PREPARATION OF 8,16-IMINO-8*H*,16*H*-DINAPHTHO[2,1-*b*:2,1-*f*]-[1,5]DIOXOCIN

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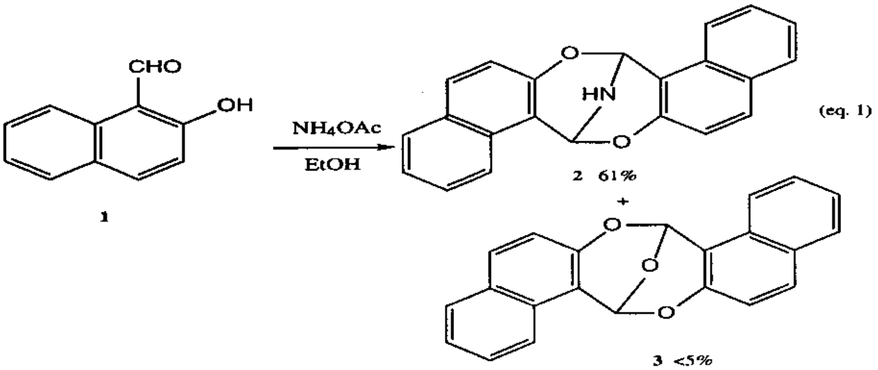
<u>Abstract</u> - A procedure for the synthesis of 8,16-imino-6*H*,14*H*-di-naphtho[2,1-*b*:2,1-*f*][1,5]dioxocin from the reaction of 2-hydroxy-1naphthaldehyde with ammonium acetate is described.

We[1] showed previously that the condensation of malononitrile with 2-hydroxy-1-naphthaldehyde (**1**) in the presence of ammonium acetate gives derivatives of 2*H-benzo*[f]chromenes in generally good yields. To see if this condensation could be extended to arylacetonitriles, we refluxed a solution containing **1**, several arylacetonitriles and ammonium acetate in ethanol for two h. After the usual workup, only 8,16-imino-8*H*,16-H-dinaphtho- [2,1-*b*:2,1-*f*]-[1,5]dioxocin (**2**) was obtained in 53% yield. When we treated **1** and ammonium acetate in the absence of arylacetonitrile, compound (**2**) was again obtained in 61% yield. A small amount of the 8,16-oxa derivative (**3**) was obtained. The ^{1}H nmr, ^{13}C nmr and ir spectra were consistent with the proposed structure of **2**. For example, the ^{1}H nmr spectra of **2** revealed



mutually coupling resonances at 5.1(t, $J = 2.9$ Hz, 1 H) and 6.71 (d, $J = 2.9$ Hz, 2 H), characteristic of a HC-NH-CH group. Additionally, the ^{13}C nmr spectrum exhibited ten resonances in the aromatic region (δ 113-150 ppm) and one at δ 75 ppm, characteristic of the C-8 and C-16 carbon atoms in the eight-membered ring, and the ir spectrum showed an imide absorption band at 3342 cm^{-1}. The structure of **2** was also confirmed by X-ray diffractometry. The identification and location of the atoms in **2** are shown in the ORTEP[2] drawing (see Figure 1) and the bond lengths, bond angles, and torsion angles are listed in Tables 1-3 (see experimental section). As shown, compound (**2**) exists in a folded conformation with a dihedral (folding) angle of 92 °.

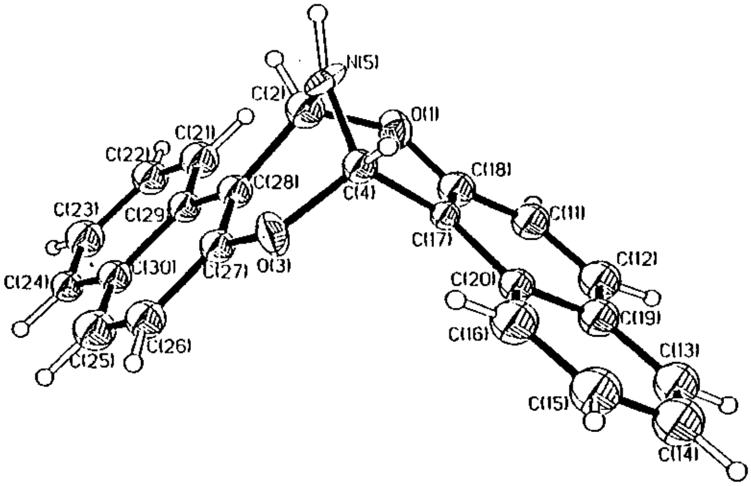


Figure 1 ORTEP Drawing of Compound (**2**)

