Preparatively Useful Oxidation Reactions of Hexamethylhexaazatriphenylene

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Derivatives of hexaazatriphenylene (HAT) have been used in charge transfer complexes,[1] polymer synthesis,[2] and the synthesis of coordination complexes.[3] Preparatively useful syntheses of HAT derivatives provide new potential building blocks. While HAT hexacarboxylic acid and its derivatives have been reported,[4] no derivatives of HAT at the aldehyde oxidation state are known. We now report the preparation of three new compounds in this class.[10]

Hexamethyl HAT (**1**) was prepared by the condensation of hexaaminobenzene with 2,3-butanedione in an EtOH/AcOH/H_2O solvent system according to the literature method.[5] The reactivity of **1** is anticipated to be analogous to that of dimethylquinoxaline. Studies have shown[6] that a tautomeric equilibrium exists in alkylquinoxalines between alkyl and enamine tautomers (Figure 1). The equilibrium lies toward the alkyl tautomer; however, the enamine tautmomer affords nucleophilic reactivity to the molecule. Dimethylquinoxaline is known to be reactive to bromination by *N*-bromosuccinimide in the presence of light.[7] Similarly, dimethylpyridine is reactive toward bromination with bromine in acetic acid.[8] We have now shown **1** to be similarly reactive toward halogenation using either bromine or sulfuryl chloride to give symmetrically substituted hexakis(dihalomethyl) HAT derivatives.

Reaction of a solution of **1** in acetonitrile/H_2O (99:1 v/v) with excess bromine and refluxing for 3 days gives crude **2** as an orange powder in 54% yield (Scheme 1). The ^1H NMR spectrum ($CDCl_3$) of **2** displays a singlet for the methine protons at 7.42 ppm, which has been shifted downfield almost 5 ppm as compared to the starting material. The ^{13}C NMR spectrum ($CDCl_3$) shows the expected doublet for the alkyl carbons at 36.7 ppm, a singlet for the external aromatic carbons at 140.4 ppm, and a singlet for the internal aromatic carbons at 152.1 ppm. Additional characterization of **2** was performed by FAB mass spectral and elemental analyses. The ^1H NMR spectrum ($CDCl_3$) of crude **2** indicates the major impurity to be an asymmetrically brominated HAT, 3,6,7,10,11-pentakis(dibromomethyl)-2-(tribromomethyl) HAT, with proton resonances at δ 7.41 (s, CH), 7.50 (s, CH), 7.57 (s, CH), 7.58 (s, CH), and 7.87 (s, CH). The asymmetric HAT has neither been isolated to homogeneity nor completely characterized.

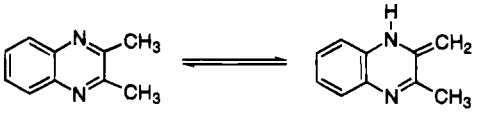
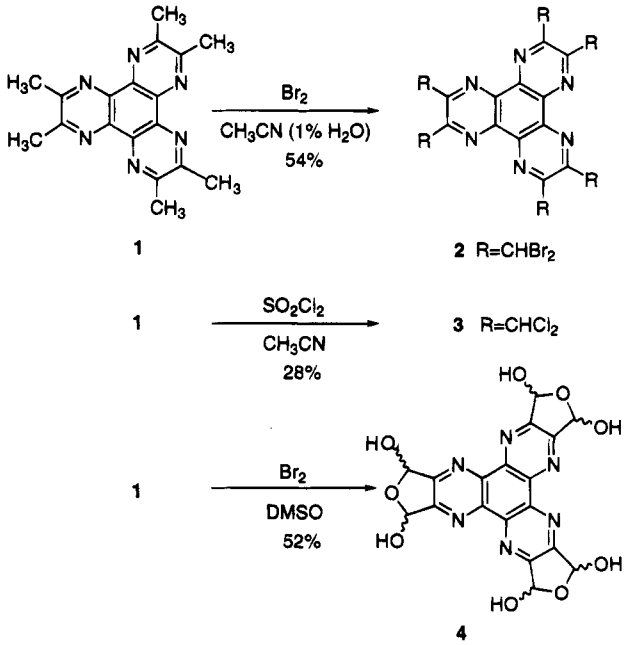


Figure 1. Dimethylquinoxaline tautomeric equilibrium.

