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Synthesis of a Trifluoromethylindolocarbazole, Novel Cyclic 27- and 36-Membered *N*-Benzyltri- and -tetraindoles, and an *N*-Benzyltetraindolyltrimethane

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Summary. 5,11-Dihydro-5,11-dibenzyl-6-trifluoromethylindolo[3,2-*b*]carbazole (**6**) and the cyclic N-benzylindole trimer **4** were synthesized from both *N*-benzylindole-3-methanol (**1**) and N,N′-dibenzyl-3,3′-diindolylmethane (**2**) by treatment with trifluoroacetic anhydride. The former also gave the 36-membered cyclic N-benzylindole tetramer **7**, and the latter furnished N-benzyl-3-trifluoroacetylindole (**8**). Heating **1** in aqueous methanol also yielded the trimer **4** along with **2**, the N-benzylitriindolyldimethane **3**, and the N-benzyltetraindolyltrimethane **5** whose structure and solid-state conformation were determined by X-ray crystallographic analysis. The results are discussed and plausible mechanisms of the reactions leading to **3–8** are presented.

Keywords. Trifluoromethylindolocarbazole; Cyclic N-benzylindole tetramer; N-Benzyltetraindolyltrimethane; X-Ray crystallographic analysis.

Synthese eines Trifluormethylindolocarbazols, neuer cyclischer 27- und 36-gliedriger *N*-Benzyltri- und -tetraindole sowie eines *N*-Benzyltetraindolyltrimethans

Zusammenfassung. 5,11-Dihydro-5,11-dibenzyl-6-trifluormethylindolo[3,2-*b*]carbazol (**6**) und das cyclische N-Benzylindoltrimer **4** wurden aus N-Benzylindol-3-methanol (**1**) und N,N′-Dibenzyl-3,3′-diindolylmethan (**2**) durch Behandeln mit Trifluoracetanhydrid synthetisiert. Ersteres ergab auch das 36-gliedrige cyclische N-Benzylindoltetramer **7**, letzteres N-Benzyl-3-trifluoracetylindol (**8**). Erhitzen von **1** in wässrigem Methanol führte zum Trimer **4** – zusammen mit **2**, dem N-Benzyl-triindolylmethan **3** und dem N-Benzyl-tetraindolyltrimethan **5**, für welches Struktur und Konformation im festen Zustand durch Röntgenstrukturanalyse abgeleitet wurden. Die Resultate werden diskutiert, und plausible Mechanismen für die Reaktionen, die zu den Verbindungen **3–8** führen, werden vorgestellt.

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Introduction

Indolocarbazoles are known to possess important biological activities [1–3]. Fluoroorganic compounds have been of great interest to synthetic and medicinal chemists for a long time due to the unique chemical and biological properties imparted by fluorine and also because of their utilization as drugs, pesticides, dyes, diagnostic agents, *etc*. [4–9]. Moreover, although several methods are known for the synthesis of 5,11-dihydroindolo[3,2-*b*]carbazoles and 5,7-dihydroindolo[2,3-*b*]carbazoles [10–13], these often involve many steps, and the yields are usually low. So far as we are aware, fluorine-containing indolocarbazoles are not known in the literature. Accordingly, we sought to devise a method for the synthesis of trifluoromethylindolocarbazoles. For this purpose, we chose the reaction of N,N′-dibenzyl-3,3′-diindolylmethane (**2**) with trifluoroacetic anhydride, since the former can supply two nucleophilic indole moieties, and the latter can provide an electrophilic carbonyl carbon atom and a trifluoromethyl group as required for constructing the skeleton of the desired compounds. Our results are presented herein.

Results and Discussion

To prepare the N-benzyldiindolylmethane **2**, the indole-3-methanol **1** was heated in aqueous methanol (cf. Ref. [14]). In addition to **2**, the reaction furnished the triindolyldimethane **3**, the tetraindolyltrimethane **5** and the 27-membered cyclic triindole **4**. The structures of **3**–**5** were established from their NMR and mass spectroscopic data, and that of **5** was confirmed by X-ray crystallographic analysis.

Crystallographic data and data collection parameters for **5** are summarized in Table 1. A view of the solid-state conformation, with the crystallographic atom numbering scheme, is presented in Fig. 1; fractional atomic coordinates are given in Table 2. Bond lengths and angles within the benzylindole moieties agree well and are, as well as the others, in accord with expectations [15]. The C3–C15–C2′–C3′–C15″–C3″–C2″–C15‴–C3‴ backbone has a helical form characterized by the following torsion angles (ω_{ij}, $\sigma \pm 0.2$–0.4°) about the bonds between atoms *i* and *j*: $\omega_{15,2'} = -105.9$, $\omega_{2',3'} = -11.7$, $\omega_{3',15''} = 144.7$, $\omega_{15'',3''} = -74.3$, $\omega_{3'',2''} = 2.3$, $\omega_{2'',15''} = 102.4^\circ$. Strain involved in the minimization of unfavourable non-bonded intramolecular interactions associated with this conformation is reflected in the significant departures of some of the directly bonded atoms from the least-squares planes through atoms of each of the approximately planar indole units (C8 0.104, C15 0.133 Å to the same side of the N1–C7a plane; C8′ 0.082, C15″ 0.079 Å to the opposite side of the N1′–C7a′ plane from C15 ($\Delta = 0.238$ Å); C8″ 0.367 Å from the N1″–C7a″ plane; C8‴ 0.133, C15‴ 0.109 Å to opposite sides of the N1‴–C7a‴plane). Furthermore, whereas methylene carbon atoms C8, C8′, and C8‴ ($\Delta = 0.013$, 0.006, 0.013 Å, respectively) lie essentially in the least-squares planes through the phenyl rings to which they are bonded, C8″ is displaced by 0.046 Å from the C9″–C14″ plane. The associated indole N atoms in each case also lie close to, but deviate by significant amounts from, the corresponding phenyl ring planes (N1 0.068, N1′ 0.086, N1″ 0.279, N1‴ 0.043 Å).

