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Thermal oligomerisation of aryl isocyanides: formation of pyrazino[1,2-*a*:4,5-*a*′]diindoles and indigo diarylimines

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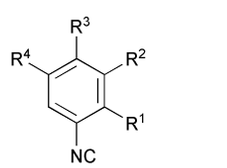
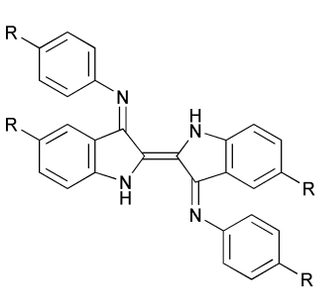
The aryl isocyanides **1**–**4** are converted at 150 °C into the hexameric pyrazino[1,2-*a*:4,5-*a*′]diindoles **15**–**19**. 4-Fluorophenyl isocyanide, when heated at 135 °C, gave the hexamer **19** and the tetrameric indigo di-arylimine **9**, and when kept at ambient temperature gave mainly the tetramer **9** in low yield. The structures of the hexamer **19** and the tetramer **9** were established by X-ray crystallography. Mechanisms are proposed for the oligomerisation reactions.

Introduction

Phenyl isocyanide **1**, the first aryl isocyanide to be prepared,[1a,b] rapidly becomes blue at ambient temperature. The colour, originally attributed to the isocyanide itself, arises from the tetramer **8** which gradually crystallises in the liquid isocyanide **1**.[1c] The tetramer also appears to have been present in the crude products obtained by other workers[1d–f] from polymerised phenyl isocyanide. The tetramer **8** was found to be identical with the product from the condensation of indigo with aniline; this established the structure of the tetramer **8** .[1c,2] The isocyanides **2** and **3** and 4-chlorophenyl isocyanide become green, indicating formation of the corresponding di-arylimines of indigo, but to a small extent as solids are not formed.[1c,d,3] In contrast, at temperatures above *ca*. 200 °C, aryl isocyanides isomerise into the corresponding nitriles.[1b,d,4a–e] We now report that aryl isocyanides are converted into a new type of oligomer when heated in the temperature range 130–160 °C.



1 $R^1 = R^2 = R^3 = R^4 = H$
2 $R^1 = R^2 = R^4 = H$, $R^3 = Me$
3 $R^1 = R^2 = R^4 = H$, $R^3 = MeO$
4 $R^1 = R^3 = H$, $R^2 = R^4 = Me$
5 $R^1 = R^2 = R^4 = H$, $R^3 = F$
6 $R^1 = R^4 = MeO$, $R^2 = R^3 = H$
7 $R^1 = H$, $R^2 = R^3 = R^4 = MeO$



8 R = H
9 R = F

Results and discussion

The isocyanides **1**–**4**, when heated at 150 °C for several hours, gave stable orange–red crystalline oligomers in modest yields (12–18%). 4-Fluorophenyl isocyanide **5**, when heated at 135 °C, gave a red oligomer (11%) together with a smaller amount (3.2%) of a sparingly soluble compound as black crystals that have a high melting point and give blue solutions. When the isocyanide **5** was kept at ambient temperature it began to deposit crystals of the black compound within 24 h after preparation and gave eventually the black compound as the main product in low yield along with a very small quantity of the red oligomer and much intractable gummy material. The properties of the black compound pointed to its being the tetramer **9** and this was confirmed by X-ray crystallography (Fig. 1 and Table 1).

Table 1 Selected bond lengths (Å) for **9**

N2–C8	1.402(3)	N2′–C8′	1.428(3)
N2–C3	1.365(3)	N2′–C3′	1.281(3)
C3–C3a	1.442(3)	C3′–C3a′	1.479(3)
C2–C3	1.400(3)	C2′–C3′	1.503(3)
N1–C2	1.386(3)	N1′–C2′	1.323(3)
N1–C7a	1.364(3)	N1′–C7a′	1.413(3)
C3a–C7a	1.418(3)	C3a′–C7a′	1.404(3)
C2–C2′	1.411(3)		

