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2,3-DIPHENYL- AND 2,3,6,7-TETRAPHENYL-HEXA-AZATRIPHENYLENE, LIGANDS FOR TRANSITION METALS.

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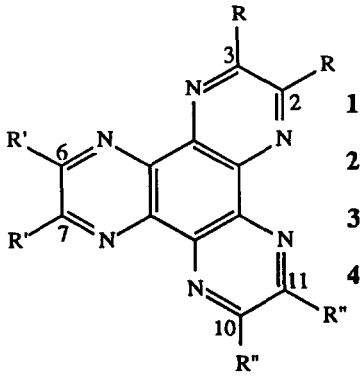
Summary. 2,3-Diphenyl-1,4,5,8,9,12-hexa-azatriphenylene **2** and 2,3,6,7-tetraphenyl-1,4,5, 8,9,12-hexa-azatriphenylene **3** can be synthesized by the direct condensation of hexa-aminobenzene with glyoxal and benzil. It is, however, not possible to make specifically one of the compounds, which is always accompanied by the parent compound **1** and the fully substituted hexaphenyl-hexa-azatriphenylene **4**. It is nevertheless possible to optimize the yields of **2** and **3** by a careful choice of the experimental conditions.

The first synthesis of dipyrazino[2,3-f; 2',3'-h]quinoxaline or 1,4,5,8,9,12-hexa-azatriphenylene **1** (abbreviated as HAT) was inefficient and required 10 steps [1]. Later work by Rogers [2] and by Praefcke's and our laboratories [3, 4] considerably improved the synthesis of hexa-aminobenzene **5** and its condensation with glyoxal or masked forms of glyoxal, and access to **1** is now rather straightforward as well as to its symmetrically hexasubstituted derivatives [5]. As part of our search for tris-chelating ligands for transition metals able to selectively bind to different ions, we report now on the synthesis of 2,3-diphenylHAT **2** and 2,3,6,7-tetraphenylHAT **4** from **5**.

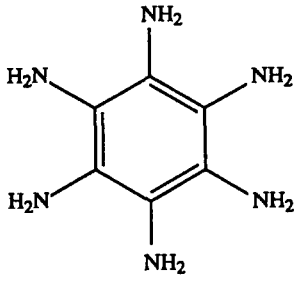


1 : R = R' = R" = H

2 : R = Ph , R' = R" = H

3 : R = R' = Ph, R" = H

4 : R = R' = R" = Ph



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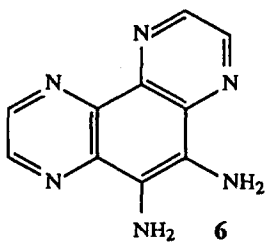
The unsubstituted HAT **1** was shown previously to give polymetallic complexes of Cr^0 [1] and Ru^{2+} [6]. The new ligands should thus open the way to the selective synthesis of mixed polymetallic complexes containing for example Cu(I) and Ru(II), where the metal centres would share a common conjugated system. Previous examples of ligands having two or more different chelating centres are known, but the metal atoms chelated by these ligands are not conjugated to each other. This is the case for the macrocycle described by Chambron and Sauvage [7]: in this molecule, the two metal atoms are separated by a polyoxyethylene chain and are thus independent of each other. Ligands **2** and **3**, on the other hand, are expected to yield heterometallic complexes [*e.g.* Cu(I)/Ru(II)] where the metal ions are conjugated to each other.

Whereas HATs carrying six identical substituents are well known [5, 8, 9], the synthesis of unsymmetrically substituted compounds such as **2** or **3** from **5** raises the problem of competing condensation reactions.