Table 1. Crystallographic data for **5**

Molecular formula	$C_{63}H_{52}N_4$
Formula weight	865.14
Crystal system	triclinic
Space group	$P\bar{1}(C_i^1)$-No. 2
a/Å	11.960(1)
b/Å	19.651(2)
c/Å	11.251(1)
α/°	106.01(1)
β/°	109.68(1)
γ/°	92.17(1)
V/Å^3	2368(1)
Z	2
D_{calcd}/g · cm^{-3}	1.213
Radiation (λ/Å)	CuK_α (1.5418)
Absorption coefficient μ/cm^{-1}	5.1
T/K	298
Crystal dimensions (mm)	0.10×0.20×0.34
T_{max} : T_{min} (relative)	1.00: 0.94
Scan type	ω–2θ
Scan width (°)	0.80+0.14tanθ
θ_{max}/°	75
Intensity control refls.:	$24\bar{3}$, $2\bar{4}\bar{2}$, 141, 330
Variation; repeat time (h)	<1.0%; 2
Total no. of refls. (+*h*, ±*k*, ±*l*) recorded	10245
No. of non-equiv. refls. recorded	9724
R_{merge} (on *I*)	0.033
No. of refls. retained (I>2.0$\sigma(I)$)	5212
No. of parameters refined	605
Extinction correction	1.9(1)×10^{-6}
R (R_w)[a]	0.047 (0.062)
Goodness-of-fit[b]	1.46
Max. shift: esd in final least-squares cycle	0.03
Final $\Delta\rho$(e/Å^3) max.; min.	0.15; −0.17

[a] $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$; $\sum w\Delta^2 (w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$ was minimized; [b] goodness-of-fit = $(\sum w\Delta^2/(N_{observations} - N_{parameters})^{1/2}$

In order to synthesize the trifluoromethylindolocarbazole **6**, **2** was treated with trifluoroacetic anhydride, and in addition to **6**, **4** and the trifluoroacetylindole **8** were also obtained. Since **2** was prepared from **1**, we envisaged that this conversion could more conveniently be done *in situ* and our objective might be fulfilled by replacing **2** by **1**. Thus, the reaction of **1** with trifluoroacetic anhydride afforded **4** and **6** along with the novel 36-membered cyclic tetraindole **7**. Macrocylic indoles of the type **4** and **7** having suitable substituents and structural variation may be manipulated to promote molecular recognition and ion binding [16, 17].

Table 2. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **5** (esd values in parentheses)

Atom	x	y	z	B_{eq}/Å^2
N(1)	0.4363(2)	0.3720(1)	0.1965(2)	3.96(4)
C(2)	0.4256(2)	0.3097(1)	0.0973(2)	3.87(5)
C(3)	0.5358(2)	0.2956(1)	0.0948(2)	3.58(5)
C(3a)	0.6216(2)	0.3524(1)	0.2003(2)	3.44(5)
C(4)	0.7464(2)	0.3677(1)	0.2502(2)	4.34(6)
C(5)	0.8012(2)	0.4295(2)	0.3543(3)	5.42(7)
C(6)	0.7340(3)	0.4764(2)	0.4088(3)	5.59(7)
C(7)	0.6108(2)	0.4627(1)	0.3624(2)	4.58(6)
C(7a)	0.5557(2)	0.3998(1)	0.2592(2)	3.63(5)
C(8)	0.3369(2)	0.4076(1)	0.2162(2)	4.53(6)
C(9)	0.3046(2)	0.4629(1)	0.1441(2)	4.12(5)
C(10)	0.2143(3)	0.5017(2)	0.1612(3)	6.42(7)
C(11)	0.1813(3)	0.5528(2)	0.0965(4)	8.42(9)
C(12)	0.2362(3)	0.5638(2)	0.0127(3)	7.46(9)
C(13)	0.3244(3)	0.5251(2)	−0.0063(3)	5.85(7)
C(14)	0.3586(2)	0.4741(1)	0.0588(2)	4.76(6)
C(15)	0.5606(2)	0.2341(1)	−0.0038(2)	4.12(5)
N(1′)	0.3854(2)	0.2338(1)	−0.2051(2)	4.46(5)
C(2′)	0.4472(2)	0.1974(1)	−0.1186(2)	3.62(5)
C(3′)	0.3813(2)	0.1329(1)	−0.1476(2)	3.31(4)
C(3a′)	0.2720(2)	0.1281(1)	−0.2567(2)	3.59(5)
C(4′)	0.1673(2)	0.0783(1)	−0.3265(2)	4.30(6)
C(5′)	0.0751(3)	0.0938(2)	−0.4247(3)	5.35(7)
C(6′)	0.0849(3)	0.1566(2)	−0.4569(3)	5.88(8)
C(7′)	0.1860(3)	0.2065(1)	−0.3904(2)	5.53(7)
C(7a′)	0.2784(2)	0.1918(1)	−0.2890(2)	4.09(5)
C(8′)	0.4279(3)	0.3010(1)	−0.2161(2)	5.24(6)
C(9′)	0.4707(2)	0.2929(1)	−0.3312(2)	4.62(6)
C(10′)	0.5054(3)	0.3540(2)	−0.3549(3)	6.77(8)
C(11′)	0.5449(3)	0.3502(2)	−0.4575(3)	8.33(9)
C(12′)	0.5486(3)	0.2867(2)	−0.5400(3)	6.79(8)
C(13′)	0.5140(3)	0.2245(2)	−0.5210(3)	6.81(8)
C(14′)	0.4739(3)	0.2281(2)	−0.4159(3)	6.12(7)
N(1″)	0.1864(2)	0.0008(1)	−0.0134(2)	3.85(4)
C(2″)	0.2710(2)	0.0563(1)	−0.0288(2)	3.63(5)
C(3″)	0.3257(2)	0.0343(1)	−0.0606(2)	3.45(5)
C(3a″)	0.2762(2)	−0.0389(1)	−0.1340(2)	3.53(5)
C(4″)	0.2975(2)	−0.0904(1)	−0.2357(2)	4.71(6)
C(5″)	0.2324(3)	−0.1582(1)	−0.2833(3)	5.81(8)
C(6″)	0.1480(3)	−0.1759(1)	−0.2322(3)	5.86(8)
C(7″)	0.1258(2)	−0.1268(1)	−0.1336(3)	5.03(6)
C(7a″)	0.1899(2)	−0.0583(1)	−0.0848(2)	3.79(5)
C(8″)	0.1355(2)	−0.0024(1)	0.1130(2)	4.77(6)
C(9″)	0.2197(2)	0.0237(1)	0.2266(2)	4.65(6)
C(10″)	0.1937(3)	0.0143(2)	0.3386(3)	7.63(8)
C(11″)	0.2668(4)	−0.0364(2)	0.4418(3)	11.1(1)