A possible mechanism for the formation of **2** is shown in Scheme 1. First, **1** reacts with free ammonia to form aldimine (**4**). The aldimine then condenses with another molecule of **1** forming adduct (**5**), which cyclizes forming the amino alcohol (**6**). Inter-mediate (**6**) then undergoes a further intramolecular cyclization yielding product (**2**). Apple[3] and coworkers have shown that 13-alkyl-8,16-imino-8*H*,16*H*-dibenzo[*b,f*][1.5]dioxocins are readily formed by the condensation of salicylaldehyde with its *N*-organylaldimine. Conceivably, intermediate (**6**) could be formed by the ammonolysis of the diol adduct formed by the self condensation of **1**. To test this proposed mechanism the following reactions were carried out.

First, **1** was converted to 2-acetoxynaphthalene (**7**) to see if by tying up the OH group the base-mediated condensation reaction would be encouraged. However, as shown in Eq. 2,

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)
O(1)	425(9)	6551(4)	1714(12)	36(4)
C(2)	-595(14)	6675(6)	2823(19)	38(4)
O(3)	706(9)	6693(4)	6850(13)	38(4)
C(4)	1085(13)	7068(5)	5443(18)	28(4)
N(5)	-168(10)	7200(4)	3938(15)	38(5)
C(11)	2773(12)	6332(5)	1876(19)	37(4)
C(12)	4166(14)	6338(5)	2811(21)	42(4)
C(13)	6095(14)	6549(6)	5712(21)	46(4)
C(14)	6520(16)	6766(6)	7503(21)	54(5)
C(15)	5537(15)	6977(6)	8407(21)	49(4)
C(16)	4129(14)	6978(6)	7528(20)	44(4)
C(17)	2188(13)	6773(5)	4603(17)	20(3)
C(18)	1805(14)	6559(6)	2798(20)	34(4)
C(19)	4657(14)	6538(6)	4730(21)	37(4)
C(20)	3639(14)	6759(5)	5666(18)	27(4)
C(21)	-2218(14)	5593(6)	1385(19)	42(4)
C(22)	-3060(13)	5110(6)	766(19)	40(4)
C(23)	-3326(14)	4697(6)	2075(20)	45(4)
C(24)	-2706(12)	4771(5)	3972(19)	31(4)
C(25)	-1203(13)	5318(6)	6650(22)	45(4)
C(26)	-348(13)	5791(5)	7335(20)	37(4)
C(27)	-141(14)	6220(6)	6062(20)	28(4)
C(28)	-732(13)	6179(6)	4152(19)	30(4)
C(29)	-1579(13)	5686(6)	3372(19)	29(4)
C(30)	-1812(13)	5247(6)	4712(20)	32(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

