

Overcrowded Molecules. V  
3,10-Dimethyl-1,12-bis(2-pyridyl)benzo[*c*]phenanthrene-2,11-diol

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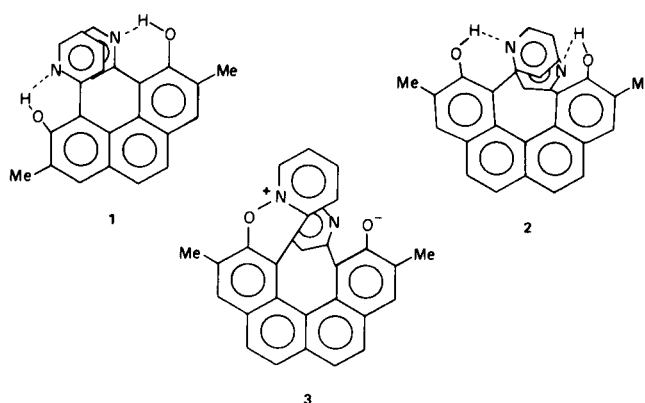
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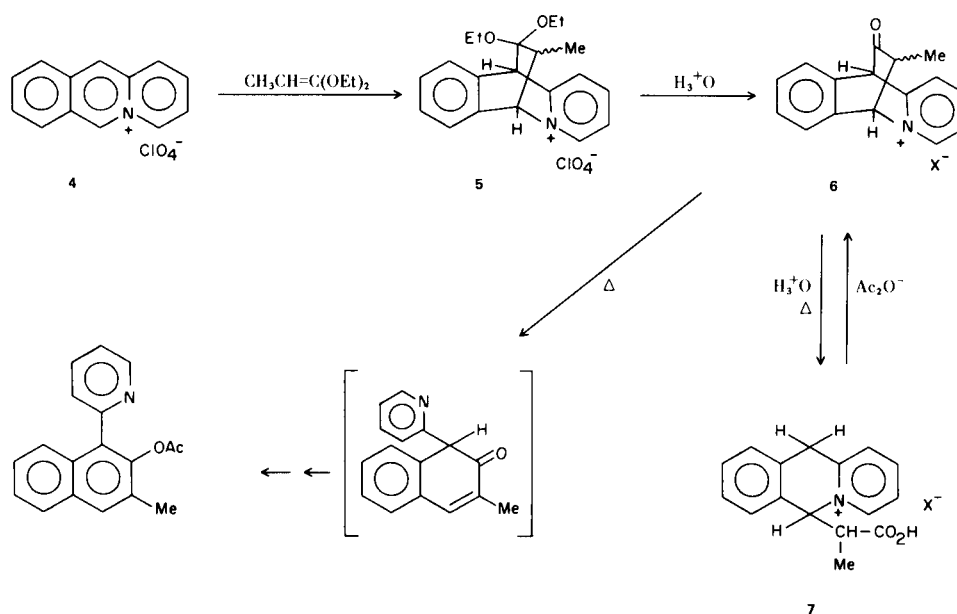
The bis ketene acetal adduct of 4a,10a-diazoniaanthra[1,2-*a*]anthracene diperchlorate (**10**) was used to prepare the highly overcrowded benzo[*c*]phenanthrene **2** by a known procedure. Its oxidation with cupric chloride provided the isoxazolium zwitterion, **3**, via an intramolecular cyclization.

We have recently described a convenient synthesis of certain 2-pyridyl-substituted 2-naphthols and phenanthrols, emphasizing its use as a method of preparing several classes of highly overcrowded molecules (**1**). Among these is the highly strained, chiral, 2,7-dimethyl-4,5-bis(2-pyridyl)phenanthrene-3,6-diol (**1**) (**1b**). The present communication deals with an extension of this synthesis to the preparation of a closely related structure, 3,10-dimethyl-1,12-bis(2-pyridyl)benzo[*c*]phenanthrene-2,11-diol (**2**), as well as its novel oxidation product, betaine **3**.

For descriptive simplification, the steps involved in the synthesis are illustrated in Scheme I for the preparation of the acetyl derivative of 3-methyl-1-(2-pyridyl)-2-naphthol (**1b**).