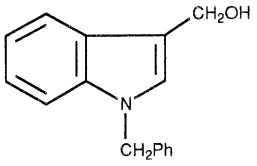
Table 2 (*continued*)

Atom	*x*	*y*	*z*	B_{eq}/Å^2
C(12″)	0.3648(4)	−0.0660(2)	0.4343(3)	12.3(1)
C(13″)	0.3912(3)	−0.0764(2)	0.3220(3)	11.2(1)
C(14″)	0.3179(3)	−0.0556(2)	0.2178(3)	7.27(8)
C(15″)	0.4221(2)	0.0770(1)	−0.0800(2)	4.26(5)
N(1‴)	0.0352(2)	0.2145(1)	−0.0393(2)	4.60(5)
C(2‴)	0.1100(2)	0.1622(1)	−0.0394(2)	4.44(6)
C(3‴)	0.1875(2)	0.1714(1)	0.0861(2)	3.70(5)
C(3a‴)	0.1595(2)	0.2320(1)	0.1709(2)	3.60(5)
C(4‴)	0.2048(2)	0.2662(1)	0.3083(2)	4.28(6)
C(5‴)	0.1552(2)	0.3242(2)	0.3583(3)	5.35(7)
C(6‴)	0.0652(2)	0.3506(2)	0.2753(3)	5.61(7)
C(7‴)	0.0175(2)	0.3180(1)	0.1396(3)	4.96(6)
C(7a‴)	0.0653(2)	0.2583(1)	0.0893(2)	4.02(5)
C(8‴)	−0.0633(3)	0.2184(2)	−0.1557(3)	5.76(7)
C(9‴)	−0.0374(2)	0.2750(1)	−0.2147(2)	4.70(6)
C(10‴)	−0.1264(3)	0.2804(2)	−0.3267(3)	6.83(9)
C(11‴)	−0.1084(4)	0.3302(2)	−0.3861(3)	8.2(1)
C(12‴)	−0.0014(3)	0.3755(2)	−0.3347(3)	7.6(1)
C(13‴)	0.0869(3)	0.3710(2)	−0.2238(3)	7.05(9)
C(14‴)	0.0691(3)	0.3205(2)	−0.1640(3)	6.01(8)
C(15‴)	0.2872(2)	0.1282(1)	0.1282(2)	4.42(6)

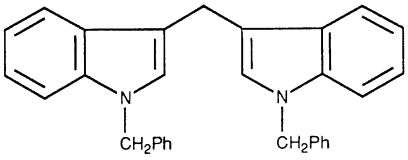
The protons and the carbon atom of one *N*–CH_2 of **6** were shifted downfield in its ^{1}H and ^{13}C NMR spectra relative to those of the other N–CH_2 moiety, presumably because the protons and the carbon of one *N*–CH_2 bear six-bond and five-bond relationships [18, 19], respectively, with the fluorine atoms of its CF_3 group, whereas there exists no such relationship with those of the other *N*–CH_2 group. This observation led us to propose structure **6**. This assignment was confirmed by the fact that the 7-H of **6** resonated further downfield that its 1-H in the ^{1}H NMR spectrum. Similarly, 2-H of **8** also resonated downfield and showed coupling with fluorines in its ^{1}H NMR spectrum. Solutions of **6** in various solvents exhibited blue-violet fluorescence.

Suggested mechanisms of the reactions leading to **3**–**8** are indicated briefly in Schemes **1**–**3**; they have some analogy to those reported in the literature [20].

This work presents simple methods for the synthesis of macrocyclic indoles **4** and **7**, trifluoromethylindolocarbazole **6**, and tetraindolyltrimethane **5**, all of which appear to be unreported in the literature, from readily available materials and reagents. Formation of **8** from **2** provides unambiguous experimental evidence to show that acylation of 3-alkylindoles occurs by initial electrophilic attack at the 3-position followed by migration of the acyl group from the 3- to the 2-position to furnish the observed 2-acyl-3-alkylindoles as *Jackson et al*. [20] have speculated, and contradicts the suggested mechanism [21, 22].



