dried and chromatographed on silica gel using CH_2Cl_2 as eluent, yield 205 mg (53%) m.p. 186–187°).

Method B—*cyclocondensation of* N-*methylindoxyl*-O-*acetate*. N-Methylindoxyl-O-acetate (1.77 g) was refluxed in trifluoroacetic acid for 2 hr, whereupon the acid was distilled off and the residue washed with water and chromatographed on silica gel using CH_2Cl_2 as eluent. After evaporation the residue was crystallized from MeOH/MeOAc. Some rather insoluble material (0.22 g) was collected during this operation (*vide infra*), yield 0.62 g (48%) m.p. 186–187°.

Method C. Same as method A, but replace **8** with **7** (391 mg) and double the amount of DDQ, yield 43%, m.p. 186–187°.

Method D. To a soln of compound **7** (1.29 g, 3/100 mol) in THF (50 ml) was added 2 equivs of BuLi. After a reflux period of 2 hr dry $CoCl_2$ (0.5 g) was added and the mixture refluxed for 4 hr whereupon the solvent was evaporated and the mixture extracted with hot EtOAc. After concentration to *ca.* 10 ml and cooling crystals of **3** were obtained, yield 40% m.p. 186–187°. MS[*m/e*(% rel. int.)]: 389(M + 2, 5), 388(M + 1, 31), 387(M, 100), 373(12), 372(40), 366(4), 358(9), 357(31), 356(13), 355(7), 354(4). Only peaks higher than 3% above *m/e* 200 are listed. m*: 357.5 (387→372), 342.6 (372→357). NMR ($CDCl_3$): δ_H 4.20 (6, NCH_3, s), 4.52 (3, NCH_3, s), 7.3–7.7 (12, arom., m). IR: 3020(w), 1569, 1471, 1390, 1322, 1134, 1093, 735.

Cleavage of 3,3-*bis*(N-*methyl*-3-*indolyl*)-N-*methylindoline with strong acid.* Compound **7** (389 mg) was dissolved in a mixture of EtOH and conc HCl (4:1). During the dissolution a transient blue-violet colouration was observed. After *ca.* 10 min crystals separated from the clear homogeneous soln. The crystals, 182 mg (70%) m.p. 185–187°, were identified as 3,3'bi (N-methylindolyl) by comparison with an authentic sample.[20] Treatment of the mother liquor with aqueous hydroxide gave a mixture of the dimer and trimer of N-methylindole.

Cleavage of 3,3-*bis*(3-*indolyl*)*indoline with strong acid.* The procedure described above was used yielding 3,3'-biindolyl (55%) m.p. 285–287°, which was identified by comparison with an authentic sample.[21]

3(2-*Methyl*-3-*indolyl*)*oxindole* (**13**). 3-Hydroxyoxindole[22]

(1.49 g) and 2-methylindole (1.31 g) were refluxed for 3 hr in AcOH (15 ml). After cooling the mixture was poured into water. The solid formed was collected, dried and recrystallized from acetonitrile, yield 1.85 g (70%) m.p. 192–194°. MS[*m/e*(% rel. int.)]: 263(M + 1, 19), 262 (M, 100). 261(29), 247(37), 233(62), 219(66), 218(21), 131(22), 130(58). Only peaks higher than 18% above *m/e* 100 are listed.

2-Methyl-3,3'-biindolyl (14). 3(2-Methyl-3-indolyl)oxindole (1.31 g) was reduced with LAH (0.3 g) in refluxing ether (75 ml) for 6 hr. After work up the crude product was recrystallized from EtOH, yield 0.97 g (78%), m.p. 252–254°.

Synthesis of compound **11b**. 2,3'-Biindolyl[23] (2.32 g) and 3-hydroxyoxindole[22] (1.49 g) were refluxed for 3 hr in AcOH (25 ml), whereupon the solvent was evaporated under reduced pressure. The residue crystallized from toluene yielded 2.62 g (79%) m.p. 258–260°. IR: 3400, 3048, 1714, 1615. 1469, 1452, 1331, 1240, 738. MS[*m/e*(% rel. int.)]: 363(M, 8), 334(8), 232(30), 231(10), 92(73), 91(100). Only peaks higher than 7% above *m/e* 70 are listed.

Reduction of compound **11b** *with LAH.* Compound **11b** was reduced with LAH as described. The product (yield 82%) was identical with 2,3-bis(3-indolyl)indole (described).