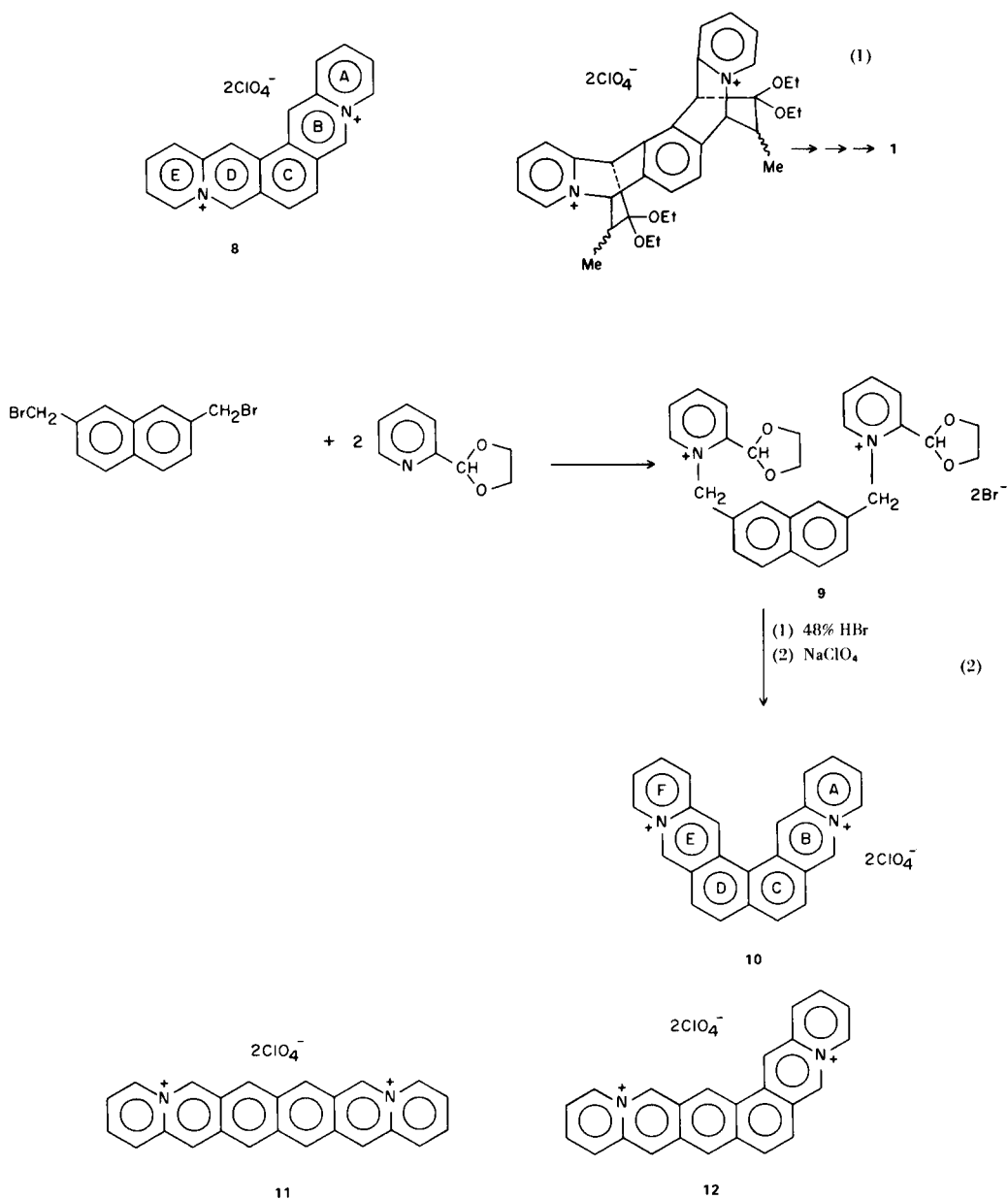
SCHEME I



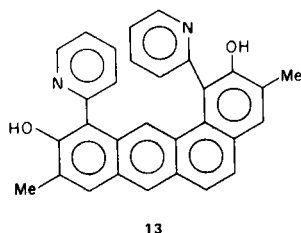
1,1-Diethoxypropene readily cycloadds regioselectively (2) across the B-ring (9,10-positions) of 4a-azoniaanthracene (4) to give the 1:1 adduct, 5, in excellent yield (3). Heating 5 in 6 *N* hydrochloric acid results in the expected hydrolysis to bicyclic ketone 6, but, under these reaction conditions, this is followed by its hydrolytic cleavage to 7 (4). Acid 7 usually is not isolated, but is converted directly to the acetyl derivative of the desired 2-naphthol by heating it in acetic anhydride in the presence of sodium acetate. The acetic anhydride treatment promotes the sequential intramolecular acylation back to ketone 6, elimination, enolization, and finally acetylation reactions