1



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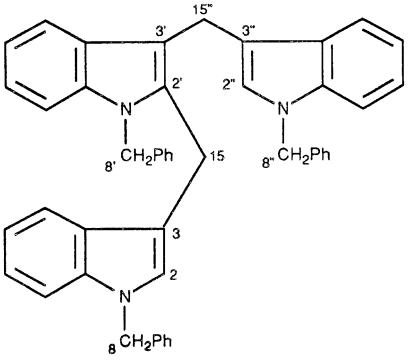
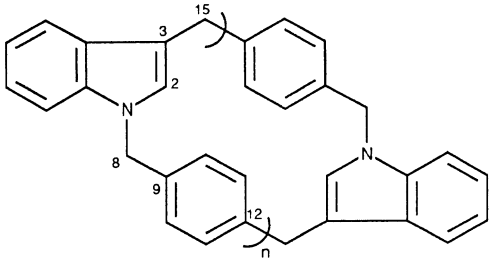
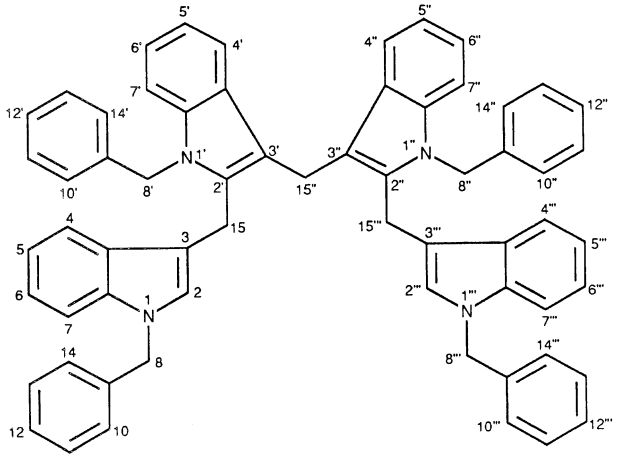


3



4 (n = 2)
7 (n = 3)



5

Experimental

Melting points are uncorrected. UV spectra were recorded in ether or ethanol on a Varian Technotron Series 634 spectrophotometer, IR spectra were taken as KBr pellets on a Perkin Elmer 782 instrument, ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were determined on a Bruker AM 300L (300 MHz) spectrometer using *TMS* and $CDCl_3$ as internal standards, and mass spectra were obtained on Jeol SX-102 or Jeol D-300 instruments. Trifluoroacetic anhydride was prepared immediately prior to use. Petroleum ether indicates the fraction boiling from 60–80°C. Silica gel (60–120 mesh) was used for column chromatography. ^{1}H and ^{13}C NMR spectroscopic data for only one indole moiety of **4** and **7** and two of **5** are given; data for the other indole moieties are the same. Elemental analysis data agreed with the calculated values within experimental error. Indole-3-methanol **1** was prepared by

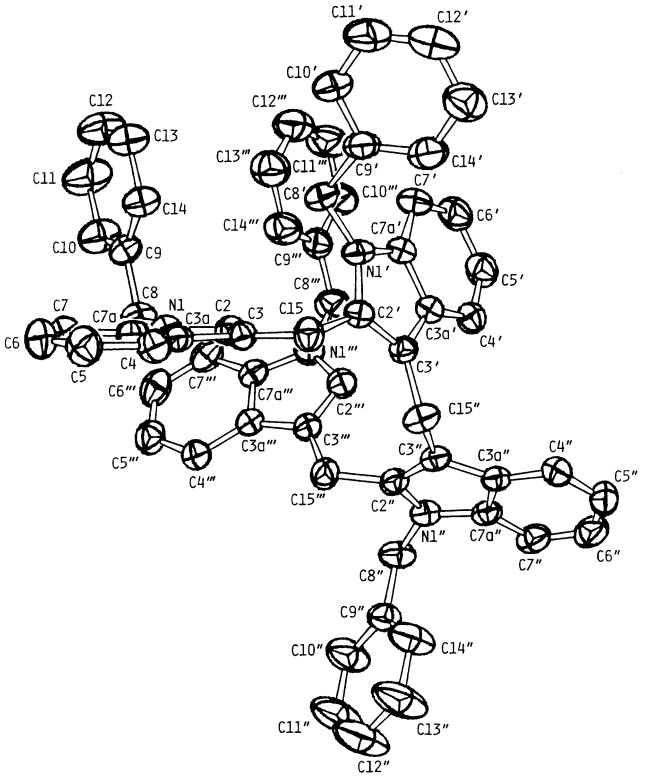


Fig. 1. ORTEP diagram (40% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation of compound **5**; hydrogen atoms have been omitted for clarity

reduction of *N*-benzylindole-3-carboxaldehyde (0.6 g, 2.5 mmol) with sodium borohydride (190 mg, 5 mmol) in ethanol following the procedure given in Ref. [23].

N-Benzylindole-3-methanol (**1**; $C_{16}H_{15}NO$)

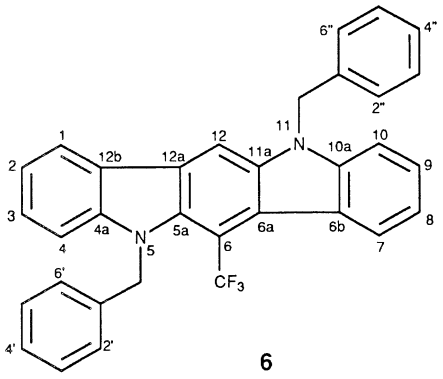
M.p.: 92°C; colourless needles (benzene-petroleum ether); yield: 0.59 g (98%); IR: $\nu = 3360\,cm^{-1}$ (hump, OH); ^1H NMR ($CDCl_3$): $\delta = 4.81$ (2H, s, 3-C*H*$_2$OH), 5.22 (3H, s, N-CH$_2$, 3-CH$_2$O*H*), 7.06–7.26 (9H, m, Ar–H), 7.66–7.69 (1H, m, 4-H) ppm.

