

2,3:6,7-Bis(2',3'-quinolino)pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane

Alan P. Marchand^{*}, Pendri Annapurna

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068

Judith L. Flippen-Anderson^{*}, Richard Gilardi, and Clifford George

Naval Research Laboratory, Laboratory for the Structure of Matter, Code 6030
Washington, D. C. 20375-5000

Summary: The title compound (**4**) was synthesized by two sequential Friedlaender condensations between pentacyclic bis(ketoester) **2** and *o*-aminobenzaldehyde. The dihedral angle between the two quinoline rings in **4** is 76.4°; the nonbonded N...N interatomic distance in **4** is 4.32 Å.

Thummel and coworkers have utilized sequential Friedlaender condensations between aromatic *ortho*-aminoaldehydes and cyclic 1,2-diketones to synthesize polyaza cavity shaped molecules.^{1,2} More recently, they reported that this same approach, when applied to tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-3,6-dione, afforded a novel, rigid syn-orthocyclophane, **1** (Scheme I).³ As part of a program that is designed to exploit the synthesis and chemistry of novel polycyclic cage hydrocarbon systems,⁴ we have undertaken a study of the reaction of diethyl 3,6-dioxopentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane-2,7-dicarboxylate (**2**)⁵ with *o*-aminobenzaldehyde. Thus, when an intimate mixture of **2**, *o*-aminobenzaldehyde (3 equivalents), and boric anhydride⁶ (2 equivalents) was heated at 150 °C under nitrogen, decarboxylation of **2** occurred with concomitant Friedlaender condensation. When the reaction was carried out for 48 h, a mixture of mono- (**3**)⁷ and diadducts (**4**) was obtained in 40% and 20% yield, respectively. If instead the reaction mixture was heated at 150 °C for 72 h, only diadduct **4**, mp 278-280 °C (dec.), was formed (40% yield). These results are summarized in Scheme II.⁸

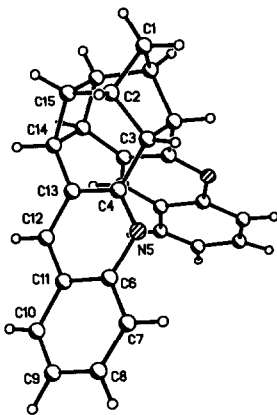
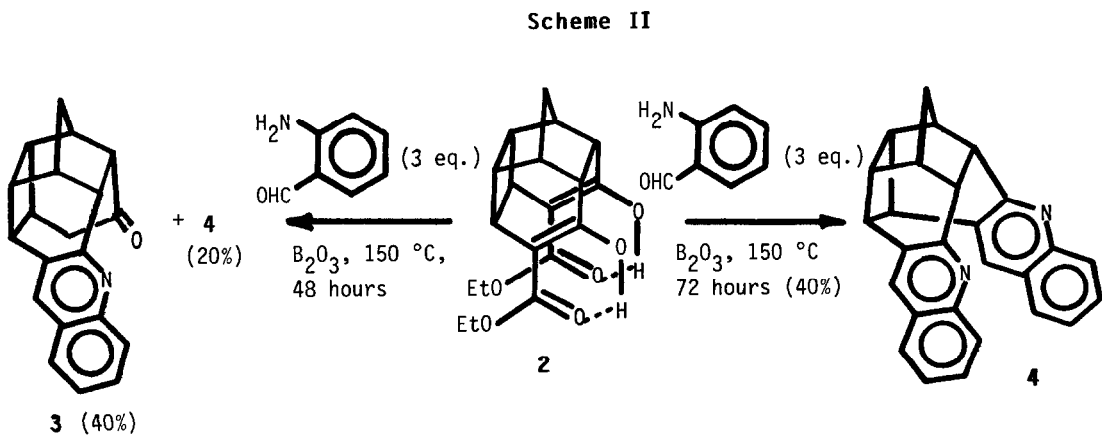
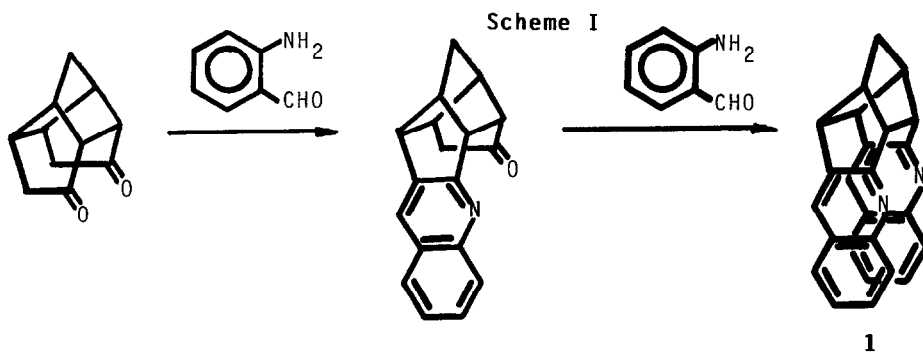


Figure 1. Molecular structure of **4** as determined by X-ray crystallography. Only the crystallographically independent atoms are labeled.