The attempted condensation of **5** with two equivalents of glyoxal gave poor yields of 9,10-diamino-1,4,5,8-tetra-aza-phenanthrene **6** [1], and using only one equivalent of benzil gave the very unstable and difficult to purify 2,3-diphenyl-5,6,7,8-tetra-aminoquinoxaline **7**



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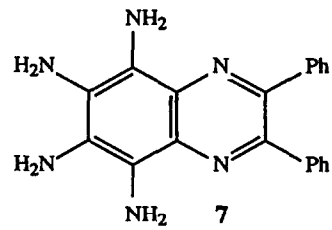

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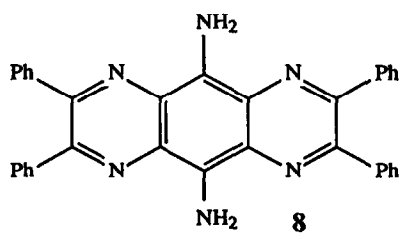
It was thus decided to resort to one-pot syntheses by adding adjusted amounts of glyoxal and benzil in the best order. In all cases a mixture of the four HATs **1** - **4** was isolated, and it was attempted to optimize the yield of the required compound.

After systematic variations of the temperature, pH, concentration and addition order of the reagents, a 96 % overall yield of the four compounds **1** - **4** was obtained, with 2,3-diphenylHAT **2** contributing 34 % [10]. It is especially worth mentioning that before the addition of the first equivalent of glyoxal, the medium should contain excess ammonia in order to avoid the fast formation of HAT **1**.

When the same procedure was adapted to the synthesis of 2,3,6,7-tetraphenylHAT, a new compound was isolated in up to 58 % yields: 2,3,7,8-tetraphenyl-5,10-diamino-1,4,6,9-tetra-aza-anthracene **8** [11].



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2,3,6,7-TetraphenylHAT **3** [12] was finally isolated with a yield of 35 % based on **5**. Here again, a fairly high initial concentration of ammonia is critical.

Access to unsymmetrically substituted HATs is thus now fairly straightforward, especially since it was found that the Birch reduction of 2,4,6-trinitro-1,3,5-triaminobenzene to hexa-aminobenzene can be greatly improved. We have observed indeed that the yield of this reduction, performed according to Rogers [2], critically depends on the rate of addition of the sodium metal to the medium: the yield of **5** raises from 4 % to over 90 % when the time to add 2.4 g of sodium is shortened from 30 min to less than 3 min.

Interestingly, all attempts using masked forms of glyoxal such as N,N'-dimethyl-[2,3;7,8;4a, 10a;5a,9a]-octahydro-di-[1,4]-oxazino-[2,3-b;2',3'-e]-di-[1,4]-oxane [13] (Le Rouzic's reagent) or glyoxal-di(cyclohexylimine) [14, 15] gave no result in the synthesis of these unsymmetrically substituted HATs, contrary to what was found previously for the formation of the unsubstituted **1**.

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Notes and References.

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(10) ^{1}H NMR spectra were recorded with a Bruker Cryospec WM spectrometer at 250 MHz. Chemical shifts, relative to internal TMS, are given in ppm; couplings in Hz. Mass spectra were recorded with a VG Micromass 7070F spectrometer.A solution of hexa-aminobenzene (1.5 mmol.L^{-1}) in aqueous ammonia (0.62 mol.L^{-1}) is kept at 50° C, and exactly one equivalent of 30 % aqueous glyoxal diluted with an equal volume of ethanol is added. After 2 h, exactly one equivalent of benzil, dissolved in an EtOH/AcOH/H_2O (10:4:1) mixture is added, still at 50° C. After 1 h, the last equivalent of glyoxal in water-ethanol is added, an the medium is stirred, still at 50° C, for 2 more hours. Dilution with water, extraction with chloroform, drying and concentration gives a dark solid which is chromatographed through silicagel with chloroform/ethanol 98:2. The four compounds **1**, **2**, **3** and **4** are obtained in ratios of 29 : 35 : 27 : 9 for a total yield of 96 %. 2,3-DiphenylHAT: very pale yellow solid, isolated with a 34 % yield based on **5**; MP: >330° C. ^{1}H NMR ($CDCl_3$): 9.32 (d, 2H, $H_{7,10}$); 9.28 (d, 2H, $H_{6,11}$); $J_{6,7} = J_{10,11} =$

