

spectra and experimental data (dashed lines). Because of the complexity of the overlap, it is only possible to calculate the spectra for the relatively resolved resonance which moves from about 150 to 140 ppm as a function of exchange. The exchange spectra were computed assuming a two-site exchange (see caption to Figure 1), and no correction was made for possible spectral distortions due to the fact that the exchange rate and magic angle sample spinning rate are similar.<sup>15</sup> Spectra were calculated as a function of exchange rate using 55:45 as the population ratio of the two sites at room temperature and visually compared to the experimental data until a reasonably good fit was obtained. Errors in estimated exchange due to magic angle sample spinning interferences are probably less than 10% and those due to overlap and broad lines are about the same magnitude. It is probable that the errors in this work are greater than those obtained from <sup>15</sup>N studies of this and similar compounds because of the simplicity of the <sup>15</sup>N spectra. The results are indicated in Figure 1. Because of the extremely poor solubility of phthalocyanine, to our knowledge no liquid-state studies have been performed. However, our results can be compared to the ones obtained for dissolved tetra-*tert*-butyltetraazaporphyrin, where a very similar exchange rate was found.<sup>17</sup>

In conclusion, we have demonstrated the utility of 2-D exchange spectroscopy in a case where the 1-D spectra are impossible to interpret. It has generally been believed that the only way to get kinetic information on these systems is through difficult isotopic labeling.

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(15) We would like to point out that exchange rates obtained from a line fit of exchange-broadened MAS spectra are only approximations to the true exchange rate (see ref 16).

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### Convenient Synthesis and Structural Aspects of 1,3,5-Tri[2,6]pyridacyclohexaphane-2,4,6-trione and Precursors<sup>1</sup>

George R. Newkome,\*† Young J. Joo, Kevin J. Theriot, and Frank R. Fronczek

Department of Chemistry, Louisiana State University  
Baton Rouge, Louisiana 70803-1804

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Analogues of porphyrins, in which one or more of the pyrrole subunits have been substituted by an electron-rich heterocycle (such as furan<sup>2</sup> and/or thiophene<sup>3</sup>), have been prepared<sup>4</sup> by the acid cyclocondensation of an appropriately substituted heterocycle with either aldehydes or ketones. However, the incorporation of an electron-poor heterocycle, e.g., pyridine, has not been accomplished since traditional electrophilic procedures are not applicable.

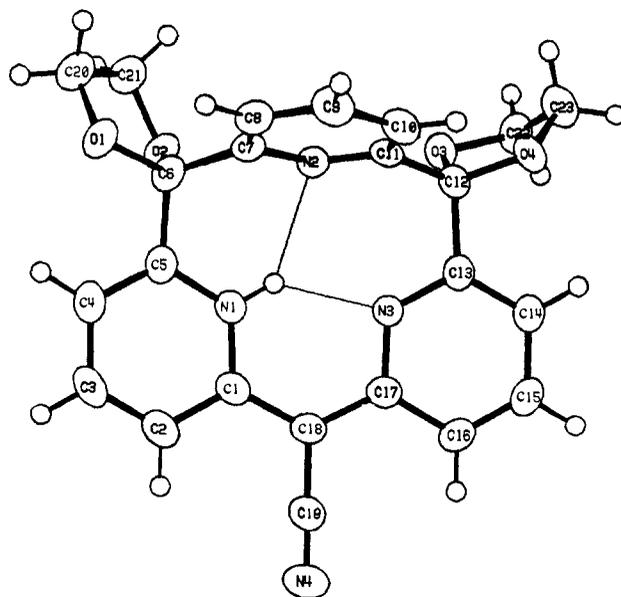
\* Current address: Department of Chemistry, University of South Florida, Tampa, FL 33620.