Scheme 1



The chlorination of **1** is effected by treating an acetonitrile solution with an excess of sulfuryl chloride and refluxing for 3 days (Scheme 1). Aqueous precipitation of the reaction mixture yields crude **3** as a white powder. The crude compound is crystallized slowly from benzene to give fine colorless needles of hexakis(dichloromethyl) HAT (**3**) in 28% yield. The ^1H NMR spectrum ($CDCl_3$) displays two singlet proton resonances at 7.36 (**3**) and 7.64 ppm (cocrystallized benzene). Additional characterization of **3** was accomplished using ^{13}C NMR, FAB mass spectral, and elemental analyses. The ^1H NMR spectrum of crude **3** ($CDCl_3$) indicates that an asymmetrically chlorinated HAT, 3,6,7,10,11-pentakis(dichloromethyl)-2-(trichloromethyl) HAT, is obtained as a side reaction. Five singlets are observed at 7.58, 7.60, 7.67, 7.73, and 7.94 ppm in addition to a singlet at 7.36 ppm for **3**. As with the asymmetrically brominated HAT, the asymmetrically chlorinated HAT has neither been isolated to homogeneity nor completely characterized.

An aldehyde derivative of **1** was found to be accessible via a Nace-type reaction.[9] A suspension of **1** in dimethyl

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sulfoxide reacts exothermically upon addition of bromine (11.5 equiv). The reaction is then heated at 75 °C for 1 h giving a deep red solution that smells strongly of dimethyl sulfide. Aqueous precipitation of the crude reaction mixture affords HAT hexaaldehyde, obtained from the reaction as trihydrate **4** (Scheme 1). Purification was accomplished by reprecipitation from DMSO to give **4** as a tan powder in 52% overall yield. Analysis of **4** by ^{1}H NMR was interpreted by analogy to the ^{1}H NMR of quinoxalinedicarboxaldehyde hydrate reported by Moriconi and Fritsch.[8] The two multiplets of **4** at 6.42 and 6.65 ppm are assigned to the methine protons, and the two doublets at 7.56 and 7.69 ppm are assigned to the hydroxyl protons. The two multiplets and two doublets exist in a 1:1 ratio.

Two NMR experiments support this assignment. D_2O addition to the NMR sample of **4** in $(CD_3)_2SO$ yields deuterium exchange of the hydroxyl signals and concomitant sharpening of the methine multiplets to singlets. Furthermore, when the temperature of the ^{1}H NMR spectrum of **4** in $(CD_3)_2SO$ is raised to 303 K, the spectrum shows a multiplet and doublet at 6.43 and 6.75 ppm and two doublets at 7.57 and 7.72 ppm. Raising the temperature further to 353 K causes the downfield peaks to become one broad resonance indicative of rapid proton exchange. The upfield methine proton signals continue to sharpen and become singlets at 430 K.[10]

The ^{13}C NMR spectrum of **4** in $(CD_3)_2SO$ shows five carbon peaks as opposed to three for the polyhalo HAT derivatives. Two alkyl carbons appear at 95.5 and 96.2 ppm and three aromatic carbons at 142.4, 155.8, and 156.2 ppm. The occurrence of five carbon resonances is attributed to the two local isomers possible for the hydroxyl groups, cis and trans with respect to the plane of the ring system. Additional characterization of **4** was carried out by FAB mass spectral and elemental analyses that likewise confirmed the structural assignment.