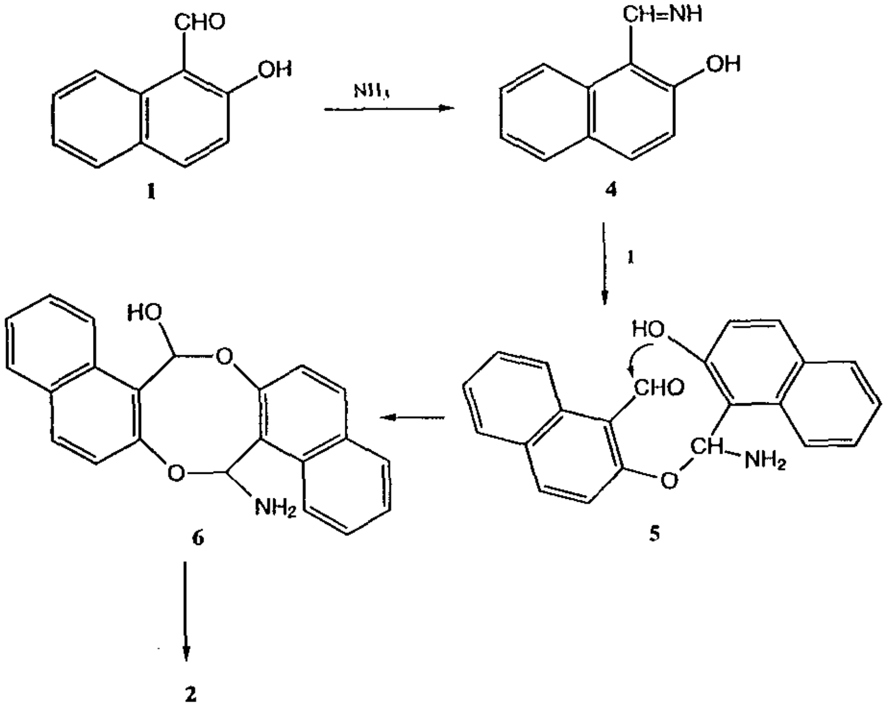
Table 2. Bond lengths (Å)

O(1)-C(2)	1.468 (18)	O(1)-C(18)	1.383 (15)
C(2)-C(28)	1.512 (20)	O(3)-C(4)	1.451 (17)
O(3)-C(27)	1.387 (15)	C(4)-C(17)	1.530 (19)
N(5)-C(2)	1.439 (17)	N(5)-C(4)	1.452 (14)
C(11)-C(12)	1.363 (17)	C(11)-C(18)	1.396 (21)
C(12)-C(19)	1.426 (20)	C(13)-C(14)	1.352 (20)
C(13)-C(19)	1.411 (18)	C(14)-C(15)	1.387 (23)
C(15)-C(16)	1.367 (18)	C(16)-C(20)	1.404 (18)
C(17)-C(18)	1.356 (18)	C(17)-C(20)	1.437 (16)
C(19)-C(20)	1.439 (21)	C(21)-C(22)	1.377 (18)
C(21)-C(29)	1.433 (18)	C(22)-C(23)	1.407 (20)
C(23)-C(24)	1.365 (18)	C(24)-C(30)	1.408 (17)
C(25)-C(26)	1.375 (18)	C(25)-C(30)	1.390 (20)
C(26)-C(27)	1.394 (20)	C(27)-C(28)	1.362 (19)
C(28)-C(29)	1.422 (17)	C(29)-C(30)	1.450 (20)

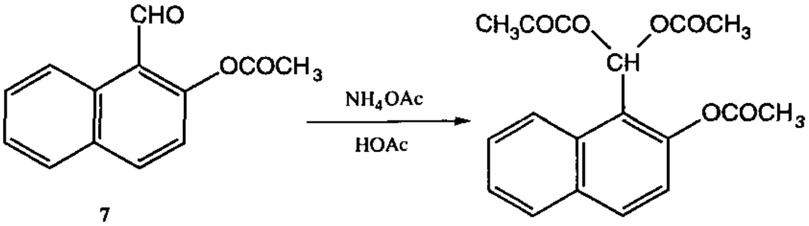
Table 3. Bond angles (°)

