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Synthesis of Naphth[1,2,3-*cd*]indol-6(2*H*)-one Derivatives and Their Fluorescence Properties

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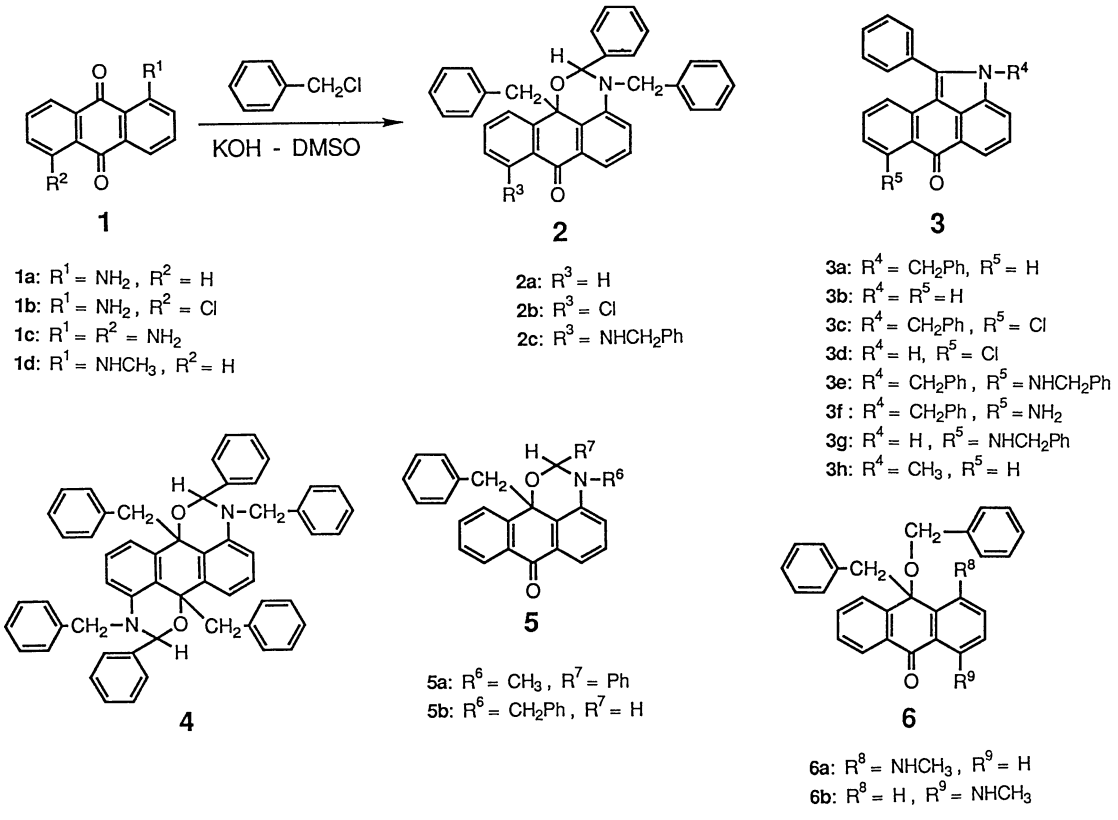
Highly fluorescent 1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (**3b**) and its 7-chloro and 7-amino derivatives were synthesized by reaction of 1-aminoanthraquinones with benzyl chloride in KOH–DMSO system, followed by treatment with aluminium chloride. The compound **3b** was easily *N*-alkylated with various alkyl halides in KOH–DMSO system. The fluorescence quantum yields (Q_f) of naphth[1,2,3-*cd*]indol-6(2*H*)-one derivatives **3** were high (0.5—0.7), except for 7-amino derivatives which did not fluoresce. The Q_f of 7-chloro derivative (**3d**) was strongly dependent on solvent: 0.37 in ethanol; 0.02 in acetonitrile; 0 in benzene. The compounds **3** were demonstrated to be efficient laser dyes for 500—550 nm region.

