Synthesis of Hexahalogeno-1,8-diazabiphenylenes; Separation of Steric and Electronic Effects in Extrusion of Dinitrogen from Benzo[*c*]cinnoline Systems, and the *X*-Ray Crystal Structure of Octachlorobenzo[*c*]cinnoline

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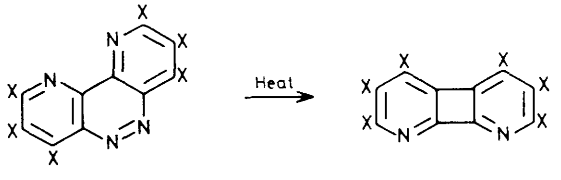
Thermal extrusion of dinitrogen from hexafluoro- and hexachloro-4,5,9,10-tetra-azaphenanthrenes gives hexafluoro- and hexachloro-1,8-diazabiphenylenes under conditions which contrast with the relatively easy dediazatation of octachlorobenzo[*c*]cinnoline whose *X*-ray crystal structure shows severe distortion.

Extrusion of dinitrogen from 9,10-diazaphenanthrenes {benzo[*c*]cinnolines} by flash vacuum pyrolysis is a useful route to biphenylenes,[1a] and their aza-, diaza-,[1b] and thia-nor[1c] analogues. Sartori and co-workers[2] obtained a mixture of hexafluoro-2,6- and -2,7-diazabiphenylene *via* trifluoro-3,4-pyridyne, and hexachloro-2,7-diazabiphenylene has been prepared by thermal extrusion of sulphur dioxide.[3] We report the synthesis of pure perfluoro- and perchloro-diazabiphenylenes (**2**, X = F or Cl) by flash vacuum pyrolytic extrusion of dinitrogen from the tetra-azaphenanthrenes (**1**, X = F or Cl).

Chlorination of 4,5,9,10-tetra-azaphenanthrene with phosphorus pentachloride (6 mol, 240 °C, 18 h, stainless steel autoclave) gave hexachloro-4,5,9,10-tetra-azaphenanthrene (**1**, X = Cl),† m.p. 325—330 °C (from acetonitrile) in 33% yield, ν_{max} (KBr, strongest band) 1107 cm^{-1}; λ_{max} (cyclohexane) 244.5 (log ϵ 4.40), 271.5 (4.67), 291 (4.42), 309.5 (4.09), 321.5 (4.01), 334 (3.61), 350.5 (3.72), and 367.5 nm (3.73). Pyrolysis of the tetra-azaphenanthrene (**1**, X = Cl) on silica wool at 850 °C and 4 × 10^{-2} mbar and chromatographic separation of the breakdown products gave hexachloro-1,8-diazabiphenylene (**2**, X = Cl)† in 11% yield, m.p. 293—294 °C, ν_{max} (KBr, strongest band) 1270 cm^{-1}, λ_{max} (cyclohexane) 259 (log ϵ 4.72), 268 (4.71), and 379 nm (4.35).



(**1** X = H, F, or Cl) (**2**)

The u.v. spectrum of this diazabiphenylene (**2**, X = Cl) is very like that of 1,8-diazabiphenylene (**2**, X = H), with a shift to longer wavelength of *ca.* 30 nm. A similar correlation exists between the u.v. spectrum of 2,7-diazabiphenylene and its hexachloro-derivative.[4]

Fluorination of hexachloro-4,5,9,10-tetra-azaphenanthrene (**1**, X = Cl) with anhydrous potassium fluoride (36 mol, 260 °C, 18 h, stainless steel autoclave) gave hexafluoro-4,5,9,10-tetra-azaphenanthrene (**1**, X = F)† in 40% yield, m.p. 303—304 °C (from acetonitrile), ν_{max} (KBr, strongest band) 1460 cm^{-1}, λ_{max} (cyclohexane) 243 (log ϵ 3.40), 314 (1.95), and 326 nm (1.95). Pyrolysis of hexafluoro-4,5,9,10-tetra-azaphenanthrene (silica wool, 850 °C, 8 × 10^{-2} mbar) gave hexafluoro-1,8-