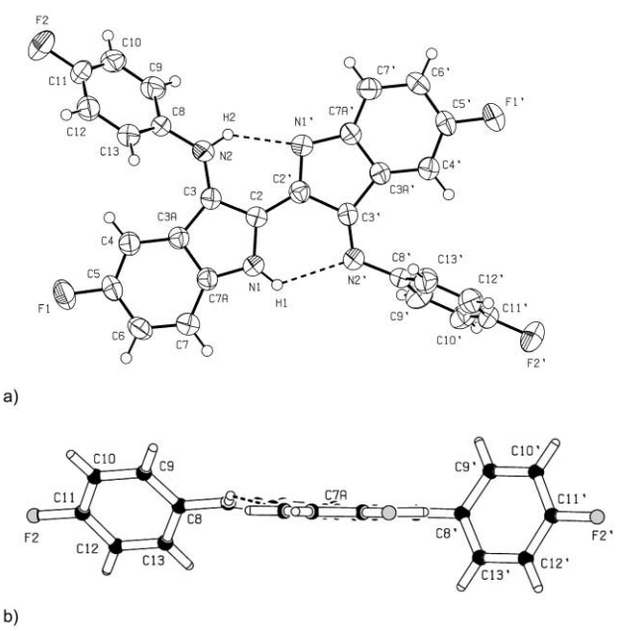


Fig. 1 Structure of **9** as determined by X-ray crystallography. a) ORTEP diagram (50% probability level) showing the intramolecular hydrogen bonding. b) An alternative view showing the planarity of the main part of the molecule.

The NMR spectra of the orange–red oligomers from the isocyanides **2** and **3** showed three ^{1}H- and three ^{13}C-methyl signals; the ^{19}F NMR spectrum of the oligomer from the isocyanide **5** showed three ^{19}F signals; and the NMR spectra of the oligomer from the isocyanide **4** showed four ^{1}H- and four ^{13}C-methyl signals. These data suggested initially that the orange–red oligomers are isocyanide trimers for which, in the case of phenyl isocyanide, we considered the indole structures **12**–**14** resulting from addition of phenyl isocyanide to the dimer **10** of phenyl isocyanide (Scheme 1). However a preliminary crystal structure determination of the red oligomer from 4-methoxyphenyl

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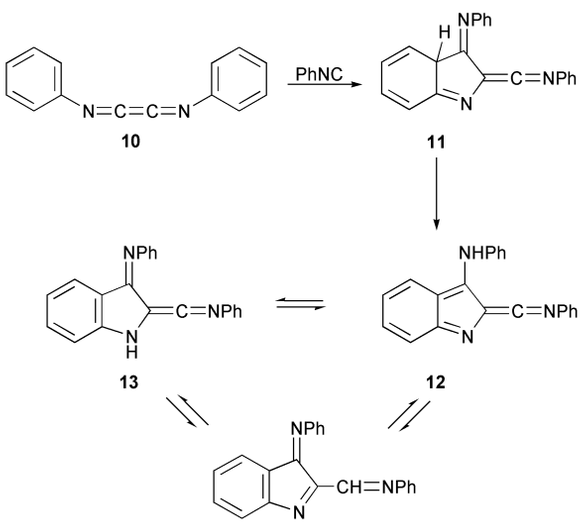
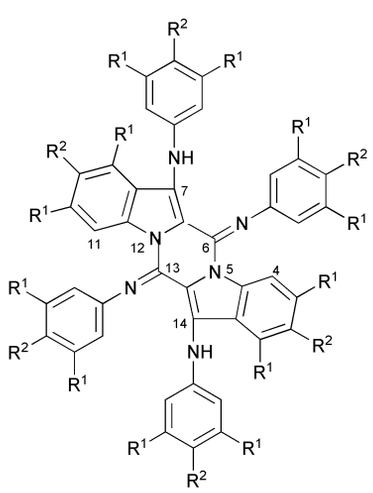
Table 2 Selected bond lengths (Å) for **19**

N2–C8	1.398(2)	N1–C2	1.419(2)
N2–C3	1.379(2)	N1–C7a	1.403(2)
C3–C3a	1.443(2)	N1–C14	1.410(2)
C3a–C7a	1.403(2)	N3–C14	1.281(2)
C3–C2	1.376(2)	N3–C15	1.413(2)

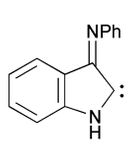


Scheme 1

isocyanide **3** established that the orange–red oligomers are the centrosymmetric isocyanide hexamers **15**–**19** based on the pyrazino[1,2-*a*:4,5-*a*′]diindole system. A good confirmatory structure determination was obtained for the solvate of the hexamer **19** with DMF (2DMF : 1 **19**) (Fig. 2 and Table 2).