2.0 Hz; 7.7 (m, 4H, phenyl H_{ortho}); 7.4 (m, 6H, phenyl $H_{meta, para}$). MS: $M^{\cdot+}$: 386 (100 %), 287 (27 %); 385 (45; $M^{\cdot+}$ - $H^{\cdot}$); 283 (21; $M^{\cdot+}$ - C_6H_5CN); 282 (24; 385 - C_6H_5CN); 193 (14; 283 - C_7H_4); 180 (12; 283 - C_6H_5CN); 154 (42; 180 - CN); 100 (12; 154 - 2 HCN). UV ($CHCl_3$): λ_{max}(nm) (10^{-4} ε): 248.5 (3.10); 289 (3.32); 350 (1.97).

(11) Adding two equivalents of benzil in the mixed solvent system EtOH/AcOH/H_2O (10:4:1) to aqueous **5** and, after two hours at 20 °C, the glyoxal in alcohol/water results in the formation of 58 % of 2,3,7,8-tetraphenyl-5,10-diamino-1,4,5,8-tetra-aza-anthracene **8**; MP:> 330 °C. The four compounds **1**, **2**, **3** and **4** are obtained in ratios of 17 : 15 : 60 : 8 for a total yield of 36 %. 2,3,7,8-tetraphenyl-5,10-diamino-1,4,6,9-tetra-aza-anthracene **8**: ^1H NMR ($CDCl_3$): 7.84 (m, 8 H, phenyl H_{ortho}); 7.41 (m, 12 H, undistinguished phenyl $H_{meta, para}$). MS: $M^{\cdot+}$: 516 (100 %), 517 (39), 518 (8); 515 (22; $M^{\cdot+}$ -$H^{\cdot}$); 288 (21; $M^{\cdot+}$ - 2,3-diphenylpyrazine + 2 H ?); 287 (10; $M^{\cdot+}$ - 2,3-diphenylpyrazine + $H^{\cdot}$?); 273 (33; 288 - NH); 258 (19; M^{++}); 246 (18).

(12) The whole synthesis is performed at room temperature. Starting with a 4.8 mmol.L^{-1} water solution of **5** containing ammonia at a concentration of 0.50 mol.L^{-1}, exactly one equivalent of benzil, dissolved in an EtOH/AcOH/H_2O (10:4:1) mixture, is added, and 1.25 h later one equivalent of glyoxal in ethanol/water is added. The second equivalent of benzil is introduced 1.5 h later, and the medium left under stirring for an additional 2 h. Dilution with water, extraction with chloroform, drying and concentration gives a dark solid which is chromatographed through silicagel with chloroform/ethanol 98:2.The four compounds **1**, **2**, **3** and **4** are obtained in ratios of 23 : 24 : 41 : 12 for a total yield of 85 %. 2,3,6,7-TetraphenylHAT: very pale yellow solid, isolated with a 35 % yield based on **5**; MP: >330° C. ^1H NMR: 9.27 (s, 2H, $H_{10,11}$); 7.8 (m, 8 H, undistinguished phenyl H_{ortho}); 7.4 (m, 12 H, undistinguished phenyl $H_{meta, para}$). MS: $M^{\cdot+}$: 538 (100 %), 539 (43), 540 (12); 537 (36; $M^{\cdot+}$ - $H^{\cdot}$); 435 (6; $M^{\cdot+}$ - C_6H_5CN); 332 (17; $M^{\cdot+}$ - 2 C_6H_5CN); 331 (17; $M^{\cdot+}$ - H - 2 C_6H_5CN); 269 (24; M^{++}); 209 (11); 166 (16). UV ($CHCl_3$): λ_{max}(nm) (10^{-4} ε):243 (2.10); 314 (2.16); plateau 356-372 (1.88 ± 0.02); similar spectrum in benzene solution.

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