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AN ANNELATED HEXAAZA[26]ANNULENE

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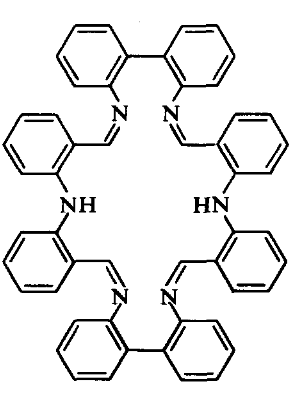
Abstract—The condensation of 2,2′-diaminobiphenyl and diphenylamine-2,2′-dicarboxaldehyde afforded Octabenzo[b,f,h,l,o,s,u,y][1,5,10,14,18,23]hexaaza[26]annulene in quantitative yield.

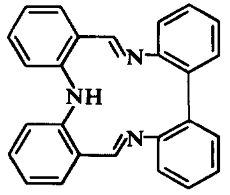
Among the various aspects of annulene chemistry, little progress has been made so far in the synthesis of heteroannulenes.[1] The present communication describes a straightforward, simple synthesis of octabenzo[b,f,h,l,o,s,u,y][1,5,10,14,18,23]hexaaza[26]annulene (1). The diamine-dialdehyde condensation applied in this synthesis took an unexpected course, leading to a 2:2-cyclization product, to the exclusion of the ordinary 1:1 cyclization. Recently Hideg and Lloyd reported the formation of either seven-membered rings or fourteen-membered rings or uncyclized adducts from the analogous reaction of ethylenediamine and $\alpha\beta$-unsaturated ketones.[2]

2,2′-Diaminobiphenyl[3] reacted with diphenylamine-2,2′-dicarboxyaldehyde[4] in methanol solution at room temperature to give (1) (yellow needles, m.p. 322° dec) in quantitative yield. The formation of the 26-membered ring (1) rather than the 13-membered ring (2) is indicated by the molecular weight of the product (746·315194; $C_{52}H_{38}N_6$ requires 746·315794). The IR spectrum displayed strong C═N absorptions at 1630, 1615, and 1596 cm^{-1} and a medium N—H absorption at 3140 cm^{-1}. The UV spectrum (λ_{max}(CCl_4) 370^s and 408 nm (ϵ 16,000 and 16,350)) resembled that of the starting dialdehyde;[4] it reflected the absence of any extended conjugation system in 1, thus a non-planar configuration. The NMR spectrum of 1 showed absorptions only in the aromatic region, thus ruling out polycyclic "hydride shift" products and supporting the (tetrakis)-Schiff base structure of 1. It is doubtful whether the absorption of the N═CH protons (singlet, 8·05 ppm) could be applied as a probe to establish whether 1 is diatropic.[1] The chemical shift of these protons would be considerably affected by their geometry relative to the neighbouring aromatic rings and by the shielding due to the *ortho* amino groups.

The diamine-dialdehyde condensation method has been employed in the heteroannulene series, e.g., for the synthesis of an annelated diaza[12]-annulene.[5,6] The method has been studied in terms of bis-Schiff base *vs* bicyclic "hydride shift" products.[6] Although a 12-membered ring has been shown previously[6] to be a sufficient minimum ring size for the formation of a bis-Schiff base, the results reported here indicate that an analogous 13-membered ring (2) could not be obtained (at least by this method). The formation of the 26-membered ring product (1) is apparently due to the preferred conformation of the diphenylamine-2,2′-dicarboxaldehyde moiety during the condensation. The nitrogen bridge (which is absent in biphenyl-2,2′-dicarboxaldehyde) reduces significantly the probability for the cyclization to 2, leading instead to the formation of the 2:2 condensation product (1).



1



2

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas and Hoover capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer. UV spectra were recorded on a Unicam SP 800 spectrophotometer. NMR spectra were recorded at 100 MHz on a Varian XL-100 spectrometer. ^1H chemical shifts are reported in parts per million, downfield from TMS. Mass spectra were recorded on a Varian MAT 711 spectrometer.

Octabenzo[b,f,h,l,o,s,u,y][1,5,10,14,18,23]*hexaaza*[26] *annulene* (1).

2,2′-Diaminobiphenyl[3] (4·4 mmole) and diphenylamine-2,2′-dicarboxaldehyde[4] (3·9 mmole) were stirred in MeOH soln at room temp for 20 hr. The product 1 separated from the soln. Recrystallization from toluene gave 1 as yellow needles (quantitative yield), m.p. 322° (dec); UV $\lambda_{max}^{CCl_4}$ 370 sh nm (log ϵ 4·20) and 408 (4·21); $\lambda_{max}^{CH_3CN}$

243 nm (log ϵ 4·77), 258 sh (4·74) and 400 (4·20); IR ν max (nujol) 3140, 1630, 1615, 1596, 1580, 1560, 1513, 1480, 1375, 1365, 1323, 1183, 1160, 1156, 755, 745, 735 cm^{-1}; NMR ($CDCl_3$) δ 6·42–7·66 ppm (m), 8·05 (s), 8·45 (s, broad). (Found: C, 83·90; H, 5·32; N, 10·98. $(C_{26}H_{19}N_3)_n$ requires: C, 83·62; H, 5·13; N, 11·25%).

REFERENCES

[1] F. Sondheimer, *Accounts Chem. Res.* **5**, 81 (1972)

[2a] K. Hideg and D. Lloyd, *Chem. Commun.* 929 (1970); [b] K. Hideg and D. Lloyd, *J. Chem. Soc.* (C), 3441 (1971)

[3] St. von Niementowsky, *Ber. Dtsch. Chem. Ges.* **34**, 3325 (1901)

[4] E. D. Bergmann, M. Rabinovitz, and I. Agranat, *Bull. Res. Council Israel* **11A**, 149 (1962)

[5] E. D. Bergmann, I. Agranat, and M. A. Kraus, *J. Org. Chem.* **32**, 600 (1967)

[6] A. P. Bindra and J. A. Elix, *Tetrahedron* **26**, 3749 (1970)