Fluorescent dyes attract continuous attention because of their application in various field.[1] Especially dye laser applications are growing. In our previous paper we reported a new synthetic method of highly fluorescent naphthindolone derivatives.[2] Thus the reaction of 1-aminoanthraquinone (**1a**) with benzyl chloride in the presence of powdered potassium hydroxide (KOH) in dimethyl sulfoxide (DMSO) afforded 3,11b-dibenzyl-2-phenyl-3,11b-dihydroanthra[1,9-*de*]-1,3-oxazin-7(2*H*)-one (**2a**). Then, the compound **2a** was treated with concd hydrochloric acid in ethanol or aluminium chloride in benzene to give 2-benzyl-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (**3a**) or 1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one(**3b**), respectively. Although naphth[1,2,3-*cd*]indol-6(2*H*)-one derivatives have been known to be good fluorophores,[3] little has been reported concerning their properties so far. We report herein the synthesis of new naphth[1,2,3-*cd*]indol-6(2*H*)-one derivatives and their fluorescence properties and lasing behavior.

Results and Discussion

Synthesis of Naphth[1,2,3-*cd*]indol-6(2*H*)-one Derivatives. In order to synthesize new substituted 1-



Scheme 1.

phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one derivatives, 1-amino-5-chloroanthraquinone (**1b**), 1,5-diaminoanthraquinone (**1c**), and 1-methylaminoanthraquinone (**1d**) were used as starting compounds. The aminoanthraquinone was first treated with powdered KOH in DMSO to yield green solution of the corresponding amide ion. Then excess benzyl chloride was added to the amide ion solution. In the reaction of **1b**, 3,6-dihydro-2*H*-1,3-oxazine compound (**2b**) was obtained in 53% yield. The reaction of **1c** also gave 3,6-dihydro-2*H*-1,3-oxazine compound (**2c**) in 16% yield, and compound **4**, which would be derived from **2c** by the further reaction, was not observed. In the case of the reaction of **1d**, mass spectrum of the isolated product does not show the signals of expected 3,6-dihydro-2*H*-1,3-oxazine compound (**5a** or **5b**: M 417) but does *m*/*z* 419. Its IR spectrum shows the presence of N–H group at 3400 cm^{-1}. ^1H NMR also suggests the presence of N–H group at around 6.3 ppm: By the addition of CD_3OD, the peak of *N*-methyl group (doublet at 2.90 ppm) was changed to singlet and the peaks at around 6.3 ppm was disappeared. ^1H NMR also shows two sets of benzylic protons, which had different chemical shifts with doublet at 4.10 ppm and AB quartet at 3.57 ppm. These results and analytical data suggest that the product is not the expected 3,6-dihydro-2*H*-1,3-oxazine compound (**5a** or **5b**) but benzyl ether-type compound: 10-benzyl-10-benzyloxy-4-methylamino-9(10*H*)-anthracenone (**6a**). Treatment of compound **6a** with concd hydrochloric acid gave compound **3h** (*vide infra*). This fact excludes the possibility of the isomeric structure, 10-benzyl-10-benzyloxy-1-methylamino-9(10*H*)-anthracenone (**6b**).

The 3,6-dihydro-2*H*-1,3-oxazine compound (**2b**) was treated with concd HCl in ethanol to afford 2-benzyl-7-chloro-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (**3c**) in 36% yield. In the reaction of **2b** with aluminium chloride in refluxing benzene the debenzylated product (**3d**) was obtained in 53% yield together with **3c** (12% yield). The reaction of **2c** with $AlCl_3$ in refluxing benzene gave the 7-amino derivatives **3e**, **3f**, and **3g** in 41, 18, and 22% yields, respectively. Treatment of **2c** with $AlCl_3$ or $FeCl_3$ at room temperature afforded only **3e** in 24 and 39% yields, respectively. The 7-benzylamino derivative **3g** was also obtained by the nucleophilic reaction of **3d** with benzylamine in 8% yield. It is noteworthy that reaction of benzyl ether-type compound **6a** with concd HCl in ethanol afforded 1-phenyl-2-methylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (**3h**) in 66% yield, which was identical with *N*-methylation product of **3b** in KOH–DMSO system (see Table 1).