as shown. Applying this procedure starting with 4a,8a-diazoniapentaphene diperchlorate (8) provides the aforementioned phenanthrenediol 1 as its diacetate, wherein analogous ring transformations are operative on both B and D ring areas of the molecule as shown in eq. 1.

Considering the desired benzo[*c*]phenanthrene 2, the necessary precursor to it was the previously unknown 4a,10a-diazoniaanthra[1,2-*a*]anthracene diperchlorate (10). The synthesis of 10 (eq. 2) proved to be straightforward, patterned after the procedure used by Bradsher and Sherer in their preparation of isomeric 14a,16a-diazoniaanthra[1,2-*a*]anthracene (5). Although un-



likely, the acid-catalyzed biscyclodehydration of the intermediary bis pyridinium salt **9** could conceivably lead to two isomers other than the desired **10**, *i.e.*, **11** and **12**. Structure **11** was ruled out based on absorption spectral considerations, *i.e.*, our isolated product has no visible absorption maximum greater than 460 nm, and **12** was discounted for a similar reason, as well as because, when subjected to the synthetic sequence of Scheme I, it would lead to the unsymmetrical benzoanthracene **13**, a compound whose expected uv and nmr spectra would be incompatible with those of the product actually obtained.



The conversion of **10** to **2** was uncomplicated. Treatment of a suspension of **10** in acetonitrile with excess 1,1-diethoxypropene at reflux temperature for 2 hours produced a light yellow solution completely free of starting **10**. The absence of absorption maxima > 330 nm indicated that the desired biscyclodehydration across the B and E rings had occurred (See eq. 3). No attempt was made to crystallize or purify the syrup obtained from this reaction. It was instead treated successively with refluxing 6 *N* hydrochloric acid and acetic anhydride-sodium acetate in the standard manner, to yield a crystalline diacetate. Deacetylation with base and purification by Florisil chromatography afforded the desired product, **2**, as bright yellow crystals in 53% over-all yield from **10**. Its structural assignment was supported by elemental analysis and by its spectral properties (nmr, mass, uv), selected results of which are detailed below.

Benzoanthracene **2** has a two-fold axis of symmetry, thereby giving a relatively simple nmr spectrum, one in which all of the individual absorptions are readily assignable when interpreted in terms of the suggested structure (See Experimental).

The electronic spectrum of **2** is depicted in Figure 1. Based on analogy with examples taken from previous related studies, molecular overcrowding of the type experienced by **2** would be expected to produce batho-

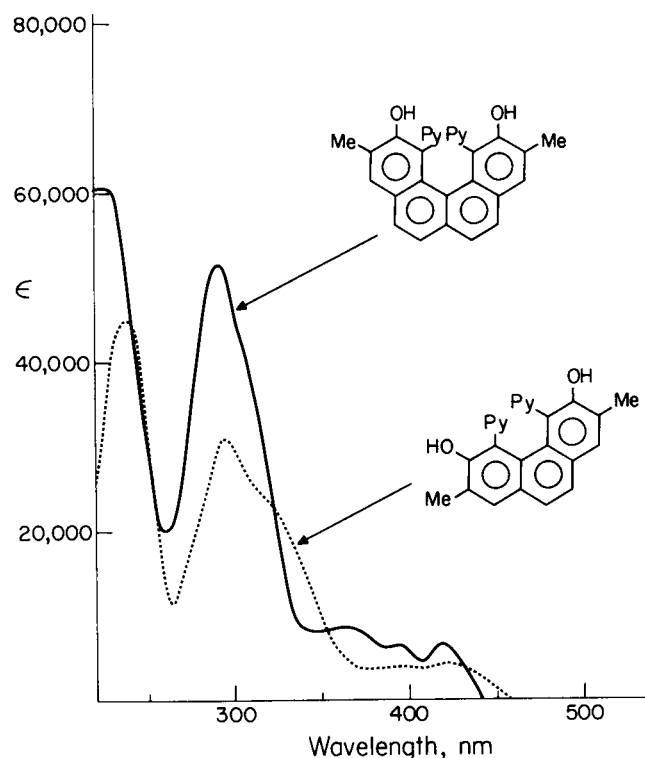
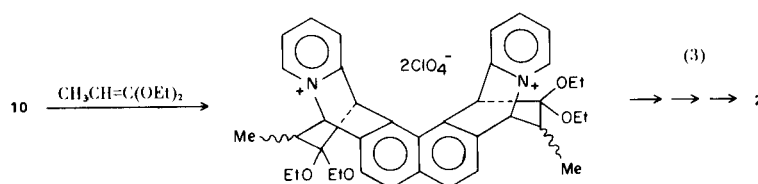
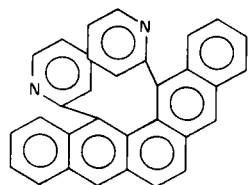


