Reaction of N^1, N^2-Diarylamidines with Chloranil and 2,3-Dichloro-1,4-naphthoquinone

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Nucleophilic attack by N^2 of N^1,N^2-diarylformamides **1a-c** on C-2 of chloranil (**2**) and subsequently by N^1 on C-1 of **2** initiates the formation of benzimidazolinones **8a-c**. In contrast, when **1b-e** is reacted with 2,3-dichloro-1,4-naphthoquinone (**9**), both chlorine atoms are successively substituted by the two nitrogen atoms and 2-(arylamino)-3-(*N*-formylarylamino)-1,4-naphthoquinones **13b-e** result, which (probably *via* their cyclic tautomers **12b-e**) may be cyclodehydrogenated to form N^1,N^3-diarylnaphtho[2,3-*d*]imidazoline-2,4,9-triones (as **14b,c**). On the other hand, N^1,N^2diarylacetamidines **15a-d** attack **2** and **9** at C-2 with N^2 but subsequently exert nucleophilic character at the acetamidine α-carbon attacking C-1 of **2** and **9**, respectively, thus forming 1-aryl-2-(arylimino)-3a-hydroxy-2,3,3a,6-tetrahydro-1*H*-indol-6-ones **18a-d** and 3-aryl-2-(arylimino)-9b-hydroxy-2,3,5,9b-tetrahydro-1*H*-benz[*e*]indol-5-ones **19b,c**, respectively. The latter may be thermally dehydrated to the fully conjugated 2,5-dihydro-3*H*-benz[*e*]indol-5-ones **20b,c**. Unambiguous structural assignments for **18b** and **20c** are made on the basis of X-ray crystal structure analyses.

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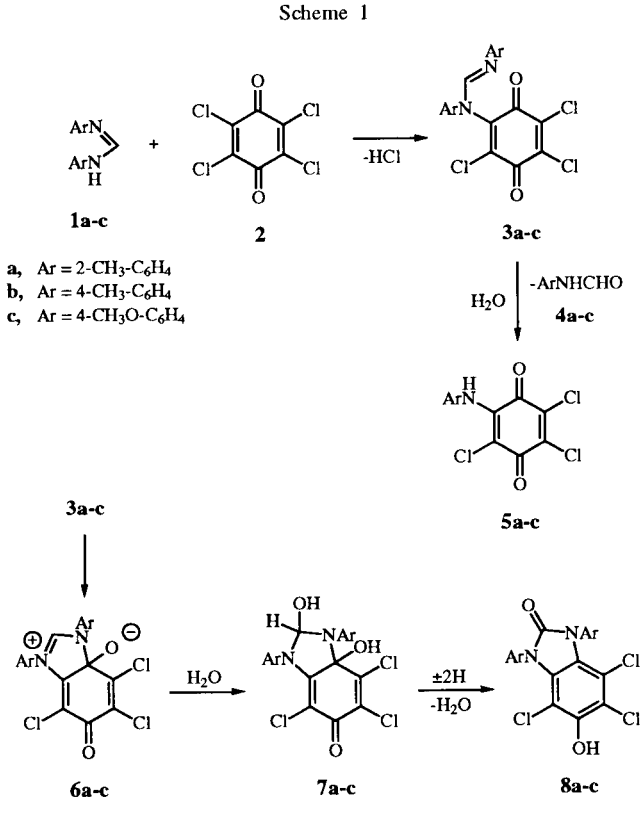
2,3,5,6-Tetrachlorobenzoquinone ("chloroanil", **2**) and 2,3-dichloro-1,4-naphthoquinone (**9**) undergo substitution of one or two chlorine atoms by primary amines [1-3], amino acids [4], and aziridines [5,6]. In the reactions of **2** and **9** with pyrazoles, imidazoles and triazoles [7] all chlorine atoms present may be replaced by the heterocyclic residues. From the reaction of **2** with *N*-aryl-*N*-(4-dimethylaminobenzylidene) amines (which are amidine phenylogues), 2-(arylamino)-3,5,6-trichloro-1,4-benzoquinone and its 2,5-bis(arylamino) analogue are ultimately isolated [8], probably due to the primary substitution products' resistance to hydrolysis. In this paper we present the results of interaction of **2** and **9**, respectively, with *N*,*N'*-diarylformamidines **1a-e** and *N*,*N'*-diarylacetamidines **15a-d**.

Addition of ethyl acetate solutions of **2** to solutions of formamidines **1a-c** (1:2) in the same solvent formed, after standing for 48 hours at room temperature, 5-hydroxy-4,6,7-trichloro-1,3-diarylimidazol-2-ones **8a-c** as major (29-60%) and 2-(arylamino)-3,5,6-trichloro-*p*-benzoquinones **5a-c** as minor products (5-12%, yields based on the amount of **2** used), together with the corresponding formamidine hydrochlorides (20-39% based on amidine used).

The structural assignment of **8a-c** is based on the following data: In their ^{13}C nmr spectra, the characteristic absorption signal of the two carbon atoms of chloranil at δ = 169.9 ppm [9] is replaced by signals at δ 152.1-152.8 ppm, which are characteristic for the 2-imidazolone carbonyl C-atom [9]. In addition, the ir spectra (in potassium bromide) showed two sharp bands at ν = 3350-3380 and 1710-1725 cm^{-1} for the hydroxyl and carbonyl groups, respectively. For more details, see the Experimental.

Formation of these products may be rationalized as follows (see Scheme 1): Replacement of one Cl-atom in **2** by

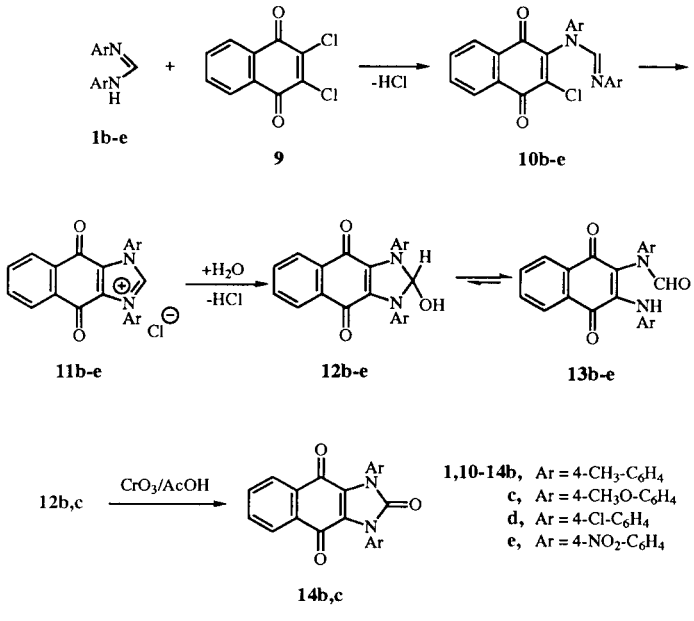
Scheme 1



1a-c yields **3a-c**, a minor fraction of which undergoes hydrolysis with liberation of formanilides **4a-c** to form the trichloroanilinoquinones **5a-c** (5-12%). The major fraction of **3a-c**, however, is transformed into **8a-c** probably *via* **6a-c** and **7a-c**, which constitutes a hydration/dehydration sequence involving also an oxidation at C-2 accompanied by a reduction at C-6.