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**Figure 1.** Macrocycle **4** illustrating one of the two disordered, bifurcated, intramolecular hydrogen bonds. Bond lengths averaged over chemically equivalent bonds: N1-C1 1.358, N1-C5 1.353, N2-C7 1.338, O1-C6 1.416, O1-C20 1.425, C1-C2 1.415, C2-C3 1.355, C3-C4 1.395, C4-C5 1.361, C5-C6 1.530, C6-C7 1.523, C7-C8 1.380, C8-C9 1.379, C20-C21 1.494, C1-C18 1.431, C18-C19 1.421, C19-N4 1.15 Å; esd's are 0.002-0.003 Å.

The simplest member of this C-bridged, electron-deficient series is 1,3,5-tri[2,6]pyridacyclohexaphane-2,4,6-trione (**1**),<sup>5</sup> which should be an ideal structure to probe the electronic and/or steric effects of N electrons within a highly rigid cavity, as well as being ideally suited to be the perfect proton sponge. Our original low-yield route into this structural family was via a low-temperature (-100 °C), nucleophilic substitution;<sup>6</sup> however, unfavorable conformational problems impeded cyclization. We herein report a procedure that circumvents this problem and affords facile entry into the construction of a convenient precursor to trione **1**.

Diketone **2**<sup>7</sup> was synthesized by treatment of 2-lithio-6-bromopyridine<sup>8</sup> with either 2,6-dicarbalkoxy- or 2,6-dicyanopyridine at <-50 °C in Et<sub>2</sub>O. Ketalization of **2** conducted under either standard acidic<sup>9</sup> or basic<sup>10</sup> conditions gave (90%) **3**. Cyclization was accomplished (50%) by treatment of bis-ketal **3** with LiCH<sub>2</sub>CN, generated from anhydrous CH<sub>3</sub>CN in 5% TMEDA-toluene with LiH. The mixture was refluxed for 2 days; then, after cooling, water was added. After standard workup, the resultant dark yellow oil was chromatographed (Al<sub>2</sub>O<sub>3</sub>; CH<sub>2</sub>Cl<sub>2</sub>) to afford the yellow crystalline macrocycle **4** (Scheme I).<sup>11,12</sup>

The <sup>1</sup>H NMR spectrum of **4** showed a broad singlet at δ 16.5 indicative of a strong N-H···N interaction;<sup>13</sup> this proton was not

(5) IUPAC nomenclature: 19,20,21-Triaza tetracyclo[13.3.1.1<sup>3,7</sup>.1<sup>9,3</sup>]he-neicos-1(19),3,5,7(21),9,11,13(20),15,17-nonaene-2,8,14-trione.

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(11) **4**: mp 268-269 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.15-4.36 (m, 8 H, OCH<sub>2</sub>), 6.95-7.06 (m, 2 H), 7.24-7.80 (m, 7 H), 16.5 (br s, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 65.9 (OCH<sub>2</sub>), 69.0 (CCN), 104.9 (OCO), 109.7 (C3'), 119.4, 119.6 (C3 and C5'), 122.6 (C≡N), 136.6 (C4'), 138.9 (C4), 150.7 (C2'), 154.4 (C6'), 157.4 (C2); MS, *m/e* 415 (M<sup>+</sup> + 1, 31), 414 (M<sup>+</sup>, 100), 370 (10), 326 (28); IR (KBr) 2162 cm<sup>-1</sup> (C≡N). Anal. Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 66.66; H, 4.38; N, 13.52. Found: C, 66.36; H, 4.09; N, 13.25.

(12) Crystal data for **4**: C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>, MW = 414.4, monoclinic P2<sub>1</sub>/n, a = 11.104 (4) Å, b = 7.544 (2) Å, c = 22.375 (4) Å, β = 91.66 (2)°, Z = 4, D<sub>c</sub> = 1.469 g cm<sup>-3</sup>, R = 0.035 for 2103 observed reflections (1° < θ < 25°, Mo Kα).