Reaction of **1** *in aqueous methanol*

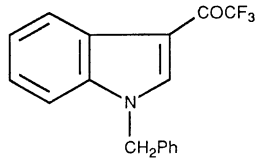
Compound **1** (2.45 g, 0.0103 mol) was refluxed with water (35 cm^3) and methanol (90 cm^3) for 25 h, and excess methanol was removed by distillation. The resulting mixture was extracted with ether and dried (Na_2SO_4). The viscous liquid obtained after removal of the solvent was chromatographed over silica gel. Elution of the column with petroleum ether-benzene (9:1) furnished **2**–**4**. Further elution of the column with petroleum ether-benzene (3:1) afforded **5**.

N,N′-Dibenzyl-3,3′-diindolylmethane (**2**; $C_{31}H_{26}N_2$)

M.p.: 135–137°C (Ref. [24]: m.p.: 137°C); colourless needles (benzene-petroleum ether); yield: 0.7 g (31.8%).



6



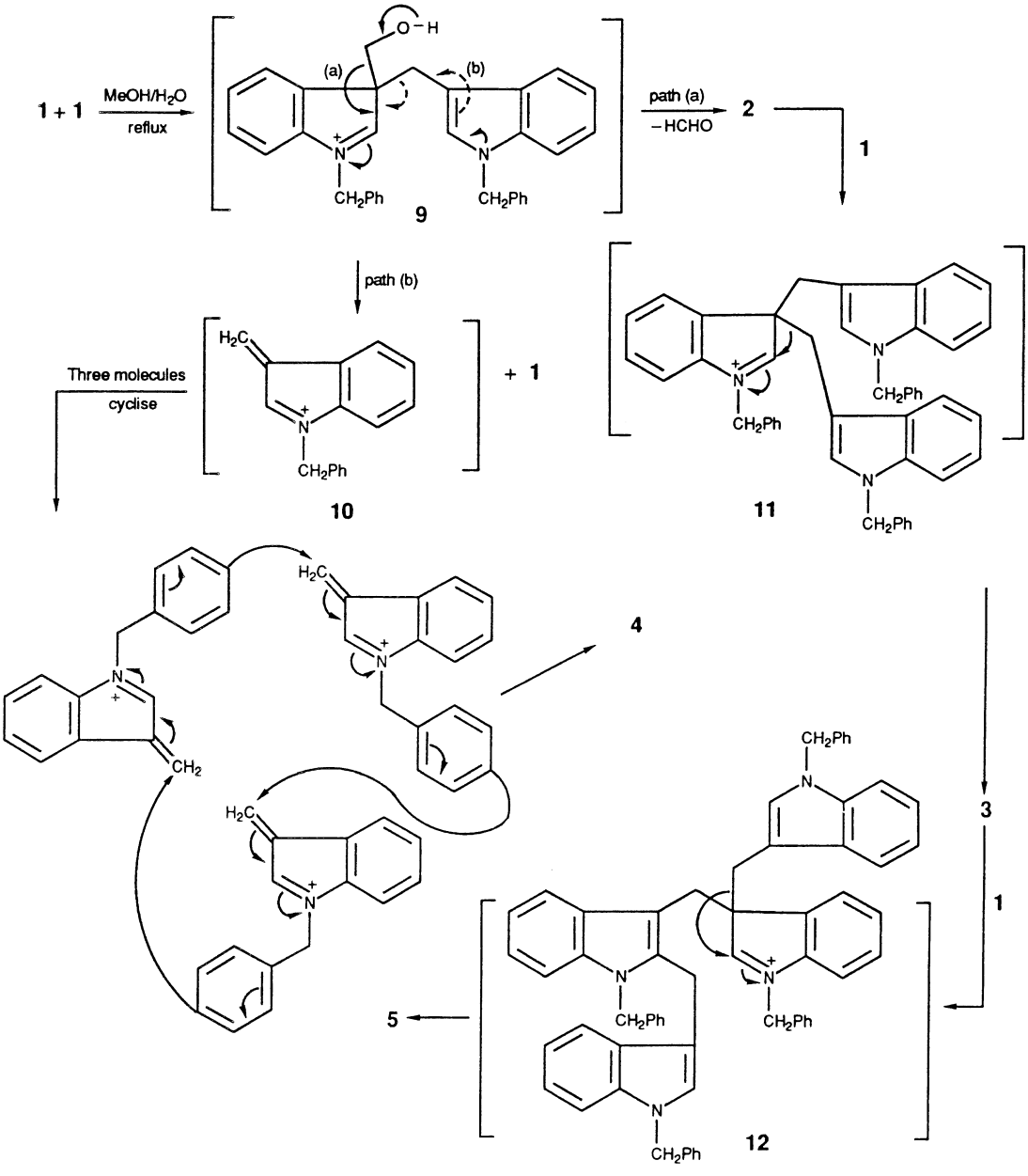
8

Triindolyldimethane (**3**; $C_{47}H_{39}N_3$)