On the other hand, 2-(arylamino)3-(*N*-formylarylamino)-1,4-naphthoquinones **13b-e** were obtained in 21-63% yield from the reaction of the formamidines **1b-e** with the 2,3-dichloronaphthoquinone (**9**) (Scheme 2). Probably *via* their cyclic tautomers **12b,c** compounds **13b,c** underwent oxidative cyclization in the presence of a chromium trioxide/acetic acid mixture to yield the naphthoimidazolinones **14b,c**.

Scheme 2



To avoid low efficiency in the use of amidines due to their reaction with the liberated hydrogen chloride, triethylamine was advantageously added to the reaction mixture.

The naphthoquinones **13b-e** exhibited two ir absorptions at 3300 (secondary amine), and 1680 cm^{-1} (formamide carbonyl), respectively. The ^{13}C nmr spectra of **13b,d** show absorption signals around 162 ppm for the formyl carbon atoms as well as two signals around 177.5 and 182 ppm for two quinonoid carbonyl C-atoms. Upon dehydrogenation of **13b,c** to **14b,c**, the formamide C=O absorption is replaced by a new ir band at 1720 cm-1, and the ^{13}C nmr spectrum exhibits two carbonyl C-atom resonances at 152 and 174 ppm, respectively. The expected molecular ion peaks in the ms and the satisfactory elemental analyses also confirm the imidazolinone stnuctures of **14b,c**.

The formation of the "open" products **13b,c** may be rationalized through the successive substitution of both chlorine atoms *via* **10** and **11**, hydration to **12** and ring $\rightleftarrows$ chain tautomerization (Scheme 2).

With two equivalents of N^1,N^2-diarylacetamidines **15a-d**, **2** reacts in ethyl acetate at room temperature to afford tetrahydroindolones **18a-d** as major (12-80%) and 2-arylamino-3,5,6-trichloro-1,4-benzoquinones **5a-c** as minor products (5-6%, yields based on **2** used), in addition to the corresponding diarylacetamidine hydrochlorides (16-40%, based on the amount of amidines used).

The ir spectra of **18a-d** show characterisitc absorption for the hydroxy groups between 3360 and 3400 cm^{-1} and between 1690-1705 cm^{-1} for the C=O groups. The ^1H nmr spectra showed AB patterns with δ_A = 2.56-2.70 and δ_B = 3.41-3.60 ppm with coupling constants between 15.17 and 15.10 Hz, which indicates that a methylene group is present adjacent to a chiral carbon atom. Moreover, the ^{13}C nmr DEPT spectra exhibited a negative signal between 37.3 and 38.6 ppm for the methylene group, and the ^1H decoupled ^{13}C nmr reveals a signal between 74.9 and 75.1 ppm for an aliphatic quaternary carbon atom bearing a hydroxyl group [9]. The X-ray crystal structure analysis of **18b** clearly demonstrates the tetrahedral arrangement around C-3a and the folding of the cyclohexadienone ring (Figure 1).

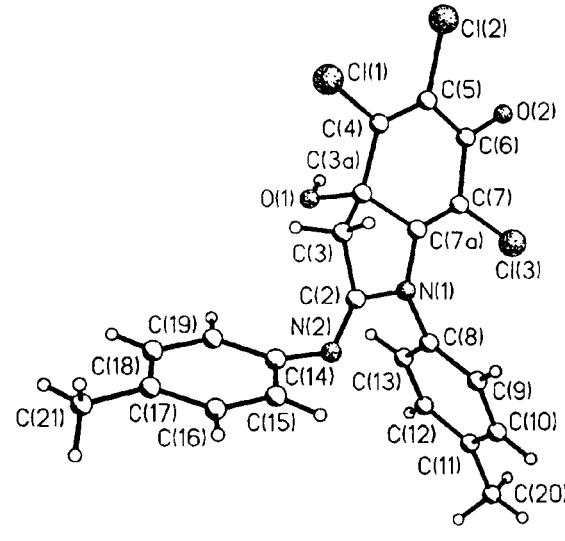
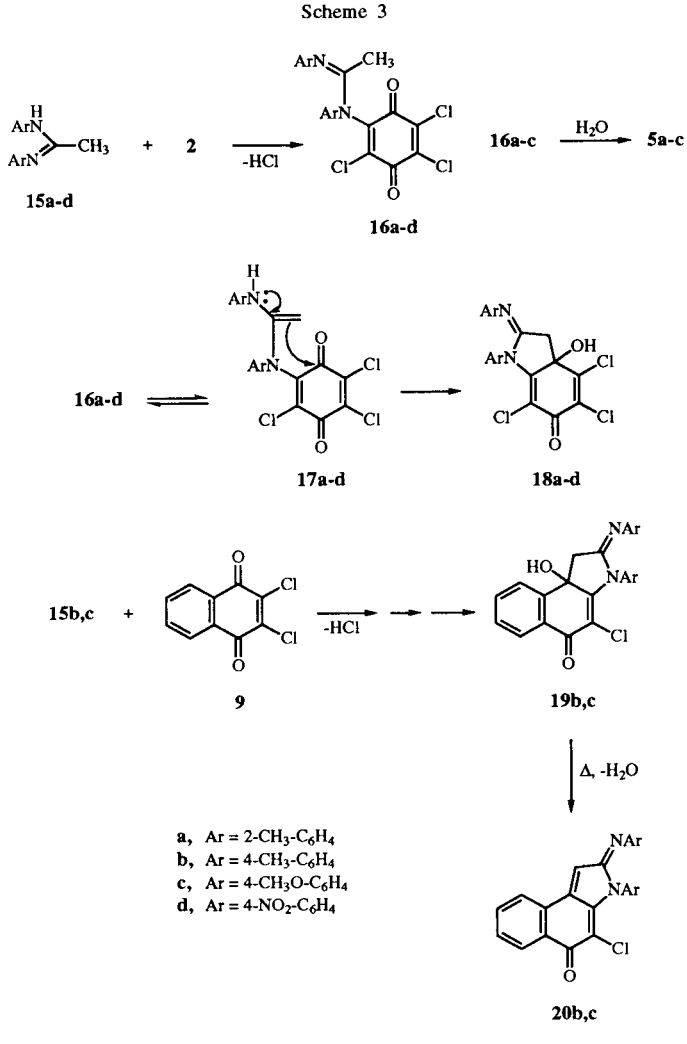


Figure 1. Molecular structure of **18b** in the crystal (the crystallographic numbering does not reflect systematic numbering).

