# 1,3,4,6,8,9b-Hexaazaphenalene

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Cyclization of 2,6-diaminopyrazine to two new heterocyclic ring systems, 1,3,5,7,9b-pentaazaphenalene and 1,3,4,6,8,9b-hexaazaphenalene is reported.

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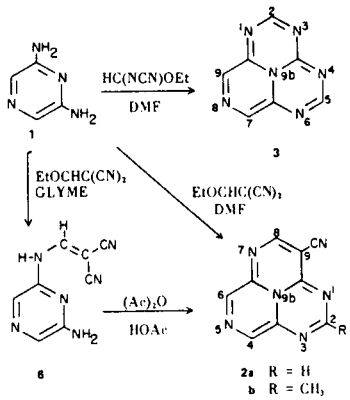
The recent literature (1-5) displays an increasing interest in the synthesis and reactions of aza-analogues of 9b-azaphenalene. The starting materials for these syntheses have been 2,6-diaminopyridine, 2,4-diaminopyrimidine and activated 2,6-dimethylpyridines. We have found that 2,6-diaminopyrazine (**1**) also can be used in these procedures and have used it to prepare 9-cyano-1,3,5,7,9b-pentaazaphenalene (**2a**), 9-cyano-2-methyl-1,3,5,7,9b-pentaazaphenalene (**2b**) and 1,3,4,6,8,9b-hexaazaphenalene (**3**), members of two new *N*-bridged heterocyclic annulenes.

Thus heating **1** with ethoxymethylenemalononitrile (**4**) in dimethylformamide (DMF) at ~150° gave **2a** in 14% yield. A similar reaction of **1** with ethyl *N*-cyanoformimidate (**5**) in DMF at ~95° gave **3** in 40% yield. An alternative path to derivatives of ring system **2** was accomplished by first refluxing **1** with **4** in 1,2-dimethoxyethane(glyme) to yield 2-cyano-3*N*-(6-amino-2-pyrazinyl)-aminopropenenitrile (**6**) in 54% yield. Ring closure of **6** to **2b** was effected in 86% yield by refluxing with acetic anhydride in acetic acid. We have not been able thus far to carry out similar reactions of **1** with **5** to provide an alternative route to derivatives of ring system **3**.

Elemental analyses, molecular weights and infrared data consistent with the proposed structures of the new ring systems are given in the experimental. Some of the pmr assignments require a few additional remarks. The pmr spectra of **2b** in deuteriochloroform shows three singlets: the 3-proton singlet at δ 1.95 is obviously the methyl group; protons $H_4$ and $H_6$ while not in equivalent environments are nonetheless in a more similar environment than is $H_8$ and thus correspond to the 2-proton singlet at δ 7.49; the remaining signal at δ 7.16 must be $H_8$. These results obtained in deuteriochloroform suggest that the two 1-proton singlets at δ 7.43 and δ 7.68 obtained for **2b** in DMSO-$d_6$ must be $H_4$ or $H_6$, since the other two singlets are reasonably close to the corresponding values obtained in deuteriochloroform. Three of the four singlet resonances of **2a** in DMSO-$d_6$ show an almost one to one correspondence to the pmr signals of **2b** in DMSO-$d_6$ and were assigned accordingly. The remaining singlet at δ 7.18 must then be due to $H_2$. The pmr spectra of **3** showed the two expected singlets of equal intensity, but they were rather surprisingly close to each other. It was assumed that in this compound as in **2a** and **2b**, the protons in the pyrazine ring ($H_7$ and $H_9$) would be those further downfield and assignments were made accordingly.

Reactions of these new ring systems will be a subject of a future paper.




## EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting-point bath and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Infracord, Model 137. Pmr spectra were determined on a Varian EM-360 spectrometer using TMS as an internal reference. Analyses were performed by Micro-Analysis Inc., Marshallton, Delaware. All evaporations were carried out on a rotary evaporator at reduced pressure.

Glyme, 1,2-dimethoxyethane and dimethylformamide were dried over calcium hydride and stored over molecular sieves. Ethoxymethylenemalononitrile (**4**) was obtained from Aldrich Chemical Company. Woelm silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc.

9-Cyano-1,3,5,7,9b-pentaazaphenalene (**2a**).