M.p.: 150°C; colourless needles (benzene-petroleum ether (40–60°C)); yield: 0.2 g (9%); UV: λ_{max} (ether) = 221(3.43), 240(4.38), 288(4.33) nm (logε); ^{1}H NMR ($CDCl_3$): $\delta = 4.12$ (2H, s, 15-CH_2), 4.28 (2H, s, 15″-CH_2), 4.89 (2H, s, 8″-CH_2), 5.01 (2H, s, 8-CH_2), 5.14 (2H, s, 8′-CH_2), 6.31 (1H, s, 2″-H), 6.69 (1H, s, 2-H), 6.74–7.59 (27H, m, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.48$ (15″-CH_2), 20.96 (15-CH_2), 46.57 (8′-CH_2), 49.58 (8-CH_2), 49.68 (8″-CH_2), 109.18, 109.43, 109.62 (C-7″, C-7, C-7′), 111.23, 112.36, 115.34 (C-3′, C-3, C-3″), 118.73, 118.73, 118.90 (C-4, C-4″, C-4′), 118.90. 118.96, 119.26 (C-6″, C-6, C-6′), 120.88, 121.43, 121.69 (C-5″, C-5, C-5′), 125.79, 126.38, 126.38 (C-11, C-13, C-11′, C-13′, C-11″, C-13″), 126.68, 126.83 (C-2, C-2″), 127.59, 128.2, 128.2 (C-3a″, C-3a, C-3a′), 127.17, 127.17, 127.28 (C-12, C-12″, C-12′), 128.41, 128.41, 128.45 (C-10, C-14, C-10″, C-14″, C-10′, C-14′), 135.42, 136.58, 136.72 (C-7a″, C-7a, C-7a′), 137.52, 137.77 (C-9″, C-9), 138.24 (C-2′, C-9′) ppm; MS (FAB): *m*/*z* (%) = 645 (M^+, 5.5), 439 (M–*N*-benzyl-3-indolyl, 100), 438 (M–N-benzylindole, 100), 347 (438 − $PhCH_2$, 100).

Cyclic trimer (**4**; $C_{48}H_{39}N_3$)

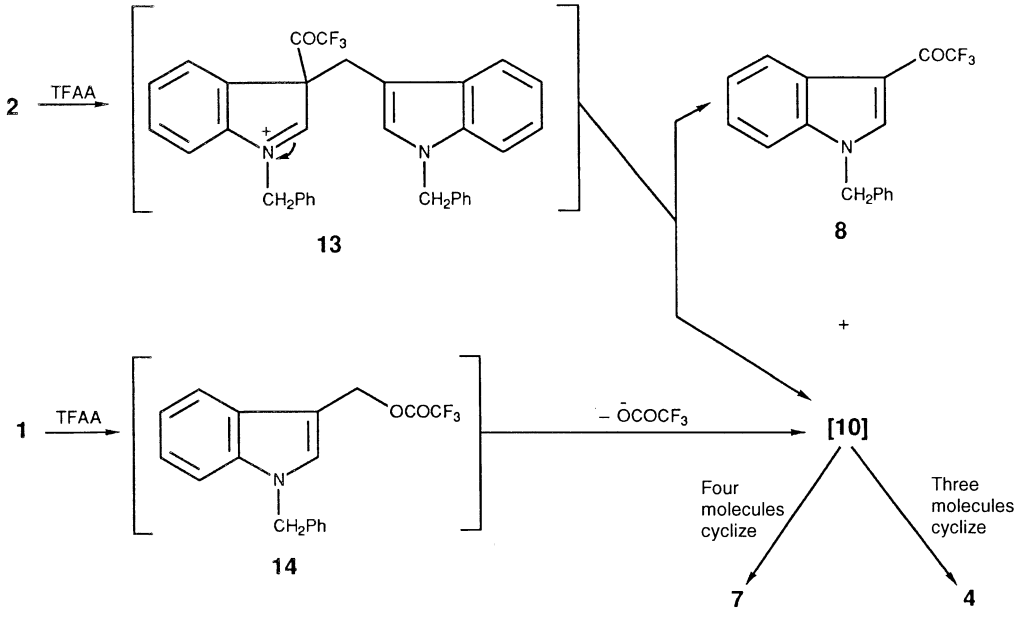
M.p.: 224°C; white spongy mass (benzene-petroleum ether); yield: 0.025 g (1.1%); UV: λ_{max} (ether) = 217 (3.68), 239 (4.45), 287.5 (4.36) nm (logε); ^{1}H NMR ($CDCl_3$): $\delta = 4.03$ (2H, s, 15-CH_2), 5.41 (2H, s, 8-CH_2), 6.83–6.99 (4H, m, Ar–H), 7.16–7.30 (5H, m, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.52$ (15-CH_2), 46.42 (8-CH_2), 107.83 (C-3), 109.21 (C-7), 117.36 (C-4), 119.13 (C-6), 121.08 (C-5), 125.99 (C-11, C13), 127.15 (C-2), 127.60 (C-3a), 128.65 (C-10, C-14), 135.60 (C-7a), 136.30 (C-12), 137.92 (C-9) ppm; MS (FAB): *m*/*z*(%) = 657 (M^+, 59), 566 (M–$PhCH_2$, 9.6) 436 (M–*N*-benzyl-3-methylindole, 12.5).