Initially, the reaction of the acetamidines **15a-d** with chloranil (**2**) is clearly analogous to the reaction of the latter with the formamidines, and thus the same

trichloroaminoquinones, namely **5a-c**, are obtained from the primary substitution products, the structures of which are probably **16a-d**, by hydrolysis. On the other hand, **16a-d** may be in equilibrium with the enamines **17a-d**, and the latter may well cyclize to **18a-d** (Scheme 3).

Scheme 3



A completely analogous sequence of steps is plausible for the formation of **19b,c** from **15b,c** and **9**. In refluxing ethyl acetate solution **19b,c** underwent dehydration to give the benzoindolone derivatives **20b,c**.

The structure assignment for **20b,c** is based upon the close similarity of their ^{13}C nmr spectra and an X-ray crystal structure analysis of **20c** (Figure 2), which demonstrates the coplanarity of the three anellated rings and the considerable torsion around the N1-(*p*-anisyl) bond due to steric hindrance between the anisyl group and the chlorine atom at C-4.

As might have been expected, *N,N'*-di(4-nitrophenyl)-formamidine (**1e**) did not react with **2** under the conditions used in this study. *N,N'*-Di(4-nitrophenyl)acetamidine (**15d**) reacted with **2** only after three hours at reflux temperature giving only a 12% yield of the indolinone **18d** compared to a 59-80% yield of **18a-c** obtained in the reactions of **2** with the more electron rich acetamidines **15a-c**.

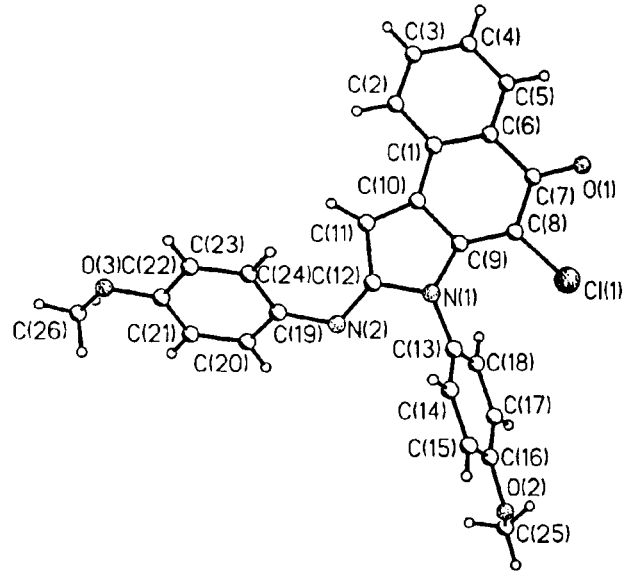


Figure 2. Molecular structure of **20c** in the crystal (the crystallographic numbering does not reflect the systematic numbering); C10-C11: 1.343(3) Å, C11-C12: 1.468(3) Å.

Conclusion.

The results show that the amidines used in this study resemble amines in their reactions with chlorinated quinones, but due to their ambident nature allow for the synthesis of benzimidazolinones and indolinones by their reactions with the subject quinones.

Acetamidines such as **15a-d** to some extent may also be considered as being analogous to enamines. Since the latter are reacted with 1,4-benzoquinone [10] or dichlorinated 1,4-benzoquinones [11,12] in the well known Nenitzescu's indole synthesis [10] to give 5-hydroxylated indoles, it is noteworthy that the cyclization reported in this study leads to oxindole derivatives **18a-d**, **19b,c** and **20b,c** [13] bearing an oxygen function on C-6 (referring to the indole numbering). Thus the Nenitzescu synthesis is nicely supplemented by this cyclization while it is not of importance that in the examples quoted [11,12] to document the former all chlorine atoms have been retained in the product.

EXPERIMENTAL

The uncorrected melting points were determined on a Kofler micro hotstage apparatus. Elemental analyses were measured on

a Carlo Erba 1106 CHN-analyzer while the ir (potassium bromide) were obtained on a Perkin Elmer 283 spectrometer. The 300 MHz ^{1}H and 75 MHz ^{13}C nmr were observed on a Bruker WM 300 with TMS as the internal standard, m = multiplet. The mass spectra (70 eV, electron impact mode) were recorded on a MAT 311 A in connection with an AMD DP-10 data processing system. Preparative layer chromatography (plc) used air dried 1.0 mm thick layers of slurry applied silica gel Merck PF_{254} on 48 cm wide and 20 cm high glass plates using the solvents listed. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light and eluted with acetone or ethyl acetate.

Starting Materials.

2,3,5,6-Tetrachloro-*p*-benzoquinone (chloranil, **2**), and 2,3-dichloro-1,4-naphthoquinone (**9**) (Aldrich) were used as received. *N,N'*-Diarylformamidines **1a-e** [14] and *N,N'*-diarylacetamidines **15a-d** [15] were prepared according to literature procedures.

Reaction of **2** with Amidines **1a-c** and **15a-d**.

A solution of **2** (0.5 mmole) in 20 ml of dry ethyl acetate is added dropwise to a solution of the amidine (1.0 mmole) in 10 ml of dry ethyl acetate at room temperature. The reaction mixture becomes deeply blue or purple and later turns into a brown or green color. It was left standing for 48 hours, filtered, and the precipitate was washed several times with cold ethyl acetate and identified as the corresponding amidine hydrochloride. The filtrate was concentrated *in vacuo* and the residue separated by plc using toluene/ethyl acetate (10:1) into three zones. The fastest zone contained unreacted **2**, the second compounds **5a-c**, and the third compounds **8a-d**, respectively.

3,5,6-Trichloro-2-(2-methylphenylamino)-1,4-benzoquinone (**5a**) [16].