The *N*-alkylation in KOH–DMSO system[4] was applied to **3b** using various alkyl halides in order to examine the properties of the *N*-alkylated compounds as fluorophore, and the alkyl substituent affected largely the lasing behavior (vide infra). After the compound **3b** was deprotonated by KOH in DMSO, alkyl halide was added. Table 1 shows that the *N*-alkylation of **3b** in KOH–DMSO system afforded the corresponding *N*-alkyl derivatives in good yields. The reaction of **3b** with 2-bromoethanol, protected with tetrahydropyranyl group, afforded the corresponding *N*-alkyl derivative (**3l**), which was easily converted to the alcohol (**3m**) by the treatment with *p*-toluenesulfonic acid.

Table 1. *N*-Alkylation of **3b** in KOH–DMSO System

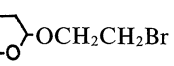
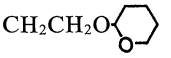
RX	Time/h	Product	Yield/%
$PhCH_2Cl$	5	**3a**	89
CH_3Br	2.5	**3h**	13
n-C_4H_9I	1	**3i**	92
$Br(CH_2)_8Br$	1	**3j**	79
$C_{16}H_{33}Br$	11	**3k**	90
	18	**3l**	47

Table 2. Absorption and Fluorescence Properties of 1-Phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-ones **3** in Ethanol

	R^4	R^5	λ_a/nm[a]	λ_f/nm[b]	Q_f[c]
3a	CH_2Ph	H	426	498	0.65±0.05
3b	H	H	430	496	0.51
3c	CH_2Ph	Cl	430	498	0.30
3d	H	Cl	433	500	0.37
3e	CH_2Ph	$NHCH_2Ph$	491	—	0
3f	CH_2Ph	NH_2	477	—	0
3g	H	$NHCH_2Ph$	493	—	0
3h	CH_3	H	431	505	0.59
3i	$(CH_2)_3CH_3$	H	430	501	0.64
3j	$(CH_2)_8Br$	H	431	501	0.61
3k	$(CH_2)_{15}CH_3$	H	431	501	0.65
3l		H	425	499	0.70
3m	CH_2CH_2OH	H	428	504	0.56

a) Absorption maximum. b) Fluorescence maximum. c) Fluorescence quantum yield.

Fluorescence Properties. Table 2 shows the wavelength of absorption and fluorescence maxima of the compounds **3** in ethanol. Varying the substituent in the 2-position does not result in large shifts in both absorption and fluorescence: The compounds **3** have their absorption maxima (λ_a) at around 430 nm and fluorescence maxima (λ_f) at around 500 nm. In the cases of 7-amino derivatives (**3e**, **3f**, and **3g**) the absorption maxima appeared at the longer wavelength region of 477—493 nm which could be assigned as an intramolecular charge-transfer band between the amino group in the 7-position and the carbonyl group. The fluorescence quantum yield (Q_f) of **3a** was found to be 0.65±0.05, 0.68±0.02, and 0.62 by using three different fluorescence standard of quinine sulfate, fluorescein, and 9,10-diphenylanthracene, respectively. Hence, in Table 2 the Q_f of compounds **3** in ethanol was compared using quinine sulfate as a standard. The Q_f are generally high (0.51—0.70). The substitution of chlorine for H at 7-position resulted in a decrease in Q_f, suggesting

Table 3. Solvent Effect on Absorption and Fluorescence Maxima and Fluorescence Quantum Yields

R^4	R^5	Solvent	λ_a/nm	λ_f/nm	Q_f
3a CH_2Ph	H	C_2H_5OH	426	498	0.65±0.05
		CH_3CN	429	479	0.65
		C_6H_6	428	461	0.24
3b H	H	C_2H_5OH	430	496	0.51
		CH_3CN	420	479	0.49
		C_6H_6	407	456	0.11
3d H	Cl	C_2H_5OH	433	500	0.37
		CH_3CN	429	479	0.02
		C_6H_6	410	—	0
3e CH_2Ph	$NHCH_2Ph$	C_2H_5OH	491	—	0
		CH_3CN	485	—	0
		C_6H_6	485	—	0
3h CH_3	H	C_2H_5OH	431	505	0.59
		CH_3CN	433	487	0.59
		C_6H_6	433	467	0.41
3i *n*-C_4H_9	H	C_2H_5OH	430	501	0.64
		CH_3CN	433	486	0.59
		C_6H_6	432	463	0.34