Figure 1. Electronic spectra of **1** and **2**.

chromic and hyperchromic shifts in the long-wavelength absorptions when compared to the spectrum of the parent benzo[*c*]phenanthrene-2,11-diol (**1**). To what extent such shifts occur in **2** has not been determined since we lack suitable model compounds of the benzo[*c*]phenanthrene type that would be instructive in this regard. The electronic spectrum of **2** does bear the expected resemblance to that of phenanthrenediol **1**.

The relative abundance of the prominent ions found in the mass spectrum of **2** are compared in Table I with like data taken from spectra of phenanthrene **1** (**1b**), and pentaphene **14** (**1c**), another pyridyl overcrowded compound. The dominant and unusual M-pyridyl frag-





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mentation found with both **1** and **14** is believed to be promoted by a relief of steric strain. The fact that it occurs to a lesser extent in **2** compared to **1** and **14** suggests that **2** is less strained and this would be anticipated since **2** has a larger skeletal framework between the interfering pyridyl substituents over which to distribute the distortions created by the pyridyl overcrowding.

TABLE I  
Important Ions in the Mass Spectra of **2**, **1**, and **14**

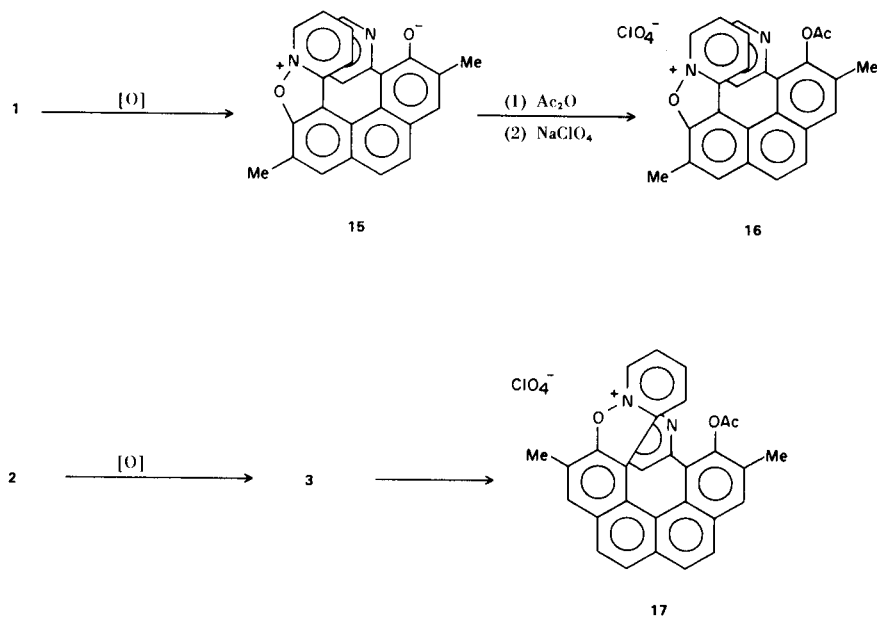
Fragment	<b>2</b>	Rel. intensity, % <b>1</b>	<b>14</b>
M	100.0	21.0	14.0
M-1	6.4	0.6	0.3
M-Pyridyl	47.0	100.0	100.0