C(2)-O(1)-C(18)	113.3(10)	C(4)-O(3)-C(27)	113.5(10)
C(2)-N(5)-C(4)	100.0(10)	O(1)-C(2)-N(5)	109.0(11)
O(1)-C(2)-C(28)	113.2(11)	N(5)-C(2)-C(28)	108.5(11)
O(3)-C(4)-N(5)	109.2(10)	O(3)-C(4)-C(17)	111.2(10)
N(5)-C(4)-C(17)	110.0(10)	C(12)-C(11)-C(18)	118.7(13)
C(11)-C(12)-C(19)	122.2(14)	C(14)-C(13)-C(19)	120.9(15)
C(13)-C(14)-C(15)	120.1(13)	C(14)-C(15)-C(16)	121.7(13)
C(15)-C(16)-C(20)	120.2(14)	C(4)-C(17)-C(18)	119.6(11)
C(4)-C(17)-C(20)	120.2(10)	C(18)-C(17)-C(20)	120.1(13)
O(1)-C(18)-C(11)	114.4(11)	O(1)-C(18)-C(17)	122.8(13)
C(11)-C(18)-C(17)	122.0(12)	C(12)-C(19)-C(13)	122.8(14)
C(12)-C(19)-C(20)	118.2(11)	C(13)-C(19)-C(20)	119.0(13)
C(16)-C(20)-C(17)	123.8(13)	C(16)-C(20)-C(19)	118.1(11)
C(17)-C(20)-C(19)	118.0(11)	C(22)-C(21)-C(29)	121.0(13)
C(21)-C(22)-C(23)	120.7(12)	C(22)-C(23)-C(24)	119.1(12)
C(23)-C(24)-C(30)	123.5(13)	C(26)-C(25)-C(30)	121.4(14)
C(25)-C(26)-C(27)	119.1(13)	O(3)-C(27)-C(26)	116.2(11)
O(3)-C(27)-C(28)	121.8(13)	C(26)-C(27)-C(28)	122.0(12)
C(2)-C(28)-C(27)	120.9(12)	C(2)-C(28)-C(29)	118.1(11)
C(27)-C(28)-C(29)	120.8(13)	C(21)-C(29)-C(28)	125.1(13)
C(21)-C(29)-C(30)	118.1(11)	C(28)-C(29)-C(30)	116.8(12)
C(24)-C(30)-C(25)	122.6(13)	C(24)-C(30)-C(29)	117.5(12)
C(25)-C(30)-C(29)	119.9(12)		

Scheme I



treatment of **7** in the presence of ammonium acetate in acetic acid gave no condensation



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8

(eq. 2)

products, but rather gave 1-bisacetoxymethyl-2-acetoxynaphthalene (**8**).

We subsequently found that **2** could be prepared in 69% yield by treating **1** with refluxing NH_3/MeOH reagent, indicating the importance of ammonia in the condensation. Again, only trace amounts (<5%) of **3** were detected.

Next, we treated naphthalimine (**4**) with **1** in refluxing ethanol a complex mixture was obtained, in which **2** was present, albeit in small amounts (less than 5%). Thus the

$$\begin{array}{cccccc} 1 & + & NH_3 & \xrightarrow{\text{MeOH}} & 2 & 3 \\ & & & & 69\% & >5\% \end{array} \qquad \text{(eq. 4)}$$

intermediacy of **4** may be involved, but the data is here is less convincing on the role of ammonia.

In conclusion, we have presented a novel and quick synthesis of 8,16-imino-8*H*,16*H*-dinaphtho[2,1-*b*:2,1-*f*]dioxocin (**2**) by the base (ammonium acetate or ammonia) condensation of **1**, which to our knowledge is the first parent imino bridged naphthodioxocin to be reported.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Company and were distilled or recrystallized prior to use. Melting points were taken on an electrochemical apparatus and are uncorrected. The ftir spectra ($CHCl_3$) were measured on a Nicolet Magna-IR™ model 550 spectrophotometer, the nmr spectra were determined on a Brucker WPSY-200 MHz spectrophotometer using TMS as internal standard, and the elemental analyses were performed by the Southern Methodist University Analytical Services.