This compound was obtained as yellow crystals (cyclohexane), mp 177°; ir: ν 3270 (NH), 1680 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.56 (s, 1H, N*H*), 2.26 (s, 3H, CH_3), 7.0-7.24 (m, 4H, aryl); ms: m/z 317 (M^+), 315, 282, 280, 252, 217, 188, 77, 65.

Anal. Calcd. for $C_{13}H_8Cl_3NO_2$: C, 49.30; H, 2.55; N, 4.42. Found: C, 49.18; H, 2.48; N, 4.19.

3,5,6-Trichloro-2-(4-methylphenylamino)-1,4-benzoquinone (**5b**) [16].

This compound was obtained as yellow crystals (cyclohexane), mp 235°; ir: ν 3200 (NH), 1670 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.20 (s, 1H, NH), 2.45 (s, 3H, CH_3), 7.10-7.35 (m, 4H, aryl); ms: m/z 317 (M^+), 315, 300, 282, 280, 252, 91.

Anal. Calcd. for $C_{13}H_8Cl_3NO_2$: C, 49.30; H, 2.55; N, 4.42. Found: C, 49.24; H, 2.61; N, 4.38.

3,5,6-Trichloro-2-(4-methoxyphenylamino)-1,4-benzoquinone (**5c**) [8,16].

This compound was obtained as brownish crystals (cyclohexane), mp 188°, ref [8] mp 188-189°.

4,5,7-Trichloro-6-hydroxy-1,3-di-(2-methylphenyl)-2,3-dihydro-1*H*-benzimidazol-2-one (**8a**).

This compound was obtained as faint brown crystals (benzene/petroleum ether), mp 220-221°, 130 mg (60%); ir: ν 3380 (OH), 1715 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.17 (s, 3H, CH_3); 2.21 (s, 3H, CH_3), 6.01 (broad, 1H, OH); 7.27-7.42 (m, 8H, aryl); ^{13}C nmr (deuteriochloroform): δ 17.7 (*C*H_3), 17.8 (*C*H_3), 102.7 (C-4), 114.1 (C-7), 121.3 (C-8), 121.5 (C-9), 126.2 (C-6), 126.6, 128.4, 129.6, 129.7 and 130.6 (aryl *C*H), 133.3 and 133.4 (C-3a and C-7a), 137.5 and 137.6 (*C*CH_3), 144.7 (C-6), 152.8 (C=O); ms: m/z 434 (M^+), 432, 397, 91.

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2O_2$: C, 58.14; H, 3.48; N, 6.46. Found: C, 58.33; H, 3.75; N, 6.32.

4,5,7-Trichloro-6-hydroxy-1,3-di-(4-methylphenyl)-2,3-dihydro-1*H*-benzimidazol-2-one (**8b**).

This compound was obtained (64 mg, 30%) as brown crystals (benzene/petroleum ether), mp 268-270°; ir: ν 3380 (OH), 1710 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.30 (2 s, 6H, CH_3), 5.77 (broad, 1H, OH), 7.20-7.24 (m, 8H, aryl); ^{13}C nmr (deuteriochloroform): δ 21.4 (2 *C*H_3), 102.7 (C-7), 113.3 (C-7a), 114.0 (C-4), 121.9 (C-3a), 126.6 (C-5), 128.9, 128.9, 129.5, and 129.6 (aryl *C*H), 131.4 and 131.6 (*C*CH_3), 139.1 and 139.3 (phenyl *C*N), 144.7 (C-6), 154.1 (C=O); ms: m/z: 434 (M^+), 432, 91.

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2O_2$: C, 58.14; H, 3.48; N, 6.46. Found: C, 58.37; H, 3.58; N, 6.29.

4,5,7-Trichloro-6-hydroxy-1,3-di-(4-methoxyphenyl)-2,3-dihydro-1*H*-benzimidazol-2-one (**8c**).

This compound (64 mg, 29%) was obtained as brown crystals (benzene/petroleum ether), mp 210-212°; ir: ν 3350 (OH), 1725 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.86 (s, 6H, OCH_3), 5.97 (broad, 1H, OH), 6.99 (m, 4H, aryl), 7.33 (m, 4H, aryl); ^{13}C nmr (deuteriochloroform): δ 55.5 (2, O*C*H_3), 102.7 (C-7), 113.3 (C-4), 114.1-114.2 (four aryl *C*H), 121.8 (C-3a or C-7a), 126.6 (C-5), 126.8 (C-3a or C-7a), 129.8-130.3 (four aryl *C*H), 144.7 (C-6), 154.4 (C=O), 160.0 and 160.1 (*C*O*C*H_3); ms: m/z 466 (M^+), 464, 430, 135, 92, 77, 36.

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2O_4$: C, 54.14; H, 3.26; N, 6.01. Found: C, 53.99; H, 3.40; N, 5.92.

4,5,7-Trichloro-3a-hydroxy-1-(2-methylphenyl)-2-(2-methylphenylimino)-2,3,3a,6-tetrahydro-1*H*-indol-6-one (**18a**, mixture of two rotamers).

This compound (133 mg, 59%) was obtained as yellow crystals (ethanol), mp 218°; ir: ν 3400 (OH), 1705 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6, 60°, δ values of major rotamer listed first where applicable): δ 1.99, 1.98 (s, 3H, CH_3), 2.27, 2.30 (s, 3H, CH_3), AB-system (δ_A 3.26, 3.32, δ_B 2.57, J = 15.26 Hz, CH_2), 6.67, 7.00, 7.19 and 7.35 (all m, 8 aryl H and OH); ^{13}C nmr (DMSO-d_6, ambient temperature, doubled set of signals): δ 16.7, 17.3, 17.4 and 17.5 (two *C*H_3), 37.3, 37.7 (C-3), 75.1, 75.3 (C-3a), 101.7, 102.8 (C-7), 119.1-130.3 (14 signals for aryl-*C*H), 128.2, 128.2 (aryl-*C*N), 130.5, 130.5 (C-7a), 134.5, 135.3, 136.5 and 136.9 (two *C*-CH_3), 144.8, 145.1 and 147.2 (three lines for C-4, C-5), 157.4, 157.7 (C-2), 158.1 (aryl-*C*N), 171.5, 171.7 (C-6); ms: m/z 448 (M^+), 446, 430, 395, 393, 130, 91, 65, 36.

Anal. Calcd. for $C_{22}H_{17}Cl_3N_2O_2$: C, 58.99; H, 3.83; N, 6.26. Found: C, 58.90; H, 3.89; N, 6.20.

4,5,7-Trichloro-3a-hydroxy-1-(4-methylphenyl)-2-(4-methylphenylimino)-2,3,3a,6-tetrahydro-1*H*-indol-6-one (**18b**).