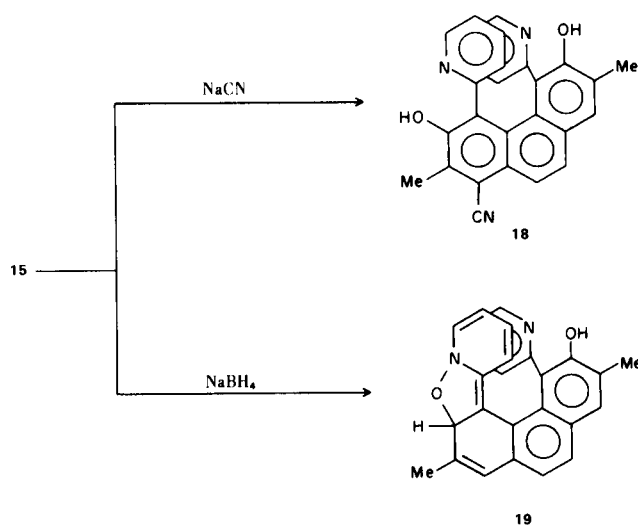
Of our studies of the chemistry of **1**, the most interesting area examined relates to its behavior upon oxidation, wherein it commonly undergoes a facile intramolecular cyclization *via* a two-electron oxidation process to give

the red, highly strained betaine **15** (**6**). Benzophenanthrene **2** is somewhat less susceptible to oxidation than **1**. Nonetheless, its oxidation using cupric chloride in refluxing ethanol does indeed occur, providing a deep purple, crystalline product believed to be betaine **3**.

Its structure is inferred from correct elemental analysis and molecular-weight determination (by mass spectrometry), method of synthesis based on analogy with the synthesis of **15** from **1**, and from the fact that acetylation followed by anion exchange yields a monoacetyl perchlorate (**17**) which would correspond to the conversion of **15** to **16** by similar treatment. Its nmr spectrum, while compatible with the assigned structure, is quite complex and thus not particularly definitive.

A few exploratory experiments dealing with the chemistry of **3** have not been encouraging. The previously described reactions of **15** with several nucleophiles were characteristically free of side reactions, leading in each case to a single novel product in high yield. For example, **15** with sodium cyanide in DMSO for 5 minutes gave the 1-cyanophenanthrene **18** in essentially quantitative yield, while its treatment with methanolic sodium borohydride provided the addition product **19**, immediately and quantitatively. Attempted analogous reaction with **3** proved rather complex, affording in each case mixtures having at least seven components (tlc). Similar unrewarding results using other nucleophiles under a variety of reaction conditions persuaded us to abandon this area of study.





## EXPERIMENTAL (7)

## 4a,10a-Diazoniaanthra[1,2-a]anthracene Diperchlorate (10).

A mixture of 2,7-bis(bromomethyl)naphthalene (8) (15.7 g., 0.05 mole) and 2-(1,3-dioxalan-2-yl)pyridine (9) (25.0 g., 0.165 mole) in 100 ml. of acetonitrile was refluxed for 2 hours, concentrated to a viscous syrup, and the syrup was dissolved in 250 ml. of 48% hydrobromic acid and heated at reflux temperature for 3 hours. The cooled solution was diluted with 150 ml. of water and treated with sodium perchlorate giving immediately a crystalline precipitate. The solid was collected, dried, and recrystallized as fine yellow needles from DMSO-methanol (Darco) (24.0 g., 90%) m.p. > 300°; uv max (acetonitrile) 237 nm (log  $\epsilon$  4.89), 275 (4.27), 310 (4.65), 344 (4.60), 355 (4.64), 383 (3.92), 404 (4.08), 425 (4.14), 449 (3.93).

*Anal.* Calcd. for  $C_{24}H_{16}Cl_2N_2O_8 \cdot 0.5H_2O$ : C, 53.4; H, 3.3; Cl, 13.2; N, 5.2. Found: C, 53.5; H, 3.5; Cl, 13.3; N, 5.0.