A mixture of 1.1 g. (0.01 mole) of 2,6-diaminopyrazine (**1**), (6) 2.69 g. (0.022 mole) of **4** in 4 ml. of dry DMF was heated at 145-153° for 0.5 hours. In order to reach this temperature, it was necessary to allow the small amount of ethanol formed in the reaction to escape. The reaction mixture, after cooling to room temperature, was diluted with 25 ml. of chloroform and chromatographed on 60 g. of silica gel using chloroform/methanol:95/5 as eluent. Evaporation of the dark blue fraction gave 0.27 g. of crude (**2a**) (14%) mp. 270-280° dec. Recrystallization from 2-methoxyethanol gave an analytical sample, dark grey-blue crystals, m.p. 298-300° dec.; ir δ (Nujol): 4.5 μm (CN), no significant absorption 2.75-3.2 μm; pmr (DMSO-$d_6$): δ 7.10 (s, 1H, $H_8$), δ 7.18 (s, 1H, $H_2$), δ 7.44 (s, 1H, $H_4$ or $H_6$), δ 7.67 (s, 1H, $H_4$ or $H_6$). Molecular weight 194 (vapor phase osmometry).

*Anal.* Calcd. for $C_9H_4N_6$: C, 55.10; H, 2.06; N, 42.84. Found: C, 55.39; H, 2.17; N, 42.71.

1,3,4,6,8,9b-Hexaazaphenalene (**3**).

A solution of 1.1 g. (0.01 mole) of **1**, 2.35 g. (0.024 mole) of ethyl *N*-cyanoformimidate (**5**) (7) and 4 ml. of dry DMF was stirred at 35-40° for 10 minutes after which time a precipitate formed. The mixture was then stirred and heated on a hot water-bath (92-98°) for 4 hours. During this time, the solid gradually dissolved and a very dark-blue solution formed. The solution was evaporated to a thick solid which upon trituration with ether, followed by filtration and recrystallization from 1-butanol gave 0.69 g. of crude (**3**) (40%), m.p. 242-247°. Two additional recrystallizations from 1-butanol gave brilliant violet crystals, m.p. 248-250°; ir λ (Nujol): no significant absorption 2.75-3.2 or 4-5 μm; pmr (DMSO-$d_6$): δ 7.39 (s, 2H, $H_2$ and $H_5$), δ 7.43 (s, 2H, $H_7$ and $H_9$): molecular weight 174 (vapor phase osmometry).

*Anal.* Calcd. for $C_7H_4N_6$: C, 48.83; H, 2.34; N, 48.82. Found: C, 48.90; H, 2.42; N, 49.01.

2-Cyano-3-*N*(6-amino-2-pyrazinyl)aminopropenenitrile (**6**).

A solution of 1.1 g. (0.01 mole) of **1** and 1.59 g. (0.013 mole) of **4** in 8 ml. of dry glyme was refluxed for 3 hours. After cooling to room temperature, the precipitate which had formed was collected by filtration and washed with a small amount of ether, 1.0 g. (54%) m.p. 235-237°. Two recrystallizations from methanol gave pale yellow crystals, m.p. 244-246° dec.; ir λ (Nujol): 2.85, 3.07 μm (NH) 4.49 μm (CN); pmr (DMSO-$d_6$): δ 6.66 [(s, 3H, NH), this signal was removed by treatment with deuterium oxide], δ 7.63 (s, 2H, pyrazine, $H_3$ and $H_5$) δ 8.45 [s, 1H, $HC=C(CN)_2$].

A value of δ 8.45 for the alkene proton may seem rather far downfield, but the corresponding proton on 2-cyano-3-*N*-(6-amino-2-pyridyl)aminopropenenitrile had a value of δ 8.60 (8).

*Anal.* Calcd. for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.82; H, 3.27; N, 45.39.

9-Cyano-2-methyl-1,3,5,7,9b-pentaazaphenalene (**2b**).

A mixture of 1.86 g. (0.01 mole) of **6** and 1.35 g. (0.0132 mole) of acetic anhydride in 17 ml. of acetic acid was refluxed for 4 hours. The residue obtained after evaporation of the reaction mixture was stirred with 25 ml. of ether for 2 hours, evaporated to 10 ml., filtered and the cake was washed with ether, 1.80 g. (86%), m.p. 205-210°. Two recrystallizations from 1-butanol gave blue-green crystals, m.p. 224-226°; ir λ (Nujol): 4.48 μm (CN), no significant absorption 2.75-3.2 μm); pmr (deuteriochloroform): δ 1.95 (s, 3H, $CH_3$), δ 7.16 (s, 1H, $H_8$), δ 7.49 (s, 2H, $H_4$ and $H_6$); pmr (DMSO-$d_6$): δ 1.87 (s, 3H, $CH_3$), δ 7.11 (s, 1H, $H_8$), δ 7.43 (s, 1H, $H_4$ or $H_6$), δ 7.68 (s, 1H, $H_4$ or $H_6$). Molecular weight 213 (vapor phase osmometry).

*Anal.* Calcd. for $C_{10}H_6N_6$: C, 57.14; H, 2.88; N, 39.98. Found: C, 57.33; H, 3.16; N, 39.81.

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