This compound was obtained (180 mg, 80%) as yellow crystals (ethanol), mp 210-212°; ir: ν 3370 (OH), 1705 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 2.26 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), AB-system (δ_A 3.48, δ_B 2.64, J = 15.09 Hz, CH_2), 6.69, 7.10,

7.20, 7.36 and 7.48 (all m, 8H, aryl), 7.25 (broad, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 20.3 (CH_3), 20.7 (CH_3), 38.1 (C-3), 74.9 (C-3a), 102.9 (C-7) 120.5, 129.0 and 129.5 (aryl *C*H), 130.4 (C-7a), 132.6 (aryl-*C*N), 132.8 and 137.8 (aryl-*C*CH_3), 145.2 and 145.6 (C-4, C-5), 157.7 (C-2), 158.4 (aryl-*C*N), 171.6 (C-6); ms: m/z 448 (M^+), 446, 432, 430, 131, 91, 65, 36.

Anal. Calcd. for $C_{22}H_{17}Cl_3N_2O_2$: C, 58.99; H, 3.83; N, 6.26. Found: C, 58.92; H, 3.92; N, 6.10.

4,5,7-Trichloro-3a-hydroxy-1-(4-methoxyphenyl)-2,4-methoxyphenylimino)-2,3,3a,6-tetrahydro-1*H*-indol-6-one (**18c**).

This compound was obtained (168 mg, 70%) as yellow crystals (ethanol), mp 130° dec; ir: ν 3360 (OH), 1690 (C=O) cm^{-1}; ^1H nmr (DMSO-d_6): AB-system (δ_A 3.48, δ_B 2.65, J = 15.17 Hz, CH_2), 3.73 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.78, 6.88, 7.05 and 7.49 (all m, 8H, aryl), 7.25 (broad, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 38.2 (C-3), 55.1 and 55.3 (OCH_3), 76.0 (C-3a), 102.6 (C-7), 113.7, 114.2 and 121.8 (aryl *C*H), 130.5 (C-7a), 141.2 and 145.1 (C-4, C-5), 155.8 (aryl-*C*N), 157.9 (C-2), 158.5 and 158.9 ($COCH_3$), 171.7 (C-6); ms: m/z 480 (M^+), 478, 464, 462, 450, 448, 333, 331,147.

Anal. Calcd. for $C_{22}H_{17}Cl_3N_2O_4$: C, 55.06; H, 3.57; N, 5.84. Found: C, 54.97; H, 3.62; N, 5.69.

4,5,7-Trichloro-3a-hydroxy-1-(4-nitrophenyl)-2-(4-nitrophenylimino)-2,3,3a,6-tetrahydro-1*H*-indol-6-one (**18d**).

This compound was obtained (30 mg, 12%) as yellowish-brown crystals (acetonitrile), mp 215° dec; ir: ν 3380 (OH), 1700 (C=O) cm^{-1}; ^1H nmr (DMSO-d_6): AB-system (δ_A 3.58, δ_B 2.70, J = 15.25 Hz, CH_2), 7.09, 7.63, 8.21 and 8.41 (all m, 8H, aryl), 7.70 (broad, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 38.6 (C-3), 74.9 (C-3a), 105.4 (C-7), 121.6, 124.1, 125.0 and 128.9 (aryl *C*H), 130.5 (C-7a), 140.6 and 143.6 (aryl-*C*N), 145.6 and 146.7 (C-4, C-5), 154.0 and 155.8 (aryl-*C*NO_2), 158.8 (C-2), 171.7 (C-6); ms: m/z 510 (M^+), 508, 494, 492, 445, 138, 108, 92, 65, 36.

Anal. Calcd. for $C_{20}H_{11}Cl_3N_4O_6$: C, 47.13; H, 2.18; N, 10.99. Found: C, 46.96; H, 2.25; N, 11.07.

Reaction of 2,3-Dichloro-1,4-naphthoquinone (**9**) with Formamidines **1b-e**.

A solution of 2,3-dichloro-1,4-naphthoquinone (**9**, 1.0 mmole) in 15 mml of dry ethyl acetate was added to a solution of the amidine **1** (1.0 mmole) and triethylamine (1 mmole), and the mixture heated under reflux for 6-8 hours, during which time it turned from faint red into deep red or orange. The precipitate (a mixture of triethylamine hydrochloride and 3-arylamino-2-(*N*-formylarylamino)-1,4-naphtho-1,4-quinones **13b-e**, was filtered off and treated with water (whereby **13b-e** were separated from triethylammonium chloride by their insolubility in water) and filtered to give the precipitate of **13b-e** which was recrystallized from the proper solvent. The filtrate was concentrated and the residue subjected to plc using toluene/ethyl acetate (10:1) as developing solvent to give two zones, the faster one contained the unreacted dichloronaphthoquinone **9**, while the second contained **13b-e**.

3-(4-Methylphenyl)amino-2-[*N*-formyl-(4-methylphenyl)-amino]-1,4-naphthoquinone (**13b**).

This compound (198 mg, 50%) formed red crystals (ethyl acetate/cyclohexane), mp 190-192°; ir: ν 3300 (NH), 1680 (C=O), 1665 (C=O), 1640 (C=C) cm^{-1}, ^1H nmr (deuteriochloroform): δ 2.24 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), several m at 6.23, 6.81, 6.87, 7.35, 7.70 and 8.20 (12 H, aryl), 7.60 (s, 1H, NH), 8.25 (s, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 20.8 and 21.0 (CH_3), 121.1-135.2 (12 signals, aryl *C*H), 128.7 and 130.0 (C-4a and C-8a), 132.9 and 134.5 (C-2 and C-3), 135.4 and 136.0 (CCH_3), 137.8 and 140.6 (aryl *C*N), 162.4 (*C*HO), 177.5 and 182.3 (C=O); ms: m/z 396 (M^+), 379, 368, 353, 262, 118, 107, 91.

Anal. Calcd. for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.64; H, 5.05; N, 7.09.

3-(4-Methoxyphenylamino)-2-[*N*-formyl-(4-methoxyphenyl)-amino]-1,4-naphthoquinone (**13c**).