15 $R^1 = R^2 = H$
16 $R^1 = H$, $R^2 = Me$
17 $R^1 = H$, $R^2 = MeO$
18 $R^1 = Me$, $R^2 = H$
19 $R^1 = H$, $R^2 = F$



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In the absence of experimental evidence it has been assumed that the dimer **10** of phenyl isocyanide is the first intermediate in the reaction sequence that gives the tetramer **8**. An early

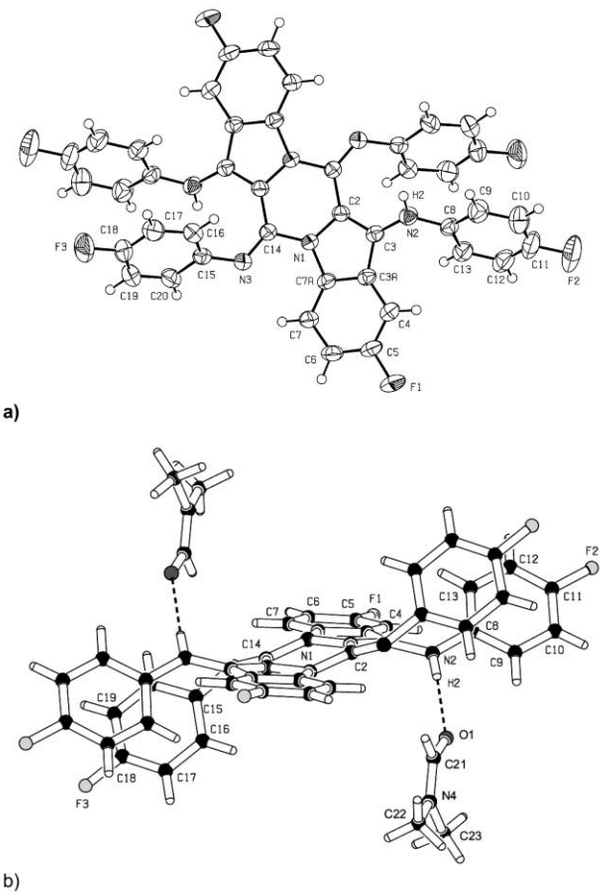
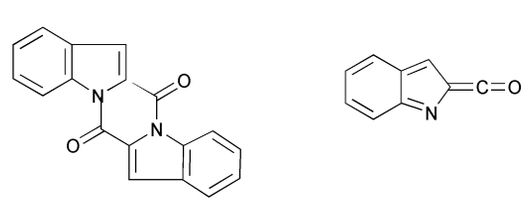


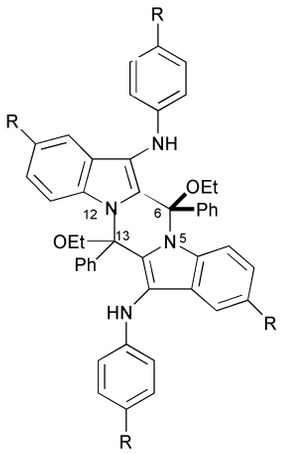
Fig. 2 Structure of **19** as determined by X-ray crystallography. a) ORTEP diagram (50% probability level). The molecules lie on an inversion centre and only the asymmetric unit has been labeled. Each molecule is hydrogen bonded to two DMF molecules as shown in (b).

mechanistic proposal[1c] was that the dimer **10** ring-closed to give the carbene **20** which dimerised to give the tetramer **8**. It was later suggested[5] that the dimer undergoes double [1 + 4]-cycloaddition of phenyl isocyanide to form the tetramer framework directly. We propose that the trimeric indolenine **12** is the key intermediate in the thermal reactions that lead to the hexamers and/or the tetramers. Further [1 + 4]-cycloaddition of phenyl isocyanide to the intermediate **12** or **13** in the manner of the sequence **10** ⟶ **11** ⟶ **12** leads to the tetramer **8**. Dimerisation of the indolenine **12** gives the hexamer **15**.