3,3-Bis[4,4-N,N-dimethylaminophenyl)]oxindole (**20b**). Isatin (7.35 g, 0.05 ml) and N,N-dimethylaniline (12.1 g, 0.1 mol) in AcOH (35 ml) was refluxed for 1 hr. Water (15 ml) was added and the mixture was allowed to crystallize, yield 17.4 g (94%), m.p. 249–251° (lit.[24] 234°). IR: 3247, 2888, 2804, 1718, 1677, 1609, 1566, 1469, 1362, 1189, 813, 802, 751.

3,3-Bis[4,4-(N,N-dimethylaminophenyl)]indoline (**20a**). Compound **20b** was reduced with diborane in diglyme as described for **6**. The crude product was crystallized from MeOH, yield 86%, m.p. 149–151°. IR: 3335, 2878, 2851, 2798, 1606, 1516, 1483, 1459, 1442, 1348, 1212, 1191, 812, 802, 739. NMR ($CDCl_3$): δ_H 2.88(12, NCH_3, s), 3.97 (2, CH_2, s), 6.4–7.3 (12, arom., m). MS[*m/e*(% rel. int.)]: 358(M + 1, 15), 357(M, 58), 238(18), 237(100), 236(27), 223(25), 193(14). Only peaks higher than 10% above *m/e* 100 are listed.

3,3-Bis(3-indolyl)-N-acetyloxindole (**12b**). N-Acetylisatin (9.15 g) and indole (11.7 g) were heated to 205°, when a vigorous reaction ensued. The cooled mixture was purified by treatment with EtOH and recrystallized from 1,2-diacetoxyethane, yield 90%, m.p. 312–314°. IR: 3424, 3322, 3058, 1749, 1718, 1461, 1370, 1348, 1298, 1268, 1246, 1169, 762, 749, 740. MS[*m/e*(% rel. int.)]: 406(M + 1, 17), 405(M, 58), 363(33), 362(100), 335(22), 334(64), 219(15), 43(19). Only peaks higher than 14% of the base peaks are listed.

3,3-Bis(3-N-methylindolyl)-N-acetyloxindole (**12c**). The method described above was used, yield 90% m.p. 302–304°. The analytical sample was recrystallized from acetonitrile. IR: 3058, 2937, 1767, 1709, 1477, 1464, 1371, 1331, 1299, 1273, 1158, 1013, 762, 752, 748. MS[*m/e*(% rel. int.)]: 434(M + 1, 21), 433(M, 63), 391(35), 390(100), 363(19), 362(66), 361(35), 360(29), 348(20). Only peaks higher than 15% of the base peak are listed.

Hydrolysis of 3,3-bis(3-indolyl)-N-acetyloxindole (**12b**). 3,3-Bis(3-indolyl)-N-acetyloxindole (808 mg) and KOH (1.0 g) in water (5 ml) and EtOH (10 ml) was refluxed for 30 min. On cooling crystals of **12a** separated, yield 695 mg (95%) m.p. 312–314° (identical with a sample using the method described above).

Hydrolysis of 3,3-bis(3-N-methylindolyl)-N-acetyloxindole (**12c**). The method given above was used, yield 94% m.p. 330–332° (identical with a sample using the method described above).

Isolation of a cyclotetramer fraction and a cyclopentamer fraction from the cyclocondensation of N-methylindoxyl-O-acetate. The insoluble material from the preparation of **3** (method B) was sublimed in a temp gradient at 10^{-3} mm Hg using a mercury vacuum pump. The fractions were analyzed by mass spectroscopy. Pentamer fraction: 645(42), 630(10), 518(24), 517(32), 516(14), 387(100). Only peaks higher than 10% above *m/e* 200 are listed. The tetramer fraction was contaminated by the trimer as well as pentamers, and the small sample (15 mg) was not studied further.

N,N'-Dimethyl-2,3'-biindolyl (**30**). To a stirred soln of N-methyloxindole (1.47 g) and N-methylindole (1.31 g) in CH_2Cl_2 (50 ml) was added $POCl_3$ (1.53 g), whereupon the soln was refluxed for 2 hr. The mixture was stirred with water (50 ml) and $NaHCO_3$ (1.0 g) for 1 hr and the organic phase was separated, dried and evaporated. The residue crystallized from MeOH gave N,N'-dimethyl-2,3'-biindolyl, yield 2.2 g (85%) m.p. 134–135° (lit.[25] 134–135°).