Preparation of 8,16-imino-8*H*,16*H*-dinaphtho[2,1-*b*:2,1-*f*][1,5]dioxocin (2). A. Ammonium Acetate Mediated. A mixture of 1.72 g (10 mmol) of 2-hydroxy-1-naphthaldehyde (**1**) and 0.77 g (10 mmol) of ammonium acetate in 15 ml of ethanol was refluxed for 2 h, then cooled to room temperature. The ethanol was removed (rotary evaporator) and the remaining material was recrystallized to yield 1.1 g (65%) of **2**, colorless crystals, mp , 240-242 °C (methanol); ir (KBr) ν_{max} 3342, 3072, 2987 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 3.12 (br s, 1 H), 6.70 (d, *J* = 2.9 Hz, 2 H), 7.03 (d, *J* = 9.0 Hz, 2 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.58 (t, *J* = 7.5 Hz, 2 H), 7.76 (d, *J* = 9.0 Hz, 2 H), 7. 79 (d, *J* = 8.2 Hz, 2 H), 8.18 (d, *J* = 8.2 Hz, 2 H); ^{13}C nmr (CDCl$_3$) δ 75.4, 113.47, 118.55, 122.47, 127.63, 127.65, 128.72, 131.04, 131.51, 150.76. *Anal.* Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found: C, 80.91; H, 4.70; N, 4.20. In addtion, a small amount (<5%) of 8,16-oxa-8*H*,16*H*-dinaphtho[2,1-*b*:2,1-*f*][1,5]dioxocin (**3**) was obtained as oil; ir (KBr) ν_{max} 3072, 2987 cm^{-1} ^{1}H nmr (CDCl$_3$) δ 6.68 (d, *J* = 2.9 Hz, 2 H), 7.03 (d, *J* = 9.0 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 2 H), 7.79 (d, *J* = 9.0 Hz, 2 H), 7. 79 (d, *J* = 8.2 Hz, 2 H), 8.20 (d, *J* = 8.2 Hz, 2 H). *Anal.* Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.91; H, 4.50.

B. Ammonia/Methanol Mediated. A mixture of 1.72 g (10 mmol) of 2-hydroxy-1-naphthaldehyde (**1**) and 0.17 g (10 mmol) of ammonia in 15 ml of ethanol was refluxed for 2 h, then cooled to room temperature. After the workup described in **A**. above, 1.18 g (69%) of **2** was obtained.

Preparation of 1-Bisacetoxymethyl-2-acetoxynaphthalene (8). A mixture containing 2.14 g (10 mmol) of 2-acetoxy-1-naphthaldehyde (**7**) and 0.77 g (10 mmol) of ammonium acetate in 25 ml of glacial acetic acid was refluxed for 2 h, then cooled to room temperature. The mixture was added to an ice/water slurry and the resulting solid was filtered, dried and recrystallized from ethanol to yield 2.31 g of **8** as colorless crystals, mp 135 °C; ^{1}H nmr (CDCl$_3$) δ 2.09 (s, 6 H), 2.45 (s, 3 H), 7.22 (d, *J* = 8.8 Hz, 1 H), 7.53 (m, 3 H), 7.86 (t, *J* = 7.0 Hz, 1 H), 8.50 (d, *J* =8.8 Hz, 1 H), 8.51 (s, 1 H); ^{13}C nmr (CDCl$_3$) δ 20.78, 20.95, 22.70, 85.67, 121.78, 125.83, 126.99, 128.61, 129.04, 131.64, 132.24, 147.18, 168.52, 169.55. *Anal.* Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.83; H, 5.12.

X-Ray Spectral Data and Data Collection and Processing. A colorless , monoclinic shaped crystal (0.5 X 0.4 X 0.3 mm) of **2** was mounted on a Nicolet R3m/V diffractometer and the following data was obtained using graphite-monochromated Mo *Kα* radiation: monoclinic $P2_1/c$, a = 9.838(5), b = 22.683(5), c = 7.263(2) Å, Β = 104.97(3)°, V = 1566(1) Å^3, Z = 4, D_{calcd} = 1.38 Mg/m^3. Of the 1607 data collected, 569 observed reflections [2Θ 3.50-40.00^{O}, F-$_{O}$ ≥ 4σ–(F $_{O}$)] were used in the solution and refinement of the structure. Oxygen atoms were anisotropically refined. Hydrogen atoms were place at geometrically idealized positions. The final values are: R = 0.069. wR = 0.067, GOF = 1.14, $\delta\rho_{(max,min)}$ = 0.28, -0.33 e Å^{-3}. SHELXTL-Plus 88[17] on microvax II was used. Final positional parameters and thermal parameters and their estimated standard deviations are available upon request.

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