appreciable deactivation from lowest excited singlet (S_1) state due to internal heavy atom effect. The 7-amino derivatives (**3e**—**g**) were almost nonfluorescent. This result could be ascribable to the intramolecular CT nature of the S_1 state.[5] As shown in Table 3, the absorption spectra of 2-alkyl derivatives (**3a**, **3h**, and **3i**) showed no significant solvent dependence, while in the cases of the derivatives (**3b**, **3d**, and **3e**) bathochromic shift was observed with increasing solvent polarity. Fluorescence emissions also underwent bathochromic shifts with increasing solvent polarity. Larger Stokes shifts were observed in polar solvents than in nonpolar solvents. These results indicate the excited states of compounds **3** are more stabilized by polar solvents. Fluorescence quantum yield of the 7-chloro derivative (**3d**) was largely dependent on solvent polarity: It has a diminished Q_f in acetonitrile and was almost nonfluorescent in benzene. Hence **3d** would be a useful probe for examining the polarity of the environment around the fluorescent species.

Lasing Behavior. Highly fluorescent compounds **3** were examined for application to laser dyes. The excimer laser operating on XeCl at 308 nm was used as an excitation source. By using this pump laser radiation with 13 ns pulse width, the lasing pulse of **3b** at 506 nm with 7.8 ns was observed, indicating a pulse compressing effect by lasing phenomena. The methanol solution of **3l** and **3m** also exhibited intense laser radiation by XeCl pumping. The tuning curves for **3b**, **3l**, and **3m** in methanol are shown in Fig. 1. The lasing maxima of compound **3b**, **3l**, and **3m** were 506, 508, and 512 nm, respectively. The compound **3m** exhibits a lasing action over a wide range of a 50 nm (500—550 nm). The compound **3l**, which shows a similar tunability to **3b**, has relatively good efficiency of energy conversion from the pump source.

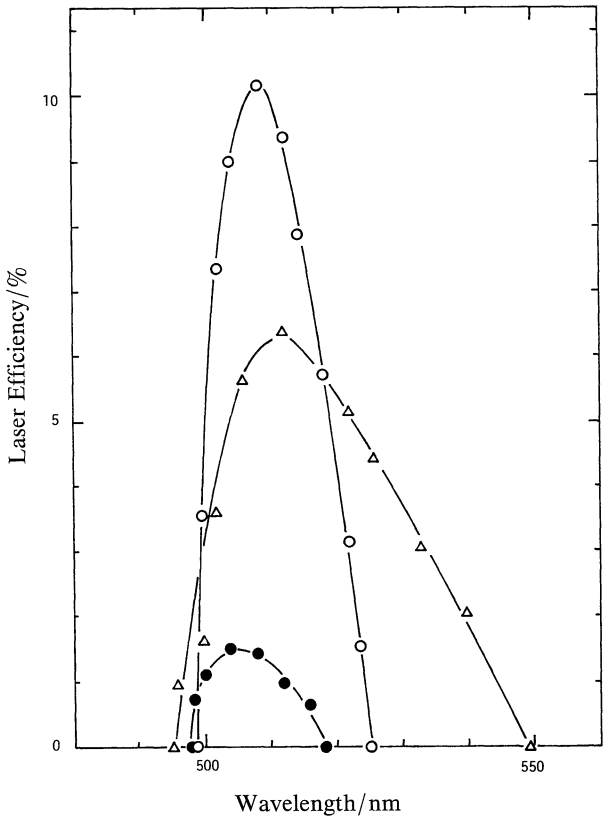


Fig. 1. Tuning curves for naphth[1,2,3-*cd*]indol-6(2*H*)-one derivatives (**3b**, **3l**, and **3m**) in Methanol. ●: **3b**, ○: **3l**, △: **3m**.