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† Satisfactory microanalytical and spectrometric data were obtained for all new compounds.

diazabiphenylene, (**2**, X = F)† in 55% yield, m.p. 130—132 °C (from hexane), ν_{max} (KBr, strongest band) 1415 cm^{-1}, λ_{max} (cyclohexane) 231 (log ε 4.37), 229 (4.38), 322 (3.67), and 338 nm (3.91); ^{19}F n.m.r. (CDCl$_3$, 84.6 MHz) δ −6.9 (m, F-3, F-6), −41.5 (m, F-4, F-5), and −79.6 p.p.m. (m, F-2, F-7) (downfield from C_6F_6). The second order multiplets (AA′MM′XX′) reveal coupling between the fluorine atoms of the two pyridine rings; detailed analysis of the spectrum is in hand. Cross-ring coupling has been observed in octafluorobiphenylene[5] and in Sartori's compounds.[2]

We have noted the relatively mild conditions (100% conversion at 700 °C) needed to extrude dinitrogen from octachlorobenzocinnoline compared with benzocinnoline (60% conversion at 920 °C with comparable hot-zone contact time) and discussed the possible steric or electronic effects responsible for this difference.[1a] Hexachloro-4,5,9,10-tetra-azaphenanthrene (**1**, X = Cl) lacks the steric interaction of chlorine atoms at C-4 and C-5 and is presumably planar, but replacement of C–Cl groups by N probably leaves a similar electron demand on the pyridazine ring to that in the octachloro-compound.

X-Ray crystallography confirms the severe distortion of the octachlorobenzocinnoline molecule revealed by the perspective diagram (Figure 1).‡ The angle between the calculated best planes of the benzene rings is 150.6°. While the greater part of this deflection is obtained by distortion of the pyridazine ring, presumably with significant loss of aromatic stabilisation, torsion angles within the benzene rings reach a maximum of 16.8° (C-1–C-10a–C-4a–C-4, phenanthrene numbering) which shows that they are also considerably twisted.

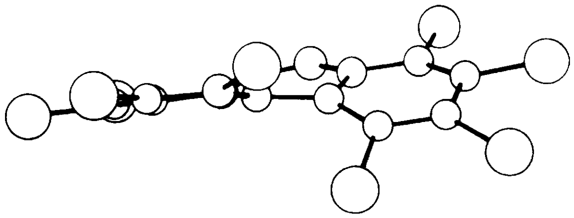

Figure 1

Since the diaza-compound (**1**, X = Cl) needs pyrolysis conditions similar to those required to extrude dinitrogen from benzocinnoline,[1a] we conclude that the steric and not the electronic effect is dominant. Further, the increased electron demand of the hexafluoro-derivative (**1**, X = F) leads to relatively minor reduction in the severity (86% conversion at 850 °C, 8 × 10^{-2} mbar) of the conditions needed to extrude dinitrogen from the hexachloro– or the unsubstituted analogues (**1**, X = Cl or H).

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‡ The atomic co-ordinates for this work are available from the Director of the Cambridge University Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data: $C_{12}Cl_8N_2$, $M = 456.1$, monoclinic, space group $P2_1/c$, $a = 10.325(1)$, $b = 7.006(1)$, $c = 21.401(2)$ Å, $\beta = 105.73(2)°$, $U = 1490$ Å^3, $F(000) = 888$, $D_c = 2.03$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) = 14.9 cm^{-1}. Reflections were measured out to $\theta = 30°$ and of these 2098 with $I > 3\sigma(I)$ were used in the refinement. The structure was solved using the SHELX centrosymmetric direct method program and refined by full-matrix least-squares with anisotropic temperature factors to an *R*-value of 5.9%. Individual bond lengths (e.s.d. 0.005—0.008 Å) and angles (e.s.d. 0.4—0.5°) were all within expected limits.