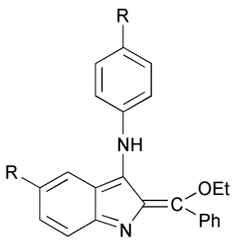
In support of this mechanism we cite several reactions in which indolenines structurally similar to the postulated intermediate **12** dimerise to give pyrazino[1,2-*a*:4,5-*a*′]diindole derivatives. Thus the dione **21** is formed by dimerisation of the transient ketene **22** which is generated (a) by FVP at 650–850 °C of indole-2-carboxylic acid or its methyl ester,[6] (b) by the reaction of (i) indole-2-carboxylic acid with DCC–pyridine,[7] (ii) indole-2-carboxylic acid chloride with Et_3N.[8] Also, Aumann has shown[9] that the 6,13-dihydropyrazino[1,2-*a*:4,5-*a*′]diindoles **23** and **24** are formed when the isocyanides **1** and **2**, respectively, react with $Ph(EtO)C{=}Cr(CO)_5$ under aprotic conditions. Evidence was adduced that the indolenines **25** and **26** are reaction intermediates which dimerise to give the diindoles **23** and **24**.



21 **22**

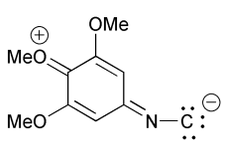


23 R = H
24 R = Me



25 R = H
26 R = Me

2,5-Dimethoxyphenyl isocyanide **6** and 3,4,5-trimethoxyphenyl isocyanide **7** are stable at ambient temperature. They did not give oligomeric products corresponding to the hexamers **15**–**19** or the tetramers **8** and **9**, when heated at 150–155 °C. We attribute this to the effect of charge repulsion between the isocyanide group carbon atoms, as in **27**, which prevents dimerisation and subsequent polymerisation from occurring. The effect of high temperatures (>*ca*. 200 °C) on the isocyanide monomer **1**–dimer **10** equilibrium will be to reduce the concentration of the dimer and consequently inhibit oligomerisation.



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X-Ray crystallography

The structure of **9** is shown in Fig. 1. Though one might expect the molecule to be the centrosymmetric tautomer (see formula **1**), the solid state structure is instead the non-centrosymmetric tautomer with respect to the hydrogen atom positions as well as bond lengths (Table 1). Analysis of the bond lengths between N2, C3, C2, C2′ and N1′ reveals the presence of significant conjugation between these atoms with the C2–C2′ bond having partial double bond character. In addition there are two intramolecular hydrogen bonds (N1–H1 ··· N2′: 2.29 Å, 123°; N1 ··· N2′: 2.847(3) Å and N2–H2 ··· N1′: 2.16 Å, 133; N2 ··· N1′: 2.812(3) Å). These hydrogen bonds as well as the partial double bond character of the C2–C2′ bond ensures that the central part of the molecule is quite flat (Fig. 1b).

The structure of **19** is shown as Fig. 2 with selected bond lengths given in Table 2. The crystal structure is really one of a solvate in which the main molecule is hydrogen bonded to two DMF molecules (Fig. 2b; N2–H2 ··· O1[x, y + 1, z]: 2.11 Å, 173°; N2 ··· O1: 2.969(2) Å) with the main molecule lying on a centre of symmetry. In addition one can also see that the central ring, made up of C14, N1, and C2 and further completed by the inversion centre, is significantly distorted from planarity.

Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined with a Bruker DRX spectrometer at 400 MHz and 100 MHz, respectively, using $CDCl_3$ solutions, unless otherwise stated. ^{1}H NMR chemical shifts δ_H are given in ppm downfield from TMS as internal reference. J values are given in Hz. ^{13}C NMR chemical shifts δ_C are given in ppm relative to the central peak of the $CDCl_3$ triplet taken as δ 77.0 and are proton-decoupled values. ^{19}F NMR spectra were determined at 282.4 MHz with a Bruker 300 AVANCE spectrometer, using $CDCl_3$ solutions. ^{19}F chemical shifts δ_F are given in ppm upfield from CCl_3F as external reference and are decoupled values.