Experimental

Materials. 1-Amino-5-chloroanthraquinone was prepared as follows: The mixture of sodium anthraquinone-1-sulfonate (4.68 g, 15.4 mmol), 95% H_2SO_4 (16 cm^3), and nitric acid (Sp. Gr. about 1.38; 2 cm^3) was heated at 95 °C for 5 h to afford 5-

nitroanthraquinone-1-sulfonic acid, which was treated with sodium chlorate (0.28 g) in hydrochloric acid to give 1-chloro-5-nitroanthraquinone. The reduction of the crude 1-chloro-5-nitroanthraquinone was carried out with sodium sulfide (11 g) in aqueous NaOH solution at 80 °C for 10 h. The product was purified by silica-gel column chromatography with benzene as eluent, followed by recrystallization from benzene to afford 1-amino-5-chloroanthraquinone as red crystals (1.428 g, 36% from sodium anthraquinone-1-sulfonate): Mp 217—219 °C (lit,[6] 219 °C); Found: C, 65.22; H, 2.97; N, 4.94%. 1,5-Diaminoanthraquinone and 1-methylaminoanthraquinone (Sumitomo Chemical Co.) were purified by recrystallization from toluene. Dimethyl sulfoxide was distilled twice under reduced pressure and stored under a nitrogen atmosphere. Benzyl chloride was distilled under a nitrogen atmosphere.

The solvents used in all spectroscopic and lasing measurements were spectrograde or purified according to the literature procedure.[7]

Instruments. Melting points obtained on a Mitamura melting point apparatus are uncorrected. UV and visible spectra were recorded with a Hitachi 220A spectrometer. ^{1}H NMR data were recorded on a Hitachi R-24 (60 MHz) and JEOL FX90Q (90 MHz) spectrometers with Me_4Si as an internal standard. IR spectra were measured on a JASCO IRA-1 spectrometer. Mass spectra were recorded with a JEOL JMS-DX 300 spectrometer by the electron impact (EI) ionizing technique at 70 eV and by the fast-atom bombardment (FAB) with *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed on a Yanaco MT2 CHN corder. Fluorescence spectra were measured on a Hitachi MPF-4 spectrofluorometer. Quinine sulfate (Q_f=0.55 in 0.5 mol dm^{-3} sulfuric acid aqueous solution),[8] fluorescein (Q_f=0.79 in 0.1 M NaOH aqueous solution),[9] or 9,10-diphenylanthracene (Q_f=1.0 in cyclohexane)[10] was used as a standard for the determination of fluorescence quantum yields.

Lasing experiments were performed using excimer laser (Lumonics Hyper EX-400) operating on XeCl at 308 nm as excitation source. The dye laser (Lumonics HyperDye-300) output was measured using a joule meter (Scientech model 38-0101).

The compounds **2** and **3** were obtained by the two-step method described previously.[2]

8-Chloro-3,11b-dibenzyl-2-phenyl-3,11b-dihydroanthra[1,9-*de*]-1,3-oxazin-7(2*H*)-one (2b). 1-Amino-5-chloroanthraquinone (**1b**: 513 mg, 1.99 mmol) was reacted with benzyl chloride (2.69 g, 21.2 mmol) in the presence of powdered KOH (1.03g, 18.4 mmol) in DMSO (60 cm^3) at 30 °C for 1 h. The reaction mixture was poured into water (1000 cm^3) and extracted with benzene. After the benzene extract was concentrated, the residue was purified by silica-gel column chromatography with benzene as eluent, followed by recrystallization from ethanol to afford **2b** (316 mg, 53%) as yellow crystals: Mp 194—195 °C; IR (KBr) 1670, 1595, 1580, 1480, 1447, 1295, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.1—4.8 (4H, m, CH_2) and 6.1—7.9 (22H, m, ArH); MS *m*/*z* 527 and 529 (M^+); Found: C, 79.48; H, 4.71; N, 2.53%. Calcd for $C_{35}H_{26}NO_2Cl$: C, 79.61; H, 4.96; N, 2.65%.

8-Benzylamino-3,11b-dibenzyl-2-phenyl-3,11b-dihydroanthra[1,9-*de*]-1,3-oxazin-7(2*H*)-one (2c). After the mixture of 1,5-diaminoanthraquinone (477 mg, 2 mmol) and KOH (1.12 g, 20 mmol) in DMSO (60 cm^3) was stirred for 30 min, benzyl chloride (5.06 g, 40 mmol) was added to the mixture. The solution was stirred overnight at RT. The reaction mixture was poured into water (1000 cm^3) and the organic materials were extracted with benzene. The benzene extract was evaporated. The residue showed 5 spots on TLC (SiO_2, benzene). The largest spot (R_f=0.70) was separated by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford **2c** (192 mg, 16%) as orange crystals: Mp 174.4 °C; UV (C_2H_5OH) 417 (log ε 3.96) and 244 nm (4.41); IR (KBr) 1630, 1590, 1520, 1493, 1282, 792, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.47 (2H, ABq, *J*=12 Hz, CH_2), 4.39 (2H, ABq, *J*=16 Hz, NCH_2), 4.46 (2H, d, *J*=6 Hz, $NHC\underline{H}_2$), 6.2—7.2 (27H, m, ArH), and 9.63 (1H, t, *J*=6 Hz, NH); MS *m*/*z* 598 (M^+); Found: C, 84.06; H, 5.62; N, 4.31%. Calcd for $C_{42}H_{34}N_2O_2$; C, 84.25; H, 5.73; N, 4.68%.