N,N',N"-Trimethyl-2-(3-indolyl)3-(2-indolyl)indole (**31**). The procedure described above was used replacing N-methylindole with N,N'-dimethyl-2,3'-biindolyl (2.60 g). The title compound separated directly from the mixture (without work-up). The solid formed was washed with Na_2CO_3aq followed by water and dried, yield 3.12 g (80%), m.p. 201–203°. The analytical sample was recrystallized from acetonitrile. MS[*m/e*(% rel. int.)]: 390(M + 1, 30), 389(M, 100), 388(12), 374(18), 260(82), 244(32). Only peaks higher than 10% above *m/e* 200 are listed.

Preparation of the tetramer **32**. A mixture of **31** (389 mg), N-methyloxindole (131 mg) and $POCl_3$ in tetrachloroethylene was refluxed for 3 hr. The solid formed on cooling was collected and washed with Na_2CO_3aq and water, dried and recrystallized from EtOAc/EtOH, yield 212 mg (41%) m.p. 282–284°. MS[*m/e*(% rel. int.)]: 518(M, 1.4), 389(63), 388(84), 260(100), 194(13), 130(18), only peaks higher than 10% are listed (except the M^+ peak).

Sym. *Tris (N-methylindolo)benzene* (**1**). Compound **31** was dehydrogenated with DDQ using the procedure (Method C) for **3**, yield 45% m.p. 265–267° (lit.[2] 265°).

Tris-(benzo[b]thiopheno)benzene (**27**). 3-Acetoxybenzothiophene (1.92 g) was refluxed in trifluoroacetic acid (25 ml) for 3 hr. The solid formed was collected, washed with water, dried and recrystallized from xylene, yield 0.97 g (25%) m.p. > 360° (lit.[13] m.p. 422–425°).

REFERENCES

[1]J. Bergman and N. Eklund, *Tetrahedron* **36**, 1439 (1980).
[2]H. Müller, Dissertation, Heidelberg (1964).
[3]R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes*, p. 295. AP, New York (1967).
[4]G. I. Zhungietu and L. P. Sinyavskaya, *Khim. Get. Soedin* 204 (1976).
[5]P. Seidel, *Chem. Ber.* **83**, 20 (1950).
[6]B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.* **73**, 713 (1951).
[7]V. G. Avramenko, V. D. Nazina and N. N. Suvorov, *Khim. Get. Soedin* 1071 (1970).
[8]K. M. Biswas and A. H. Jackson, *Tetrahedron* **25**, 227 (1969).
[9]J. Bergman, R. Carlsson and S. Misztal, *Acta Chem. Scand.* **B30**, 853 (1976).
[10]M. Isobe, K. Harano and T. Taguchi, *Yakugaku Zasshi* **94**, 343 (1974); *Chem Abstr.* **81**, 77766 (1974).
[11]K. Takayama, M. Isobe, K. Harano and T. Taguchi, *Tetrahedron Letters* 365 (1973).
[12]J. Bergman and B. Egestad, *Ibid.* 3143 (1978).
[13]C. E. Dalgliesh and F. G. Mann, *J. Chem. Soc.* 910 (1945).
[14]R. Proetzsch, D. Bieniek and F. Korte, *Z. Naturforsch.* **31B**, 529 (1976).
[15]A. N. Kost, V. A. Budylin, E. D. Matveeva and D. O. Stergilov, *Zhur. Org. Khim.* **6**, 1503 (1970).
[16]E. Giovannini and F. Karrer, *Chimia* **21**, 517 (1967).
[17]J. Bergman, B. Egestad and D. Rajapaksa, *Acta Chem. Scand.* **B33**, 405 (1979).
[18]J. Bergman and B. Egestad, unpublished results.
[19]W. Steinkopf and H. Wilhelm, *Liebigs Ann.* **546**, 211 (1941).
[20]J. Bergman, *Acta Chem. Scand.* **22**, 1883 (1968).
[21]J. Bergman, *Ibid.* **25**, 1277 (1971).
[22]C. Marschalk, *Ber. Dtsch. Chem. Ges.* **45**, 582 (1912).
[23]J. Bergman, *J. Het. Chem.* **10**, 121 (1973).
[24]A. Haller and A. Guyot, *C. R. Acad. Sci., Paris* 947 (1907).
[25]M. Kunori, *Nippon Kagaku Zasshi* **80**, 407 (1959).
[26]T. Kaneko, M. Matsuo and Y. Iitaka, *Heterocycles* **12**, 471 (1979).