Organic solvent extracts were dried over sodium sulfate or magnesium sulfate. Column chromatography was carried out with silica (80–200 mesh). Petroleum denotes an alkane mixture consisting mainly of hexane, of boiling range 60–80 °C. Benzene, dichloromethane, hexane and petroleum were dried by standard procedures and distilled before use. Solvent mixtures are described in ratios by volume.

Preparation of aryl isocyanides

The isocyanides **1**–**4** were prepared by reaction of the corresponding *N*-arylformamides with Ph_3P–CCl_4–Et_3N following the literature method:[10] **1**, 40%; **2**, 60%; **3**, 67%; **4**, 71%. 2,5-Dimethoxyphenyl isocyanide **6** and 3,4,5-trimethoxyphenyl isocyanide **7** were prepared from the corresponding arylamines by the phase-transfer method,[11] using $CHCl_3$, 50%(w/w) NaOH–H_2O and benzyltriethylammonium chloride in CH_2Cl_2. Yields and characterisation data are as follows: **6**, 39%; white needles (hexane), mp 71–72 °C (lit.[12] mp 64–65 °C); δ_H 3.76 (3H, s, OMe), 3.87 (3H, s, OMe), 6.884–6.892 (3H, m, 3-H, 4-H, 6-H); δ_C 55.8 (OMe), 56.4 (OMe), 112.8, 112.9, 116.1 (C-3, C-4, C-6), 149.3, 153.0 (C-2, C-5), 167.4 (NC), C-1 signal not obtained; δ_C (300 MHz, CD_2Cl_2, central peak of solvent quintet set at δ 53.8 as reference) 55.2 (OMe), 56.82 (OMe), 113.26, 113.29, 116.4 (C-3, C-4, C-6), 149.7, 153.5 (C-2, C-5), 168.3 (NC), C-1 signal not obtained. **7**, 35%; white needles (hexane), mp 77–78 °C; δ_H 3.85 (3H, s, 4-OMe), 3.86 (6H, s, 3- + 5-OMe), 6.62 (2H, s, 2- + 6-H); δ_C 56.3 (3- + 5-OMe), 60.9 (4-OMe), 104.0 (C-2 + C-6), 121.8 (br, C-1), 139.1 (C-4), 153.4 (C-3 + C-5), 163.1 (NC).

4-Fluorophenyl isocyanide 5. A mixture of 4-fluoroaniline (22.2 g, 200 mmol), 100%(w/w) HCOOH (80 mL, 2.1 mol) and toluene (80 mL) was boiled under reflux for 8 h. The reaction mixture was distilled at atmospheric pressure until 145 mL of distillate consisting of toluene, HCOOH and water had been collected. The remaining liquid was cooled, toluene (80 mL) was added, and 50 mL liquid was distilled off. This process was repeated. The residual liquid was cooled to *ca*. 75 °C, hexane (100 mL) was added with swirling, and the precipitated solid was filtered off, washed with hexane and dried over KOH pellets. *N-4-Fluorophenylformamide* (27.1 g, 97.6%) was thus obtained as white crystals, mp 66–67 °C (dichloromethane–hexane). The ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra showed two sets of signals corresponding to the presence of two rotamers (3.8 : 1) resulting from restricted rotation about the amide N–C bond. δ_H (400 MHz, DMSO-d_6) 7.13–7.25 (m) and 7.61–7.66 (m) (4H, ArH of major + minor isomers), 8.28 (br d, major isomer CHO), 8.72 (d, $J_{CHO,NH}$ 10.8 Hz, minor isomer CHO), 10.14 (br d, minor isomer NH), 10.23 (br s, major isomer NH); δ_C (100 MHz, DMSO-d_6): major isomer 115.4 (d, $J_{C\text{-}3(5),F}$ 22.3 Hz, C-3 + C-5), 120.9 (d, $J_{C\text{-}2(6),F}$ 7.9 Hz, C-2 + C-6), 134.6 (d, $J_{C\text{-}1,F}$ 2.5 Hz, C-1), 158.2 (d, $J_{C\text{-}4,F}$ 240.2 Hz, C-4), 159.5 (s, CHO); minor isomer 116.0 (d, $J_{C\text{-}3(5),F}$ 22.6 Hz, C-3 + C-5), 119.5 (d, $J_{C\text{-}2(6),F}$ 8.0 Hz, C-2 + C-6), 134.7 (d, $J_{C\text{-}1,F}$ C-1), 158.8 (d, $J_{C\text{-}4,F}$ 240.0 Hz, C-4), 162.7 (s, CHO); δ_F −117.0 (4-F, minor isomer), −117.3 (4-F, major isomer).