2-Benzyl-7-chloro-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3c). A mixture of **2b** (211 mg, 0.4 mmol) and concd HCl (5 cm^3) in ethanol (35 cm^3) was refluxed for 3 h. The mixture was concentrated and the residue was purified by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford **3c** (47 mg, 36%) as pale orange crystals: Mp 245—246 °C; UV (C_2H_5OH) 430 (log ε 4.13), 352 (3.61), 310 (sh), and 279 nm (4.24); IR (KBr) 1640, 1606, 1588, 1330, 1192, and 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.2 (2H, s, CH_2) and 6.5—8.2 (16H, m, ArH); MS *m*/*z* 419 and 421 (M^+); Found: C, 80.22; H, 4.51; N, 3.46%. Calcd for $C_{28}H_{18}NOCl$: C, 80.09; H, 4.32; N, 3.34%.

7-Chloro-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3d). A mixture of **2b** (517 mg, 0.98 mmol) and $AlCl_3$ (932 mg, 7 mmol) in benzene (180 cm^3) was refluxed for 1 h. The mixture was poured into ice–water. The benzene extract was evaporated and the residue was purified by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford **3d** (171 mg, 53%) as yellow crystals: Mp 330.5—331.5 °C; UV (C_2H_5OH) 433 (log ε 4.13), 357 (sh), 313 (3.88), 280 (4.15), and 248 nm (4.45); IR (KBr) 3200, 1640, 1610, 1590, 1382, 1293, 1042, and 793 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.3—8.0 (11H, m, ArH) and 12.3 (1H, br s, NH); MS *m*/*z* 329 and 331 (M^+); Found: C, 76.23; H, 3.51; N, 4.40%. Calcd for $C_{21}H_{12}NOCl$: C, 76.48; H, 3.67; N, 4.25%.

2-Benzyl-7-benzylamino-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3e). A mixture of **2c** (261 mg, 0.44 mmol) and $AlCl_3$ (382 mg, 2.9 mmol) in benzene (75 cm^3) was refluxed for 35 min. The mixture was poured into ice–water. The benzene extract was evaporated. The residue showed 3 spots (R_f=0.20, 0.10, and 0.05) on TLC (SiO_2, benzene). These products were separated by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford compounds **3e** (87 mg, 41%), **3f** (31 mg, 18%), and **3g** (39 mg, 22%). **3e** (R_f=0.20) as orange crystals: Mp 230.0—230.5 °C (decomp); UV (C_2H_5OH) 491 (log ε 4.13), 383 (sh), 350 (3.87), and 317 nm (3.70); IR (KBr) 3200, 1637, 1575, 1375, 1244, 790, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.51 (2H, d, *J*=6 Hz, NCH_2), 5.17 (2H, s, CH_2), 6.3—8.2 (21H, m, ArH), and 11.96 (1H, t, *J*=6 Hz, NH); MS *m*/*z* 490 (M^+); Found: C, 85.41; H, 5.20; N, 5.66%. Calcd for $C_{35}H_{26}N_2O$: C, 85.68; H, 5.34; N, 5.71%.

7-Amino-2-benzyl-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3f). (R_f=0.05) as orange crystals: UV (C_2H_5OH) 477 (log ε 3.99), 347 (3.83), and 289 nm (4.04); IR (KBr) 3440, 3030, 1630, 1592, 1268, and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.22 (2H, s, CH_2) and 6.1—8.2 (18H, m, ArH and NH_2); MS *m*/*z* 400 (M^+); Found: C, 83.69; H, 4.80; N, 7.15%. Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00%.