## Scheme I

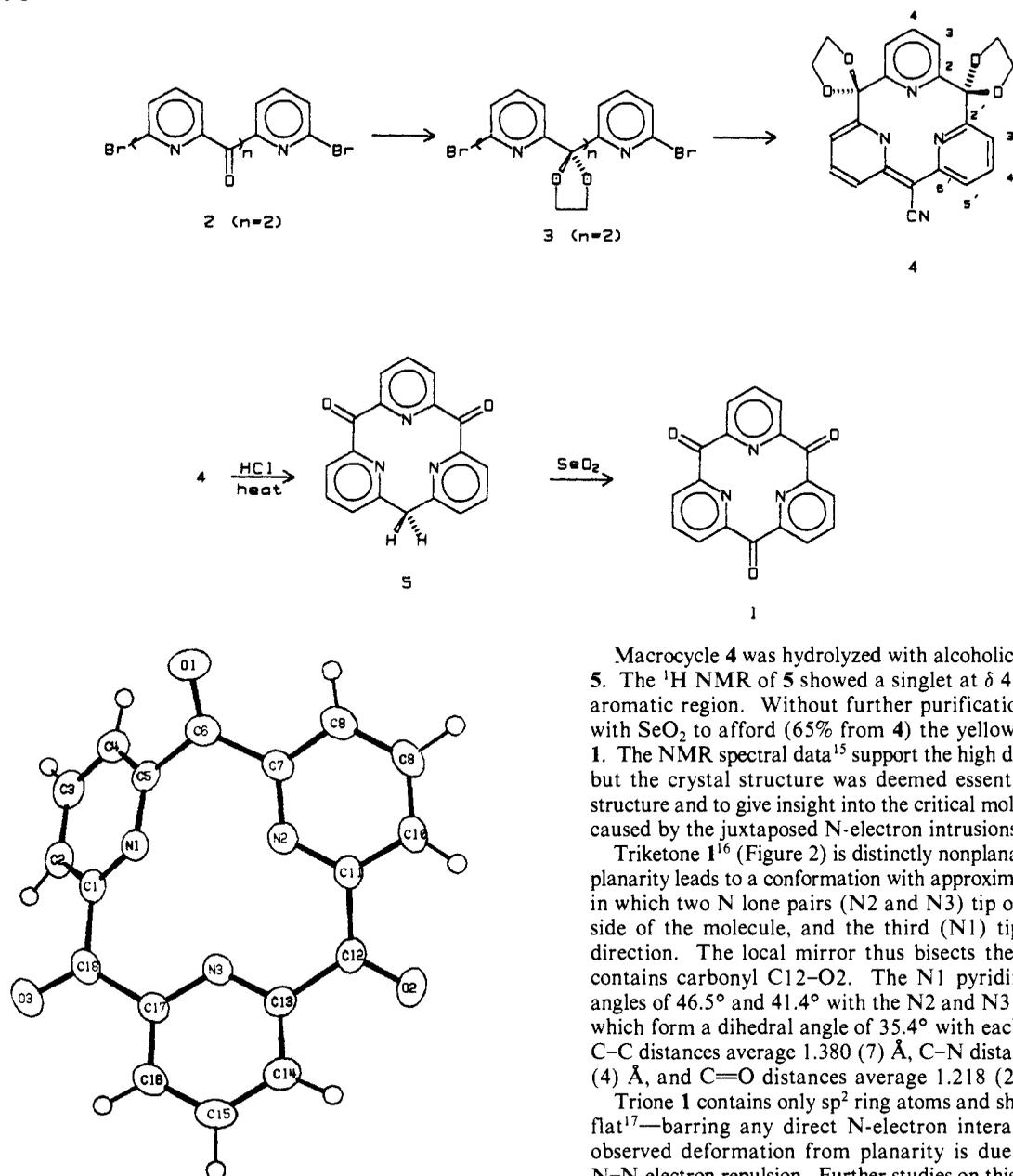


Figure 2. Triketone 1, illustrating molecular conformation and numbering scheme.

readily exchanged with D<sub>2</sub>O at 25 °C. A complex pattern was exhibited for the remaining hydrogens due to facial nonequivalence. The <sup>13</sup>C NMR of 4 confirmed the symmetrical cyclic structure, in which the pyridine carbons appeared at the usual position, except for C-3', and the bridging sp<sup>2</sup> carbon was at δ 69.0.<sup>14</sup>