A solution of triphosgene[13] (5.93 g, 20 mmol) in dichloromethane (40 ml) was added dropwise over 20 min to a stirred solution of *N*-4-fluorophenylformamide (8.35 g, 60 mmol) and triethylamine (17.5 mL, 125 mmol) in dichloromethane (80 mL) cooled in an ice bath. The resulting mixture was stirred for 3 h while the bath was allowed to warm towards room temperature. Dichloromethane (200 mL) and then water (200 mL) were added and the resulting mixture was shaken up. The aqueous

layer was extracted with more dichloromethane (200 mL) and the dichloromethane extracts were washed in turn with water (3 × 200 mL), combined and dried. The residue from the evaporated extracts was distilled at 80–120 °C/15 mmHg (heating block) giving *4-fluorophenyl isocyanide* **5** (5.60 g, 77%) as a colourless oil that rapidly becomes green on standing at room temperature; δ_H 7.05–7.12 (2H, m, 2- + 6-H), 7.28–7.40 (2H, m, 3- + 5-H); δ_C 116.5 (d, $J_{C\text{-}3(5),F}$ 23.5 Hz, C-3 + C-5), 122.7 (br t, C-1), 128.3 (d, $J_{C\text{-}2(6),F}$ 8.9 Hz, C-2 + C-6), 164.4 (d, $J_{4\text{-}C,F}$ 251.6 Hz, C-4), 164.4 (br, NC).

Preparation of the pyrazino[1,2-*a*:4,5-*a*′]diindoles 15–18 from the aryl isocyanides 1–4. The following general procedure was used. A solution of the aryl isocyanide (10 mmol) and dichlorobenzene (0.5 mL) was heated (oil bath) at 150 °C for 5 h. The cooled mixture was extracted with benzene (20 mL) and the solution was chromatographed on silica (30 × 1.9 cm). Elution was carried out with petroleum–benzene (2 : 1) until orange–red eluates emerged. Elution was continued with the solvent mixture indicated and the residual solid from the evaporated orange–red eluates was recrystallised. Heating the isocyanides alone gave lower yields of product.

7,14-Di(phenylamino)-6,13-di(phenylimino)pyrazino[1,2-*a*:4,5-*a*′]diindole 15 from phenyl isocyanide 1. Elution solvent: petroleum–benzene (2 : 1). Recrystallisation from benzene–hexane (2 : 1) gave orange crystals (125 mg, 12.1%), mp 251–254 °C (Found: C, 81.7; H, 5.2; N, 13.6. $C_{42}H_{30}N_6$ requires C, 81.5; H, 4.9; N, 13.6%); δ_H 6.62 (4H, unresolved doublet), 6.87 (2H, triplet), 6.99–7.41 (22H, m), 8.11 (2H, brs, NH); δ_C 115.9, 116.8, 117.5, 120.6, 122.0, 122.1, 123.6, 124.0, 126.6, 127.3, 128.3, 128.8, 130.0, 134.1, 140.8, 143.0, 148.6.

7,14-Di(4-methylphenylamino)-6,13-di(4-methylphenylimino)-pyrazino[1,2-*a*:4,5-*a*′]diindole 16 from 4-methylphenyl isocyanide 2. Elution solvent: benzene–petroleum (1 : 1). Recrystallisation from benzene–hexane gave orange crystals (204 mg, 17.4%), mp 258–260 °C (Found: C, 81.4; H, 5.8; N, 11.9. $C_{48}H_{42}N_6$ requires C, 82.0; H, 6.0; N, 12.0%); δ_H 2.258 (6H, s, 2 × Me), 2.273 (6H, s, 2 × Me), 2.28 (6H, s, 2 × Me), 6.54 (4H, br s, Ar–H), 6.95–7.12 (18H, m, Ar–H), 7.96 (2H, br s, ~2 × NH); δ_C 20.6 (2 × Me), 20.9 (2 × Me), 21.3 (2 × Me), 115.9, 116.5, 117.5, 118.8, 120.4, 121.4, 124.3, 126.9, 128.0, 129.2, 129.7, 130.4, 131.4, 132.5, 133.1, 140.9, 146.2.