This compound was obtained (260 mg, 61%) as red crystals (ethanol), mp 198-200°; ir: ν 3300 (NH), 1680 (shoulder), 1672 (C=O), 1635 (C=C), cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.69 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.25, 6.59, 6.75, 6.87, 7.75 and 8.15 (all m, 12 H, aryl), 7.60 (s, 1H, NH), 8.17 (s, 1H, *C*HO); ^{13}C nmr (deuteriochloroform): δ 55.3 and 55.5 (OCH_3), 113.2-135.1 (12 signals, aryl *C*H), 129.4 and 129.9 (C-4a and C-8a), 130.1 and 131.6 (C-2 and C-3), 135.3 and 140.7 (aryl *C*N), 157.6 and 157.9 ($COCH_3$), 162.5 (*C*HO), 177.5 and 182.2 (C=O); ms: m/z 428 (M^+), 426, 400, 385, 279, 264, 151, 108.

Anal. Calcd. for $C_{25}H_{20}N_2O_5$: C, 70.08; H, 4.71; N, 6.54. Found: C, 70.00; H, 4.87; N, 6.27.

3-(4-Chlorophenylamino)-2-[*N*-formyl-(4-chlorophenyl)amino]-1,4-naphthoquinone (**13d**).

This compound (119 mg, 27%) was obtained as red crystals (ethanol), mp 205°; ir: ν 3300 and 3240 (NH), 1690 (C=O), 1672 (C=O), 1635 (C=C) cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.31, 6.84, 6.90, 7.22, 7.74, 7.80 and 8.15 (all m, 12H, aryl), 7.59 (s, 1H, NH), 8.30 (s, 1H, *C*HO); ^{13}C nmr (deuteriochloroform): δ 116.0 and 129.9 (C-4a and C-8a), 122.0-135.5 (8 signals, aryl *C*H), 131.6 and 131.9 (*C*Cl), 132.6 (C-2 and C-3), 138.6 and 140.3 (aryl *C*N), 161.9 (*C*HO), 177.4 and 181.7 (C=O); ms: m/z 438 (M^+), 436, 408, 373, 282, 271, 262, 138, 132, 127, 104, 77.

Anal. Calcd. for $C_{23}H_{14}Cl_2N_2O_3$: C, 63.16; H, 3.23; N, 6.41. Found: C, 63.13; H, 3.32; N, 6.38.

2-[*N*-Formyl-(4-nitrophenyl)amino]-3-(4-nitrophenylamino)-1,4-naphthoquinone (**13e**).

This compound was obtained (95 mg, 21%) as orange powder (ethanol), mp 260-262°; ir: ν 3310 (NH), 1688 (C=O), 1674 (C=O), 1632 (C=C) cm^{-1}; ^1H nmr (DMSO-d_6): δ 6.95, 7.12, 7.99 (all m, 12H, aryl), 8.65 (d, 1H, CHO), 9.80 (broad, 1H, NH); ms: m/z 458, 456, 430, 166, 164, 139, 138, 134, 65.

Anal. Calcd. for $C_{23}H_{14}N_4O_7$: C, 60.26; H, 3.09; N, 12.22. Found: C, 60.18; H, 3.22; N, 12.15.

Cyclodehydrogenation of Compounds **13b,c**.

A solution of chromium trioxide (3 mmoles) in 10 ml of acetic acid (30% in water) is added dropwise at 5° with stirring within 30 minutes to a solution of the naphthoquinone derivative (**13b,c**, 1 mmole) in 20 ml of 60% acetic acid. The reaction mixture was filtered at once, and the solid washed with cold water followed by hot ethanol and dried.

1,3-Di-(4-methylphenyl)-2,3-dihydro-1*H*-naphth[2,3-*d*]imidazole-2,4,9-trione (**14b**).

This compound (219 mg, 56%) formed orange crystals (ace-

tone), mp 331°; ir: ν 1720 (C=O), 1660 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.44 (s, 6H, CH_3), 7.34, 7.67, 7.98 (all m, 12H, aryl); ^{13}C nmr (deuteriochloroform): δ 21.3 (two CH_3), 126.3, 127.0, 129.7 and 133.7 (aryl *C*H), 126.1 (C-4a and C-8a), 131.0 (C-3a and C-9a), 131.6 (two *C*CH_3), 139.1 (aryl-*C*N), 152.1 (C-2), 174.1 (C-4 and C-9); ms: m/z 394 (M^+), 379, 104, 91.

Anal. Calcd. for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 75.95; H, 4.66; N, 7.06.

1,3-Di-(4-methoxyphenyl)-2,3-dihydro-1*H*-naphth[2,3-*d*]imidazole-2,4,9-trione (**14c**).

This compound (291 mg, 68%), was obtained as brown crystals (acetone), mp 285°; ir: ν 1720 (C=O), 1660 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.87 (s, 6H, OCH_3), 7.02, 7.37, 7.65 and 7.98 (all m, 12H, aryl); ^{13}C nmr (deuteriochloroform): δ 55.5 (O*C*H_3), 114.3, 126.3, 128.4 and 133.7 (aryl *C*H), 126.0 (C-4a and C-8a), 131.6 (C-3a, C-9a and two aryl *C*N), 152.3 (C-2), 159.8 (two *C*O*C*H_3), 174.2 (C-4 and C-9); ms: m/z 426 (M^+), 411.

Anal. Calcd. for $C_{25}H_{18}N_2O_5$: C, 70.41; H, 4.25; N, 6.57. Found: C, 70.21; H 4.31; N, 6.50.

Reaction of 2,3-Dichloro-1,4-naphthoquinone (**9**) with Acetamidines **15a-d**.

A solution of 2,3-dichloro-1,4-naphthoquinone (**9**, 0.5 mmole) in 10 ml of ethyl acetate was added to a solution of the acetamidine **15** (1.0 mmole) and the mixture heated under reflux for 6-8 hours during which time it turned from faint red to green. The precipitate was filtered off and identified as the corresponding amidine hydrochloride. The filtrate was concentrated *in vacuo* and the residue was subjected to plc using toluene/ethyl acetate (5:1) as the developing solvent to give three zones, the fastest one contained the unreacted dichloronaphthoquinone **9**, the second zone 4-chloro-3-aryl-2-arylamino-2,5-dihydro-3*H*-benz[*e*]indol-5-one **20b,c**, while the third zone contained compounds **19b,c**.

4-Chloro-9b-hydroxy-3-(4-methylphenyl)-2-(4-methylphenylimino)-2,3,5,9b-tetrahydro-1*H*-benz[*e*]indol-5-one (**19b**).