## 3,10-Dimethyl-1,12-bis(2-pyridyl)benzo[c]phenanthrene-2,11-diol (2).

A suspension of 10 (5.00 g., 9.3 mmoles) in 12.5 ml. of acetonitrile was treated with 1,1-diethoxypropene (13.0 g., 0.1 mole) and the mixture was heated at reflux for 2 hours. Analysis of the resulting solution by ultraviolet spectroscopy showed the reaction to be complete, as indicated by the lack of absorbance at wavelengths longer than 330 nm. The solution was concentrated to a syrup and the syrup heated overnight on a steam bath in the presence of 120 ml. of 6 N hydrochloric acid. This solution was concentrated to a syrup and then costripped three times with benzene to remove residual water. A mixture of this syrup, acetic anhydride (250 ml.), and sodium acetate (2.5 g.) was refluxed for 1 hour. The residue obtained upon concentrating the reaction mixture was triturated in 250 ml. of 5% sodium bicarbonate solution, giving 2.91 g. of the diacetyl derivative of 2 as tan crystals. This product was deacetylated by stirring for 30 minutes in the presence of 0.70 g. of sodium hydroxide in 20 ml. of methanol and 5 ml. of water. The solution was acidified with 5% hydrochloric acid, basified with 5% sodium bicarbonate, and the resulting precipitate was extracted into methylene chloride. This was chromatographed on Florisil, using methylene chloride as eluent, to give 2.20 g. (53%) of 2 as yellow crystals after one recrystallization from methylcyclo-

hexane: m.p. 233-235°; mass spectrum (70 eV)  $m/e$  442 (100%)  $M^+$ , 440 (6) M-1, 364 (47) M-pyridyl, 322 (15), 295 (10), 221 (10); nmr (deuteriochloroform):  $\delta$  13.93 (broad S, 2, -OH), 8.46 (A part of AMRX,  $J_{5'6'} \cong 4.8$ ,  $J_{4'6'} \cong 2.1$ ,  $J_{3'6'} \cong 1.0$ , 1,  $H^{6'}$ ), 7.61 (S, 4,  $H^{5,6,7,8}$ ), 7.46 (Q, 2,  $H^{4,9}$ ), 6.77 (MR part of AMRX,  $J_{4'5'} = 5.3$ , 2,  $H^{4'5'}$ ), 6.07 (X part of AMRX,  $J_{3'4'} \cong 7.7$ ,  $J_{3'5'} \cong 1.4$ , 1,  $H^{3'}$ ), (D,  $J_{CH_3,H} = 0.9$ , 3,  $CH_3$ ).

*Anal.* Calcd. for  $C_{30}H_{22}N_2O_2$ : C, 81.4; H, 5.0; N, 6.3. Found: C, 81.1; H, 5.1; N, 6.2.

## Betaine 3.

A solution of 500 mg. of anhydrous cupric chloride in 5 ml. of ethanol was added in one portion to 500 mg. of 2 in 20 ml. of refluxing ethanol. The initially dark brown solution lightened to a deep yellow color within 5 minutes. The reaction mixture was concentrated free of solvent on a rotary evaporator and the residue dissolved in 200 ml. of methylene chloride and washed with 100 ml. of 5% sodium bicarbonate. The deep purple methylene chloride extract was dried over sodium sulfate and chromatographed on neutral alumina (Woelm-grade III) using methylene chloride-ethyl acetate-methanol (2:2:1 v/v) as eluent, giving 310 mg. (64%) of 3 as fine purple crystals after one recrystallization from methylene chloride-petroleum ether, m.p. 226-227°; mol. wt. 440 (mass spectrum); uv max (acetonitrile) 253 nm (log  $\epsilon$  4.63), 342 (4.31), 372 sh (4.18), 584 (3.72); nmr (DMSO- $d_6$ )  $\delta$  2.16 (D, 3, Me), 2.90 (D, 3, Me), 6.60-8.40 (M, 13), 8.90 (D of M, 1).

*Anal.* Calcd. for  $C_{30}H_{20}N_2O_2$ : C, 81.8; H, 4.6. Found: C, 81.6; H, 4.7.

Acetyl derivative 17, prepared by the procedure used for the synthesis of 16 (6), had m.p. 275-278° with dec. (acetonitrile-ethyl ether); uv max (acetonitrile) 250 nm (log  $\epsilon$  4.64), 255 (4.65), 319 (4.11), 395 (3.75); ir 1750  $cm^{-1}$  (C=O).

*Anal.* Calcd. for  $C_{32}H_{23}ClN_2O_7 \cdot 2H_2O$ : C, 61.9; H, 4.4; Cl, 5.7; N, 4.5. Found: C, 61.9; H, 4.6; Cl, 5.7; N, 4.8.

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