Figure 1 illustrates the crystal structure<sup>12</sup> of 4, which confirms a fixed tautomeric form in the crystal; C18 is planar and one of the pyridyl units is protonated. The dipyridylmethine unit is nearly planar. [Maximum deviation from planarity is 0.118 (2) Å (for N1).] The central pyridine forms a dihedral angle of 70.9° with this plane, and N2 is nearly coplanar with the dipyridylmethine [deviation 0.066 (2) Å]. The N-H hydrogen forms a bifurcated H bond, with N1...N2 distance 2.807 (2) Å and N1...N3 distance 2.643 (2) Å.

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Macrocyclic 4 was hydrolyzed with alcoholic HCl to give dione 5. The <sup>1</sup>H NMR of 5 showed a singlet at δ 4.39 and a complex aromatic region. Without further purification, 5 was oxidized with SeO<sub>2</sub> to afford (65% from 4) the yellow crystalline trione 1. The NMR spectral data<sup>15</sup> support the high degree of symmetry, but the crystal structure was deemed essential to confirm the structure and to give insight into the critical molecular deformation caused by the juxtaposed N-electron intrusions within the cavity.

Triketone 1<sup>16</sup> (Figure 2) is distinctly nonplanar. Distortion from planarity leads to a conformation with approximately C<sub>3</sub> symmetry, in which two N lone pairs (N2 and N3) tip out of plane on one side of the molecule, and the third (N1) tips in the opposite direction. The local mirror thus bisects the N1 pyridine and contains carbonyl C12-O2. The N1 pyridine forms dihedral angles of 46.5° and 41.4° with the N2 and N3 rings, respectively, which form a dihedral angle of 35.4° with each other. Aromatic C-C distances average 1.380 (7) Å, C-N distances average 1.335 (4) Å, and C=O distances average 1.218 (2) Å.

Trione 1 contains only sp<sup>2</sup> ring atoms and should be essentially flat<sup>17</sup>—barring any direct N-electron interactions. Thus, the observed deformation from planarity is due predominately to N-N-electron repulsion. Further studies on this macrocyclic series are in progress to delineate the specifics of such interactions.

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**Supplementary Material Available:** Tables of atomic coordinates, coordinates of hydrogen atoms, bond lengths, bond angles, and thermal parameters for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> and C<sub>18</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub> (11 pages). Ordering information is given on any current masthead page.

(15) 1: mp 236.0–236.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.08–8.16 (dd, 4-py H, J<sub>3,4</sub> = J<sub>4,5</sub> = 7.9 Hz, 1 H), 8.32–8.36 (d, 3,5-py H, J = 7.9 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 126.7 (C3), 138.0 (C4), 152.9 (C2), 188.1 (C=O); MS, m/e 316 (M<sup>+</sup> + 1, 21), 315 (M<sup>+</sup>, 100), 287 (M<sup>+</sup> - CO, 5), 258 (M<sup>+</sup> - 2CO, 8), 230 (M<sup>+</sup> - 3CO, 42); IR (KBr) 1667 cm<sup>-1</sup> (C=O); UV (CH<sub>3</sub>CN) λ<sub>max</sub> 227 nm (log ε = 4.43), 250 (sh, 4.32); (CH<sub>3</sub>OH) λ<sub>max</sub> 201 (4.43), 215 (sh, 4.36), 245 (sh, 4.11), 270 (sh, 4.04). Anal. Calcd for C<sub>18</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.17; H, 2.87; N, 13.11.

(16) Crystal data for triketone 1: C<sub>18</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>, MW = 315.3, monoclinic, P2<sub>1</sub>/c, a = 16.758 (2) Å, b = 3.8141 (4) Å, c = 21.357 (3) Å, β = 91.225 (11)°, Z = 4, D<sub>c</sub> = 1.534 g cm<sup>-3</sup>, R = 0.042 for 1541 observed data with 1° < θ < 25°, Mo Kα.

(17) Geometry and energies were determined by molecular mechanics calculations (MM2 force field).