This compound (144 mg, 67%) was obtained as yellow crystals (ethyl acetate/cyclohexane), mp 170-172°; ir: ν 3360 (OH), 1695 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.31 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), AB-system (δ_A 3.38, δ_B 2.85, J = 15.60 Hz, CH_2), 5.12 (s, 1H, OH), 6.73, 7.10, 7.30 and 7.50 (all m, 12H, aryl); ^{13}C nmr (deuteriochloroform): δ 20.8 and 21.4 (*C*H_3), 37.7 (*C*H_2), 73.5 (C-9b), 106.3 (C-4), 120.7-132.8 (8 signals, aryl *C*H), 130.0 (C-9a), 133.1 (C-5a), 133.2 (C-3a), 138.2 and 139.5 (*C*CH_3), 146.7 and 158.4 (aryl *C*N), 159.7 (C-2), 179.6 (C-5); ms: m/z 428 (M^+), 409, 395, 375, 321, 297, 286, 262, 106.

Anal. Calcd. for $C_{26}H_{21}ClN_2O_2$: C, 72.80; H, 4.93; N, 6.53. Found: C, 72.69; H, 4.95; N, 6.45.

4-Chloro-9b-hydroxy-3-(4-methoxyphenyl)-2-(4-methoxy-

Table 1

$C_{22}H_{17}Cl_3N_2O_2$: Coordinates and Coefficients of the Equivalent Isotropic Temperature Factors (without H atoms) [a]

Atom	x	y	z	U
Cl(1)	-0.1572(3)	0.7016(4)	0.1533(2)	0.056(2)
Cl(2)	-0.1178(4)	0.7887(3)	0.0190(2)	0.057(2)
Cl(3)	0.3579(3)	0.4868(3)	0.0367(1)	0.043(1)
O(1)	-0.0197(7)	0.4066(7)	0.1438(3)	0.032(3)
O(2)	0.1111(9)	0.6417(8)	-0.0223(3)	0.046(3)
N(1)	0.2921(9)	0.4419(9)	0.1733(4)	0.024(4)
N(2)	0.2975(9)	0.3782(10)	0.2741(4)	0.026(4)
C(2)	0.2409(12)	0.4431(11)	0.2293(5)	0.022(4)
C(3)	0.1150(10)	0.5398(10)	0.2185(4)	0.019(4)
C(3a)	0.0609(11)	0.5284(11)	0.1510(5)	0.022(4)
C(4)	-0.0291(12)	0.6375(12)	0.1164(6)	0.033(5)
C(5)	-0.0071(13)	0.6715(11)	0.0606(6)	0.033(5)
C(6)	0.1051(14)	0.6156(12)	0.0309(6)	0.039(5)
C(7)	0.2136(12)	0.5313(11)	0.0710(5)	0.027(5)
C(7a)	0.1991(11)	0.5015(11)	0.1252(5)	0.020(4)
C(8)	0.4166(13)	0.3607(11)	0.1677(5)	0.026(4)
C(9)	0.5540(14)	0.4120(13)	0.1888(6)	0.042(6)
C(10)	0.6709(14)	0.3324(12)	0.1859(6)	0.038(5)
C(11)	0.6539(15)	0.2068(13)	0.1644(6)	0.045(6)
C(12)	0.5134(13)	0.1575(11)	0.1423(5)	0.033(5)
C(13)	0.3970(14)	0.2357(10)	0.1472(5)	0.034(5)
C(14)	0.2357(12)	0.3771(11)	0.3269(5)	0.021(4)
C(15)	0.3052(12)	0.4264(11)	0.3811(6)	0.031(5)
C(16)	0.2511(14)	0.4155(12)	0.4348(5)	0.033(5)
C(17)	0.1243(14)	0.3443(12)	0.4369(5)	0.033(5)
C(18)	0.0553(12)	0.2924(12)	0.3819(5)	0.027(5)
C(19)	0.1069(12)	0.3053(12)	0.3275(5)	0.032(5)
C(20)	0.7818(12)	0.1190(14)	0.1584(6)	0.054(6)
C(21)	0.0683(13)	0.3267(13)	0.4945(5)	0.050(6)

[a] The coefficients of the equivalent isotropic temperature factors are defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

$C_{26}H_{19}ClN_2O_3$: Coordinates and Coefficients of the Equivalent Isotropic Temperature Factors (without H atoms) [a]

Atom	x	y	z	U
Cl(1)	0.0645(1)	0.3668(1)	0.4310(1)	0.028(1)
O(1)	0.1641(1)	0.1534(1)	0.4490(1)	0.032(1)
O(2)	-0.1937(1)	0.6631(1)	0.1753(1)	0.027(1)
O(3)	0.9196(1)	1.0898(1)	0.0726(1)	0.032(1)
N(1)	0.2920(2)	0.5790(2)	0.3051(1)	0.020(1)
N(2)	0.4245(2)	0.7578(2)	0.2146(2)	0.022(1)
C(1)	0.4727(2)	0.3553(2)	0.3341(2)	0.020(1)
C(2)	0.5979(2)	0.3520(2)	0.3099(2)	0.026(1)
C(3)	0.6230(2)	0.2378(2)	0.3230(2)	0.030(1)
C(4)	0.5246(2)	0.1269(2)	0.3607(2)	0.031(1)
C(5)	0.4023(2)	0.1304(2)	0.3874(2)	0.027(1)
C(6)	0.3752(2)	0.2450(2)	0.3742(2)	0.022(1)
C(7)	0.2425(2)	0.2461(2)	0.4062(2)	0.023(1)
C(8)	0.2113(2)	0.3621(2)	0.3841(2)	0.020(1)
C(9)	0.3000(2)	0.4632(2)	0.3358(2)	0.018(1)
C(10)	0.4368(2)	0.4688(2)	0.3156(2)	0.018(1)
C(11)	0.5085(2)	0.5869(2)	0.2793(2)	0.019(1)
C(12)	0.4165(2)	0.6571(2)	0.2646(2)	0.019(1)
C(13)	0.1624(2)	0.5942(2)	0.2747(2)	0.020(1)
C(14)	0.1654(2)	0.7224(2)	0.3424(2)	0.022(1)
C(15)	0.0437(2)	0.7416(2)	0.3085(2)	0.022(1)
C(16)	-0.0798(2)	0.6326(2)	0.2052(2)	0.021(1)
C(17)	-0.0849(2)	0.5030(2)	0.1388(2)	0.026(1)
C(18)	0.0380(2)	0.4853(2)	0.1747(2)	0.025(1)
C(19)	0.5522(2)	0.8374(2)	0.1786(2)	0.021(1)
C(20)	0.5326(2)	0.8600(2)	0.0565(2)	0.024(1)
C(21)	0.6525(2)	0.9410(2)	0.0159(2)	0.026(1)
C(22)	0.7942(2)	1.0048(2)	0.1010(2)	0.024(1)
C(23)	0.8159(2)	0.9864(2)	0.2257(2)	0.024(1)
C(24)	0.6961(2)	0.9029(2)	0.2639(2)	0.022(1)
C(25)	-0.2946(2)	0.5871(2)	0.0446(2)	0.033(1)
C(26)	0.9027(2)	1.0987(2)	-0.0585(2)	0.037(1)

[a] The coefficients of the equivalent isotropic temperature factors are defined as one third of the trace of the orthogonalized U_{ij} tensor.

phenylimino)-2,3,5,9b-tetrahydro-1*H*-benz[*e*]indol-5-one (**19c**).