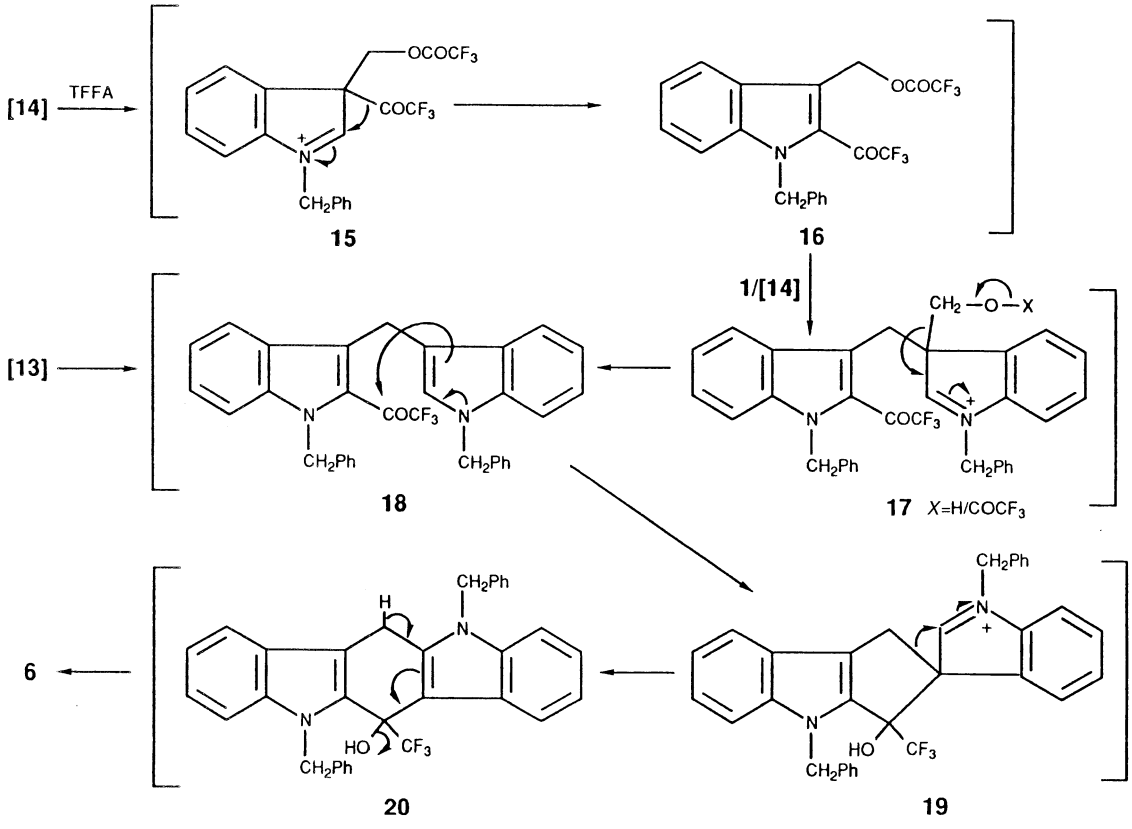
Scheme 1

Tetraindolyltrimethane (**5**; $C_{63}H_{52}N_4$)

M.p.: 169–170°C; colourless microneedles (benzene-petroleum ether); yield: 0.08 g (3.7%); UV: λ_{max} (ethanol) = 210 (4.87), 218.5 (4.87), 235 (4.94), 288 (4.52) nm (logε); ^{1}H NMR ($CDCl_3$): δ = 4.30 (2H, s, 15-CH_2), 4.62 (2H, s, 15″-CH_2), 4.88 (2H, s, 8-CH_2), 5.20 (2H, s, 8′-CH_2), 6.26 (1H, s, 2-H), 6.85 (2H, d, J = 7.45 Hz, 10-H, 14-H), 6.94 (2H, d, J = 6.56 Hz, 10′-H, 14′-H), 7.15–7.31 (12H, m, Ar–H), 7.56 (1H, d, J = 7.82 Hz, 4-H), 7.72 (1H, d, J = 7.70 Hz, 4′-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.44 (15″-CH_2), 21.04 (15-CH_2), 46.74 (8′-CH_2), 49.83 (8-CH_2), 109.25 (C-7), 109.69 (C-7′), 112.01 (C-3′), 112.59 (C-3), 118.81 (C-4), 119.06 (C-4′), 119.19 (C-6, C-6′), 120.96



Scheme 2



Scheme 3

(C-5), 121.76 (C-5′), 125.95 (C-11, C-13), 126.61 (C-11′, C-13′), 126.76 (C-2), 126.92 (C-12), 127.26 (C-12′), 128.04 (C-3a), 128.36 (C-10, C-14), 128.48 (C-10′, C-14′), 128.84 (C-3a′), 135.46 (C-7a), 136.98 (C-2′), 137.19 (C-7a′), 137.77 (C-9), 138.42 (C-9′) ppm; MS (FAB): $m/z(\%) = 864$ (M^+, 6.41), 658 (M–N-benzyl-3-indolyl, 12.06), 657 (M–N-benzylindole, 10.64), 644 (M–*N*-benzyl-3-indolylmethyl, 10.18), 566 (M–N-benzylindole $-CH_2Ph$, 6.05), 440 (M–N-benzyl-3-indolylmethyl–N-benzyl-3-indolyl+2H, 51.01), 439 (M–N-benzyl-3-indolylmethyl $-$ N-benzyl-3-indolyl+H, 91.01), 438 (M–N-benzyl-3-indolylmethyl–N-benzyl-3-indolyl, 89.94), 347 (438-CH_2Ph, 66.40), 256 (347 $-CH_2Ph$, 54.50), 220 (N-benzyl-3-indolylmethyl, 82.48), 91 (CH_2Ph, 100).

Reaction of **2** *with trifluoroacetic anhydride*

A solution of trifluoroacetic anhydride (5.6 cm^3, 30 mmol) in dry benzene (55 cm^3) was added slowly under a blanket of dry nitrogen to a stirred solution of **2** (1.3 g, 3 mmol) in dry benzene (150 cm^3) at 0–5°C, and the mixture was stirred for 4 h at room temperature. The crude product obtained after removal of solvent under reduced pressure was chromatographed over silica gel. Elution with a mixture of benzene and petroleum ether (1:9) gave **6** and **8**. Further elution of the column with a mixture of petroleum ether-benzene (3:1) furnished **4** (yield: 40 mg (2%), m.p.: 224°C).