Experimental Section

Hexakis(dibromomethyl)hexaazatriphenylene (2). Using a 1 L round-bottom flask, hexamethylhexaazatriphenylene (**1**) (2.11 g, 6.60 mmol) is dissolved in acetonitrile/H_2O (400 mL, 99:1 v/v). While stirring, a bromine/acetonitrile solution (30 mL: 100 mL) is added in one portion giving a flocculant orange precipitate. The reaction is then heated at a gentle reflux for 3 days. Initial heating dissolves the precipitate to give a clear orange solution while refluxing, which then develops a fine orange precipitate over the reflux period. The reaction is concentrated *in vacuo* resulting in an orange solid, which is triturated in 1.0 M aqueous sodium sulfite (200 mL). Vacuum filtration followed by a water wash and air drying gives 2.67 g of crude orange powder. The crude material is partially dissolved in 120 mL CCl_4 with sonication and suction filtered. The orange solid that is isolated is washed with CCl_4 (3 × 50 mL). The fine orange powder is hexakis(dibromomethyl)hexaazatriphenylene (4.27 g, 54%): mp slow decomposition to a black powder above 270 °C; ^{1}H NMR ($CDCl_3$) δ 7.52 (s, CH); ^{13}C NMR (THF-d_6) δ 36.7 (d), 140.4 (s), 152.1 (s); FAB MS *m/e* 1266.11 $(M + H)^+$. Anal. Calcd for $C_{18}H_6N_6Br_{12}$: C, 17.09; H, 0.48; N, 6.64; Br, 75.79. Found: C, 17.01; H, 0.56; N, 6.66; Br, 75.60.

Hexakis(dichloromethyl)hexaazatriphenylene (3). Hexamethylhexaazatriphenylene (**1**) (170 mg) is dissolved in acetonitrile (50 mL). While stirring, a solution of sulfuryl chloride (6 mL) in acetonitrile (10 mL) is added in one portion. The clear yellow solution is refluxed for 3 days. At the end of the reflux period the acetonitrile solution has turned to a dark amber color. The crude product is precipitated by dropwise addition of water. Suction filtration followed by water washing and air drying gives crude **3** as a white powder (310 mg). The solid is crystallized slowly from hot benzene to afford colorless needles (101 mg, 28%): mp rapid decomposition to a black powder above 260 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, ArH (residual benzene)), 7.64 (s, CH); ^{13}C NMR ($CDCl_3$) δ 67.5 (d), 128.3 (d)(residual benzene), 140.8 (s), 151.9 (s); FAB MS *m/e* 732.82 $(M + H)^+$. Anal. Calcd for $C_{18}H_6N_6Cl_{12}$: C, 29.55; H, 0.83; N, 11.49; Cl, 58.14. Found: C, 29.73; H, 0.94; N, 11.41; Cl, 57.89.

Hexaazatriphenylenehexacarboxaldehyde Trihydrate (4). Hexamethylhexaazatriphenylene (**1**) (1.27 g, 3.99 mmol) was suspended in DMSO (65 mL). While stirring in an ice bath, Br_2 (2.1 mL) was slowly added dropwise. Bromine addition is very exothermic. The reaction was then gradually heated to 75 °C for 1 h to afford a deep red solution. The red solution is cooled to 25 °C and poured into 400 mL of H_2O to give a fine powdery precipitate, which was collected by vacuum filtration. After a second precipitation from DMSO/water, the product was air-dried to afford a tan powder (951 mg, 52%): mp 175–180 °C tan powder contracts to a black residue; ^{1}H NMR ($(CD_3)_2SO$) δ 6.42 (m, 2, C-H), 6.65 (m, 1, C-H), 7.59 (d, 1, O-H), 7.73 (d, 2, O-H); ^{13}C NMR ($(CD_3)_2SO$) δ 95.5 (d), 96.2 (d), 142.4 (s), 155.8 (s), 156.2 (s); FAB MS *m/e* 457 $(M + H)^+$. Anal. Calcd for $C_{18}H_{12}N_6O_9 \cdot 3H_2O$: C, 41.63; H, 3.96; N, 16.18. Found: C, 41.75; H, 3.66; N, 16.18.

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Note Added in Proof: The free HAT-hexaaldehyde can be obtained by drying hexaazatriphenylene hexacarboxaldehyde trihydrate (**4**) under reduced pressure (45 mmHg) at refluxing toluene temperature for 2 d. Dehydration is confirmed by PMR and CMR analyses.

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