The structure of **4** was elucidated via single crystal X-ray structural analysis.¹⁰ A structure diagram of **4** is shown in Figure 1. The molecule lies on a crystallographic mirror plane which passes through the norbornyl methylene moiety and its bonded hydrogen atoms such that only half of the molecule is structurally independent. The fused ring system is highly strained; [C-C values in the cyclobutane ring range from 1.562(4) to 1.584(4) Å, and the C-C-C angle at the bridging methylene group is only 94.9(3)°]. The dihedral angle between the quinoline rings (i.e., the angle between the extension of the planes formed by the quinoline moieties) is 76.4°. The nonbonded intramolecular N(5)...N(5A) separation is 4.32 Å, and the C(12)...C(12') separation is 4.26 Å. These results indicate that the planes containing the quinoline rings in **4** are not twisted with respect to one another, and, therefore, that the dihedral angle affords a good indication of the opening of the "jaws" of the molecule. In the structurally similar compound **1**³ in which the quinoline moieties are fused to five-membered rings in a tetracycloundecane cage, the dihedral angle between the quinoline planes is 50.5° and the N...N separation is 3.65 Å. The differences between these quantities in **4** vs. **1** are due in part to the presence of the six-membered rings in **4**. Even with the added constraint imposed by the presence of the four-membered ring in **4**, the presence of the two six-membered rings allows for a greater separation between the quinoline rings in **4** as compared with **1**. Also, there is a cocrystallized H₂O molecule in the unit cell of **1** which hydrogen bonds to both N atoms, thereby drawing them closer together in **1** than they are in **4**.

Future efforts will be directed toward exploring the metal complexing ability of **4**¹¹ and also its ability to form host-guest complexes with ions and with neutral molecules. We plan to report the results of these studies shortly.

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References & Footnotes

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7. Recrystallization from ethyl acetate afforded pure **3** as a colorless microcrystalline solid: mp 214-215 °C; IR(KBr) 1685 (s), 1600 (m), 1500 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.6-2.15 (m, 4 H), 2.60 (bs, 1 H), 2.75 (bs, 1 H), 2.80-2.95 (m, 1 H), 3.00-3.15 (m, 1 H), 3.21-3.30 (m, 1 H), 3.40-3.50 (m, 1 H), 4.00-4.20 (m, 2 H), 7.5-8.3 (m, 5 H); ¹³C NMR (CDCl₃) δ 33.3 (d), 34.9 (d), 36.1 (d), 37.8 (d), 38.2 (t), 40.1 (t), 40.85 (d), 40.9 (d), 49.9 (d), 56.1 (d), 126.1 (d), 127.1 (d), 128.0 (s), 128.6 (s), 128.9 (d), 129.0 (d), 135.0 (d), 147.4 (d), 159.5 (d), 212.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 287 (molecular ion, 100); Anal. Calcd for C₂₀H₁₇NO: *M_r* 372.1627. Found (high-resolution mass spectrometry) *M_r* 372.1624.
8. It should be noted that earlier attempts at acid-promoted decarboxylation of **2** (performed in the absence of *o*-aminobenzaldehyde) led exclusively to 3-hydroxyhexacyclo-[6.5.0.0^{3,7}.0^{4,12}.0^{5,10}.0^{9,13}]tridecan-6-one via intramolecular aldol condensation.⁵
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10. Crystal data: for **4**, C₂₇H₂₀N₂, orthorhombic, space group Pbnc (non-standard setting of Pbca), a = 13.981(2), b = 6.793(1), c = 19.258(3) Å, Z = 4 (1/2 molecule per asymmetric unit), V = 1829.1(5) Å³, d_{calc} = 1.35 g·cm⁻³, μ(CuKα) = .57 mm⁻¹. The structure was solved by direct methods. Hydrogen atoms were located in difference maps and refined with isotropic thermal parameters. Final R-factor from full-matrix least-squares refinement using the 1511 observed data [F_o > 3σ(F_o)] was 0.059 (wR = 0.066). Tables of coordinates, bond lengths and bond angles are available from the Crystallographic Data Centre, Cambridge University, University Chemical Laboratory, Cambridge CB2 1EW, England.
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