7,14-Di(4-methoxyphenylamino)-6,13-di(4-methoxyphenylimino)pyrazino[1,2-*a*:4,5-*a*′]diindole 17 from 4-methoxyphenyl isocyanide 3. Elution solvent: benzene–dichloromethane (2 : 1). Recrystallisation from benzene–hexane gave red crystals (221 mg, 16.6%), mp 261–263 °C (decomp.) (Found: C, 72.4; H, 5.4; N, 9.9. $C_{48}H_{42}N_6O_6$ requires C, 72.2; H, 5.3; N, 10.5%); δ_H 3.59 (6H, s, 2 × OMe), 3.76 (6H, s, 2 × OMe), 3.78 (6H, s, 2 × OMe), 6.51–7.23 (22H, m, Ar–H), 7.76 (vbrs, 1.8H, 2 × NH); δ_C 55.4 (2 × OMe), 55.5 (2 × OMe), 55.6 (2 × OMe), 103.3, 114.2, 114.3, 115.1, 115.7, 116.0, 117.8, 120.3, 121.4, 121.9, 124.3, 125.1, 129.0, 136.3, 142.0, 154.7, 156.0.

7,14-Di(3,5-dimethylphenylamino)-6,13-di(3,5-dimethylphenylimino)pyrazino[1,2-*a*:4,5-*a*′]diindole 18 from 3,5-dimethylphenyl isocyanide 4. Elution solvent: benzene–petroleum (1 : 1). Recrystallisation from benzene–hexane gave orange crystals (187 mg, 14.3%), mp 314–315 °C (Found: C, 82.5; H, 6.9; N, 10.6. $C_{54}H_{54}N_6$ requires C, 82.4; H, 6.9; N, 10.7%); δ_H 2.13 (12H, s, 4 × Me of 7- + 14-NAr or 6- + 13-NAr), 2.19 (6H, s, 3- + 10-Me or 1- + 8-Me), 2.36 (12H, s, 4 × Me of 6- + 13-NAr or 7- + 14-NAr), 2.40 (6H, s, 1- + 8-Me or 3- + 10-Me), 5.82 (4H, s, Ar–H), 6.36 (2H, s, Ar–H), 6.73 (8H, s, Ar–H), 6.84 (2H, s, Ar–H), 8.27 (~2H, br, NH); δ_C 18.8, 21.38, 21.42, 22.0 (1- + 8-Me, 3- + 10-Me, 3- + 5-Me of 7- + 14-NAr, 3- + 5-Me of 6- + 13-NAr), 112.3, 114.0, 117.3, 118.4, 120.5, 123.8, 125.4, 125.7, 126.7, 132.2, 135.2, 137.1, 138.4, 139.7, 140.4, 146.5, 148.9.

Oligomerisation of 4-fluorophenyl isocyanide 5 at 135 °C

Freshly distilled 4-fluorophenyl isocyanide **5** (5.60 g, 46.2 mmol) was heated at 135 °C (oil bath) for 3 h. The reaction mixture on cooling set to a viscous orange–red gum and was extracted with portions of boiling benzene (total, 150 mL), leaving an insoluble solid. The solid was filtered off, washed with boiling benzene until the washings were colourless, then with hexane, and dried. This gave *5,5′-difluoroindigo-3,3′-bis-(4-fluorophenylimine)* **9** (181 mg, 3.2%) as black crystals which were used for the X-ray crystal structure determination.