7-Benzylamino-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one

(3g). A mixture of **3d** (345 mg, 1.05 mmol) and benzylamine (10 cm³) was heated at 100 °C for 130 h. The mixture was evaporated and the residue was purified by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford **3g** as red crystals (34 mg, 8%): Mp 244.0—245.0 °C; UV (C_2H_5OH) 493 (log ε 3.66), 367 (3.52), 288 (4.16), and 264 nm (4.21); IR (KBr) 3200, 2930, 2850, 1600, 1570, 1388, 1200, and 700 cm⁻¹; ^{1}H NMR (60 MHz, $CDCl_3$) δ=4.55 (2H, d, *J*=4.8 Hz, CH_2), 6.2—8.8 (17H, m, ArH and NH), and 10.8 (1H, t, *J*=4.8 Hz, N<u>H</u>CH_2); MS *m*/*z* 400 (M^+); Found: C, 83.71; H, 5.22; N, 6.91%. Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00%.

10-Benzyl-10-benzyloxy-4-methylamino-9(10*H*)-anthracenone (6a). 1-Methylaminoanthraquinone (**1d**: 475 mg, 2 mmol) was reacted with benzyl chloride (3.2 g, 25 mmol) in the presence of powdered KOH (1.1 g, 20 mmol) in DMSO (60 cm³) at 30 °C for 1 h. The reaction mixture was poured into water (1000 cm³) and extracted with benzene. After the benzene extract was concentrated, the residue was purified by silica-gel column chromatography with benzene as eluent, followed by recrystallization from ethanol to afford **6a** (344 mg, 41%) as pale orange crystals: Mp 162.1—163.2 °C (decomp); UV (C_2H_5OH) 397 nm (log ε 3.32); IR (KBr) 3390 (NH) and 1660 (C=O) cm⁻¹; ^{1}H NMR ($CDCl_3$) δ=2.90 (3H, d, *J*=5 Hz, CH_2), 3.57 (2H, ABq, *J*=13 Hz, CH_2), 4.10 (2H, d, *J*=2 Hz, CH_2), and 5.9—8.1 (18H, m, ArH and NH); MS *m*/*z* 419 (M^+); Found: C, 83.16; H, 5.90; N, 3.47%. Calcd for $C_{29}H_{25}NO_2$: C, 83.03; H, 6.01; N, 3.34%.

2-Methyl-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3h). A mixture of **6a** (195 mg, 0.46 mmol) and concd HCl (10 cm³) in ethanol (50 cm³) was refluxed for 3 h. The mixture was concentrated and the residue was purified by column chromatography (SiO_2, benzene), followed by recrystallization from ethanol to afford **3h** (94 mg, 66%): UV (C_2H_5OH) 431 nm (log ε 4.10); IR (KBr) 3060, 1628, 1590, 1480, 1292, 992, 762, and 700 cm⁻¹; ^{1}H NMR (DMSO-d_6) δ=3.58 (3H, s, CH_3) and 6.8—8.5 (12H, m, ArH); MS *m*/*z* 309 (M^+); Found: C, 85.29; H, 4.78; N, 4.49%. Calcd for $C_{22}H_{15}NO$, C, 85.41; H, 4.89; N, 4.53%.

***N*-Alkylation of 3b.** A typical procedure is described for the reaction of **3b** with butyl iodide. The compound **3b** (295 mg, 1 mmol) was stirred with powdered KOH (561 mg, 10 mmol) in DMSO (30 cm³) for 30 min at 30 °C. Then butyl iodide (1.84 g, 10 mmol) was added to the mixture and the solution was stirred for 1 h at 30 °C. The reaction was quenched with water (700 cm³). The mixture was extracted with benzene, washed with water, and evaporated. The residue was submitted to column chromatography on silica gel using benzene as eluent. The yellow fractions (R_f=0.08) were concentrated and recrystallized from ethanol to afford **2-butyl-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3i)** (323 mg, 92%) as yellow needles; mp 179.5—180.0 °C; UV (C_2H_5OH) 242 (log ε 4.42), 275 (4.24), 304 (4.07), 355 (3.61), and 430 nm (4.09); IR (KBr) 3070, 2980, 2950, 2880, 1635, 1595, 1290, 772, and 707 cm⁻¹; ^{1}H NMR ($CDCl_3$) δ=0.5—1.9 [m, 7H, -$(CH_2)_2CH_3$], 3.97 (t, 2H, N-CH_2), and 7.0—8.6 (m, 12H, ArH); MS *m*/*z* 351 (M^+); Found: C, 85.68; H, 6.00; N, 3.89%. Calcd for $C_{25}H_{21}NO_2$: C, 85.44; H, 6.02; N, 3.99%.