5,11-Dihydro-5,11-dibenzyl-6-trifluoromethylindolo[3,2-b]carbazole (**6**; $C_{33}H_{23}F_3N_2$)

M.p.: 204°C; yellow prisms (benzene-petroleum ether); yield: 0.5 g (33%), UV/Vis: λ_{max}(ether) = 259.5 (4.28), 287 (4.28), 333 (4.29), 352 (4.28), 391.5 (3.71), 412.5 (3.82) nm (logε); ^{1}H NMR ($CDCl_3$): $\delta = 5.55$ (2H, s, 11-CH_2), 5.66 (2H, s, 5-CH_2), 7.14–7.52 (16H, m, Ar–H), 8.07 (1H, d, $J = 7.33$ Hz, 1-H), 8.15 (1H, s, 12-H), 8.42 (1H, d, $J = 7.96$ Hz, 7-H) ppm; ^{13}C NMR: $\delta = 46.38$ (11-CH_2), 53.1 (5-CH_2), 103.05 (C-12), 108.7 (C-4), 111.24 (C-10), 119.21 (C-2), 119.63 (C-1), 120.1 (C-8), 120.49 (C-12a), 121.21 (C-6a), 123.23 (C-6b), 124.45 (C-12b), 124.83 (C-7), 125.91 (C-3″, C-5″), 126.09 (C-3′, C-5′), 126.58 (C-3), 126.78 (C-9), 126.99 (C-4″), 127.45 (C-4′), 128.37 (C-2″, C-6″), 128.77 (C-2′, C-6′), 136.46 (C-6), 136.77 (C-10a), 137.93 (C-4a), 141.96 (C-11a), 145.41 (C-5a) ppm; MS (EI): $m/z(\%) = 504$ (M^+, 82.4), 413 (M–CH_2Ph, 58.4), 343 (M–CH_2Ph–CF_3–H, 1.9), 322 (M–2×CH_2Ph, 12), 91 (CH_2Ph, 100).

N-*Benzyl-3-trifluoroacetylindole* (**8**; $C_{17}H_{12}F_3NO$)

M.p.: 104°C; colourless fine needles (benzene-petroleum ether); yield: 0.5 g (54%); IR: $\nu = 1660\ cm^{-1}$ (s, $COCF_3$); UV: λ_{max}(ethanol) = 211 (4.32), 251 (4.04), 317 (4.07) nm (logε); ^{1}H NMR ($CDCl_3$): $\delta = 5.40$ (2H, s, CH_2), 7.17–7.41 (8H, m, Ar–H), 7.98–7.99 (1H, m, 2-H), 8.44 (1H, dd, $J = 7.18$, 1.5 Hz, 4-H) ppm; ^{13}C NMR: ($CDCl_3$): $\delta = 51.20$ (C-8), 109.77 (C-3), 110.64 (C-7), 122.74 (C-4), 123.90 (C-6), 124.80 (C-5), 126.86 (C-11, C-13), 127.16 (C-3a), 128.41 (C-12), 129.06 (C-10, C-14), 134.65 (C-9), 136.73 (C-7a), 137.50 (C-2). **8** was found to be identical with a sample prepared in 75% yield by trifluoroacetylation of N-benzylindole [25] with trifluoroacetic anhydride in ether.

Reaction of **1** (0.6 g, 3 mmol) with trifluoroacetic anhydride (5.6 cm^3, 30 mmol) following the procedure mentioned above afforded **4** (60 mg, 11%), **6** (40 mg, 6%), and **7**.

Cyclic tetramer (**7**; $C_{64}H_{52}N_4$)

M.p.: 303–304°C; white spongy mass (benzene-petroleum ether); yield: 0.02 g (4%); UV: λ_{max}(ether) = 228, 289 nm (logε); ^{1}H NMR ($CDCl_3$): $\delta = 3.51$ (2H, br s, 15-CH_2), 6.68 (2H, br s, 8-CH_2), 6.69 (1H, s, 2-H), 7.16–7.41 (8H, m, Ar–H) ppm; ^{13}C NMR: ($CDCl_3$): $\delta = 21.28$ (15-CH_2), 44.97 (8-CH_2), 105.0 (C-3), 108.6 (C-7), 117.14 (C-4), 119.18 (C-6), 120.74 (C-5), 125.95 (C-11,

C-13), 126.86 (C-2, C-2′), 128.42 (C-10, C-14), 129.21 (C-3a), 136.03 (C-7a), 137.99 (C-9), 137.41 (C-12) ppm; MS (FAB): *m/z* (%) = 876 (M^+, 37), 785 (M–$PhCH_2$, 10), 656 (M–N-benzyl-3-indolylmethyl, 39), 565 (M–N-benzyl-3-(p-tolylmethyl)indole, 30), 431 (45), 382 (31), 289 (38), 138 (32).

X-Ray crystal structure analysis of compound **5**

X-Ray diffraction quality crystals were grown from a solution **5** in a mixture of isopropanol and dichloromethane.

Oscillation and *Weissenberg* photographs yielded preliminary unit-cell and space group information. An Enraf-Nonius CAD-4 diffractometer (CuK_α radiation, graphite monochromator) was used for all other measurements. Intensity data were corrected for the usual *Lorentz* and polarization effects; an empirical absorption correction, based on the ϕ-dependency of the intensities of several reflections with χ *ca.* 90°, was also applied. *Laue* symmetry indicated that the crystals belonged to the triclinic system, space group P1 or $P\bar{1}$; the latter was assumed at the outset and shown to be correct by the structure solution and refinement. Unit-cell parameters were derived from the diffractometer setting angles for 25 reflections ($36° < \theta < 40°$) widely separated in reciprocal space.

The crystal structure was solved by direct methods. Approximate coordinates for all non-hydrogen atoms were obtained from an *E*-map. Atomic positional and thermal parameters (first isotropic, then anisotropic) of these atoms were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions, and an extinction correction was included as a variable during the later iterations. No unusual features were present in a final difference *Fourier* synthesis.

Crystallographic calculations were performed on PDP11/44 and Micro VAX computers by use of the Enraf-Nonius Structure Determination Package (SDP 3.0) [26]. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography, vol. IV, The Kynoch Press, Birmingham, UK 1974.

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