This compound (110 mg, 48%) was obtained as yellow crystals (ethyl acetate/cyclohexane), mp 219-220°; ir: ν 3380 (OH), 1690 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): AB-system (δ_A 3.60, δ_B 2.90, J = 15.59 Hz, CH_2), 3.78 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.50 (s, 1H, OH), 6.82, 7.00, 7.45 and 7.75 (all m, 12H, aryl); ^{13}C nmr (DMSO-d_6): δ 38.2 (CH_2), 55.2 and 55.6 (OCH_3), 72.9 (C-9b), 105.0 (C-4), 113.6-135.1 (11 signals, aryl *C*H), 125.1 (C-9a), 129.0 (C-5a), 130.0 (C-3a), 154.4 and 155.5 (aryl *C*N), 158.7 (C-2), 160.5 and 160.8 ($COCH_3$), 178.0 (C-5); ms: m/z 460 (M^+), 442, 427, 408, 270, 148, 123, 108, 43, 36.

Anal. Calcd. for $C_{26}H_{21}ClN_2O_4$: C, 67.74; H, 4.59; N, 6.08. Found: C, 67.65; H, 4.66, N, 6.03.

4-Chloro-3-(4-methylphenyl)-2-(4-methylphenylimino)-2,5-dihydro-3*H*-benz[*e*]indol-5-one (**20b**).

This compound (20 mg, 10%) formed red crystals (ethanol), mp 300-302°; ir: ν 1640 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.35 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 6.83, 7.13, 7.28, 7.51, 7.72 and 8.21 (all m, 12H, aryl), 6.98 (s, 1H, 1-H); ^{13}C nmr (deuteriochloroform): δ 20.9 and 21.4 (CH_3), 108.6 (C-4), 111.7 (C-1), 122.1, 124.4, 127.9, 129.3, 129.5, 130.7 and 132.2 (aryl *C*H), 128.2, 130.0 and 132.0 (C-9b, C-9a and C-5a), 134.3 (C-3a), 138.7 and 139.3 (CCH_3), 147.0 and 148.5 (aryl *C*N), 158.6 (C-2), 178.3 (C-5); ms: m/z 410 (M^+), 409, 395, 375, 36.

Anal. Calcd. for $C_{26}H_{19}ClN_2O$: C, 75.99; H, 4.66; N, 6.82. Found: C, 75.92; H, 4.68; N, 6.80.

4-Chloro-3-(4-methoxyphenyl)-2-(4-methoxyphenylimino)-2,5-dihydro-3*H*-benz[*e*]indol-5-one (**20c**).

This compound (38 mg, 17%) was obtained as red crystals (ethanol), mp 194-197°; ir: ν 1670 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.81 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.89, 7.00, 7.32, 7.53 and 8.22 (all m, 12H, aryl), 6.96 (s, 1H, 1-H); ^{13}C nmr (deuteriochloroform): δ 55.4 and 55.5 (OCH_3), 108.4 (C-4), 111.6 (C-1), 113.9, 114.3, 123.5, 124.4, 127.9, 130.7, 130.8 and 132.2 (aryl *C*H), 128.0, 128.2 and 130.0 (C-9b, C-9a and C-5a), 139.3 (C-3a), 142.8 (aryl CN), 157.2 (C-2), 158.6 and 159.6 ($COCH_3$), 178.2 (C-5); ms: m/z 442 (M^+), 427, 408, 393, 50, 36.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_3$: C, 70.50; H, 4.32; N, 6.33. Found: C, 70.22; H, 4.48; N, 6.33.

Thermal Dehydration of **19b,c**.

A solution of **19b,c** (0.116 mmole) in 10 ml of ethyl acetate was heated to reflux for 36 hours, during which time the solution turned gradually from yellow into deep red. The solution was concentrated and separated by plc using toluene/ethyl acetate

(10:1) as eluent. The red major zone was extracted and the residue crystallized from ethanol to give 37 mg (77%) of **20b** and 47 mg (87%) of **20c**, respectively.

X-Ray Structure Determinations.

A Siemens P4RA four circle diffractometer with MoK_α radiation (λ = 0.71073 Å), graphite monochromator, rotating anode generator and scintillation counter was used (empirical absorption corrections, SHELXTL-PLUS programs, direct methods, full-matrix least-squares refinements, H atoms at idealized positions, one scaling factor, one isotropic extinction parameter). Atomic parameters are given in Table 1 (**18b**) and Table 2 (**20c**). Compound **18b** has molecular formula $C_{22}H_{17}Cl_3N_2O_2$, formula weight 447.73 amu, 150 K, monoclinic, $P2_1/n$, a = 9.427 (4), b = 10.094 (4), c = 22.208 (9) Å, β = 100.54 (3)°, V = 2077.06 Å^3, Z = 4, D_x = 1.431 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.46 mm^{-1}, transmission range 0.900-0.871, crystal dimensions 0.33 mm x 0.29 mm x 0.16 mm, ω-scan, $2\theta_{max}$ = 44°, 2343 unique reflections, R (R_w) = 0.0840 (0.0762) for 1330 observed reflections ($I > 2\ \sigma(I)$), 264 variables (two blocks), non hydrogen atoms isotropic, one common isotropic temperature factor for H. Compound **20c** has molecular formula $C_{26}H_{19}ClN_2O_3$, formula weight 442.88 amu, 150 K, trichlinic, P1, a = 10.531 (3), b = 10.687 (3), c = 10.762 (3) Å, α = 102.47 (2), β = 99.67 (2), γ = 115.62 (2)°, V = 1018.41 Å^3, Z = 2, D_x = 1.444 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.22 mm^{-1}, transmission range 0.999-0.965, crystal dimensions 0.55 mm x 0.37 mm x 0.28 mm, ω-scan, $2\theta_{max}$ = 54°, 4449 unique reflections, R (R_w) = 0.0376 (0.0429) for 3604 observed reflections ($I > 2\ \sigma(I)$), 293 variables, all nonhydrogen atoms anisotropic, one common isotropic temperature factor for H within each residue.

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