2-(8-Bromooctyl)-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3j): Yellow needles from ethanol; mp 88.0—88.5 °C; UV (C_2H_5OH) 242 (sh, log ε 4.47), 275 (4.27), 303 (4.10), 354 (3.65), and 431nm (4.10); IR (KBr) 3060, 2940, 2860, 1630, 1595, 1335, 1278, 770, and 702 cm⁻¹; ^{1}H NMR ($CDCl_3$) δ=0.8—2.0 [m, 12H, -$(CH_2)_6$], 3.38 (t, 2H, Br-CH_2), 4.18 (t, 2H, N-CH_2), and 7.0—8.7 (m, 12H, ArH); MS *m*/*z* 485 and 487 (M^+); Found: C, 72.16; H, 5.90; N, 2.86%; Calcd for $C_{29}H_{28}NO_2Br$: C, 71.90; H, 5.80; N, 2.88%.

2-Hexadecyl-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3k): Yellow crystals from ethanol; mp 82.5—83.0 °C; UV (C_2H_5OH) 243 (log ε 4.45), 275 (4.26), 304 (4.09), 354 (3.64), and 431 nm (4.10); IR (KBr) 3070, 2930, 2860, 1630, 1598, 1480, 1290, and 708 cm⁻¹; ^{1}H NMR ($CDCl_3$) δ=0.4—1.9 [m, 31H, -$(CH_2)_{14}CH_3$], 4.05 (t, 2H, N-CH_2), and 7.2—8.7 (m, 12H, ArH); MS *m*/*z* 519 (M^+); Found: C, 85.84; H, 8.67; N, 2.71%. Calcd for $C_{37}H_{45}NO_2$: C, 85.50; H, 8.73; N, 2.69%.

1-Phenyl-2-[2-(tetrahydropyranyloxy)ethyl]naphth[1,2,3-*cd*]indol-6(2*H*)-one (3l): The reaction of **3b** with 1-bromo-2-tetrahydropyranyloxyethane, which was obtained by the reaction of 2-bromoethanol with dihydropyrane in the presence of *p*-toluenesulfonic acid, afforded **3l** as pale brown oil (47%): UV (C_2H_5OH) 425 nm (log ε 4.05); IR (KBr) 2940, 1635, 1288, 1122, 1033, and 700 cm⁻¹; ^{1}H NMR ($CDCl_3$) δ=1.1—1.6 (6H, m), 3.1—4.5 (m, 7H), and 7.1—8.4 (H, m, ArH); FABMS *m*/*z* 424 (M+1)⁺; Found: C, 79.26; H, 5.79; N, 3.19%. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31%.

2-(2-Hydroxyethyl)-1-phenylnaphth[1,2,3-*cd*]indol-6(2*H*)-one (3m). A methanol (10 cm³) solution of **3l** (111 mg, 0.26 mmol) and *p*-toluenesulfonic acid (53.2 mg, 0.27 mmol) was stirred for 16 h at RT. After the mixture was dried, the residue was recrystallized from methanol to afford **3m** as yellow needles (61.8 mg, 69%); mp 216—217 °C; UV (C_2H_5OH) 428 nm (log ε 3.97); IR (KBr) 3400, 1610, 1580, 1474, 1275, 1080, and 702 cm⁻¹; ^{1}H NMR ($CDCl_3$+CD_3OD) δ=3.84 (2H, t, *J*=5.6 Hz, NCH_2), 4.21 (2H, t, *J*=5.6 Hz, CH_2O), and 7.1—8.5 (12H, m, ArH); FAB-MS *m*/*z* 340 (M+1)⁺; Found: C, 81.20; H, 5.11; N, 4.17%. Calcd for $C_{23}H_{19}NO_2$: C, 81.39; H, 5.05; N, 4.13 %.

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