The combined benzene filtrates and washings were concentrated to 100 mL and hexane (100 mL) was added. A reddish brown sludge precipitated and the supernatant solution was decanted onto a column of silica (55 × 2.2 cm). Elution gave the following fractions: (i) hexane–benzene (3 : 1), pale orange, 500 mL, contained isocyanide **5**, discarded; (ii) hexane–benzene (2 : 1), deep orange–red, 1000 mL; (iii) hexane–benzene (2 : 1), orange, 300 mL; (iv) hexane–benzene (1 : 1), pale orange, 600 mL. Fraction (ii) was concentrated to *ca.* 10 mL and hexane (100 mL) was added. *7,14-Di(4-fluorophenylamino)-6,13-di-(4-fluorophenylimino)pyrazino[1,2-a:4,5-a′]diindole* **19** (571 mg) crystallised as small red crystals which melt at 170–175 °C, resolidify and remelt at 243–245 °C. The filtrates from fraction (ii) were combined with fractions (iii) and (iv), solvent was removed, and the residue was recrystallised from hexane to give a further 44 mg of compound **19** (total yield, 615 mg, 11%). NMR: δ_H 6.69 (br), 6.79 (dd), 6.91–7.05 (m), 7.84 (vbr, NH); δ_C 107.0 (d, $J_{C,F}$ 24.9 Hz), 115.2 (d, $J_{C,F}$ 25.4 Hz), 115.7 (d, $J_{C,F}$ 22.7 Hz), 116.1 (s), 116.7 (d, $J_{C,F}$ 22.6 Hz), 118.1 (d, $J_{C,F}$ 8.8 Hz), 119.9 (brs), 121.9 (d, $J_{C,F}$ 7.6 Hz), 124.3 (d, $J_{C,F}$ 9.8 Hz), 127.8 (vbrs), 130.4 (s), 138.1 (d, $J_{C,F}$ 2.5 Hz), 140.3 (s), 144.2 (d, $J_{C,F}$ 3.0 Hz), 158.1 (d, $J_{C,F}$ 242.2 Hz), 158.4 (d, $J_{C,F}$ 241.1 Hz), 159.4 (d, $J_{C,F}$ 244.9 Hz); δ_F −118.4, −118.6, −121.8 (br). Compound **19** crystallised from a small volume of DMF to give a solvate as granular red crystals having the composition 2DMF : 1 **19**; these were used for the X-ray crystal structure determination.

Oligomerisation of 4-fluorophenyl isocyanide 5 at ambient temperature

Freshly distilled 4-fluorophenyl isocyanide (2.42 g, 20 mmol) was kept at ambient temperature in a sealed tube. Black needle crystals formed within 24 h. The mixture was kept for 63 days and gradually formed a reddish brown gum. It was then extracted with portions of boiling benzene (200 mL) until the gum had dissolved. The residual insoluble black solid was filtered off, washed with boiling benzene until the washings were colourless, giving 5,5′-difluorophenylindigo-3,3′-bis(4-fluorophenylimine) **9** (147 mg, 6.1%) as blue–black needles (DMF) which do not melt but decompose gradually >270 °C. The combined benzene extracts were evaporated, the residue was redissolved in benzene (15 mL) and hexane (10 mL), and the solution was chromatographed on silica (45 × 1.5 cm) to give orange–red hexane–benzene (3 : 1) eluates followed by orange–red hexane–benzene (2 : 1) eluates (700 mL). Recrystallisation from hexane of the residue from the combined and evaporated eluates gave red crystals (25 mg, 1%) which were shown to be identical with compound **19** obtained in the preceding experiment.

Crystal structure determination of compound 9 †

Crystal data. $C_{28}H_{16}F_4N_4$, M = 484.45, triclinic, a = 9.6207(11),

† CCDC reference numbers 205332 and 205333. See http://www.rsc.org/suppdata/ob/b3/b302340k/ for crystallographic data in .cif or other electronic format.

b = 10.9214(13), c = 11.3237(13) Å, a = 109.183(2), β = 101.783(2), γ = 98.254(2)°, U = 1071.1(2) Å^3, T = 293(2) K, space group $P\bar{1}$ (No.2), Z = 2, μ_{Mo-Ka} = 0.115 mm^{-1}, 6401 reflections measured, 4160 unique (R_{int} = 0.0279) which were used in all calculations. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0508, w$R(F^2)$ = 0.1138.

Crystal structure determination of compound 19 †

Crystal data. $C_{48}H_{38}F_6N_8O_2$, M = 872.86, triclinic, a = 7.9770(11), b = 10.8182(15), c = 13.3466(19) Å, a = 109.812(2), β = 93.863(2), γ = 95.079(3)°, U = 1073.5(3) Å^3, T = 293(2) K, space group $P\bar{1}$ (No.2), Z = 1, μ_{Mo-Ka} = 0.103 mm^{-1}, 7601 reflections measured, 5195 unique (R_{int} = 0.0190) which were used in all calculations. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0505, w$R(F^2)$ = 0.1095.

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