Synthesis of Fluorescent Labeled Derivatives of Aminopropylpyrimidines

W. A. Summers, J. Y. Lee, and J. G. Burr*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069

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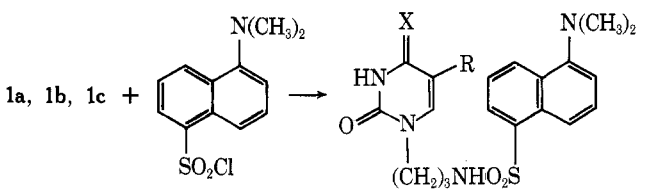
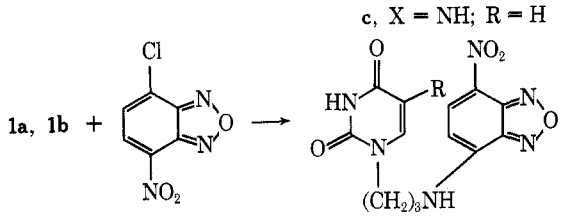
The preparation of some 1-(3-aminopropyl)pyrimidines (1) is discussed and their conversion to fluorescent compounds (2 and 3) with *N,N*-dimethylaminonaphthalenesulfonyl chloride and 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole, respectively, is elaborated.

In order to explore the energy donor capabilities of the excited states of the pyrimidines, uracil, thymine, and cytosine, we have prepared a series of compounds in which the pyrimidine is bound via a trimethyleneamino chain to an appropriate fluor. The fluors chosen for the work reported here were 5-dimethylaminonaphthalenesulfonyl[1] and 7-nitrobenzo-2-oxa-1,3-diazole.[2] The compounds thus prepared are shown as **2a–c** and **3a,b.** Energy transfer in



1a, **1b**, **1c** +

2a, X = O; R = CH_3
b, X = O; R = H
c, X = NH; R = H



1a, **1b** +

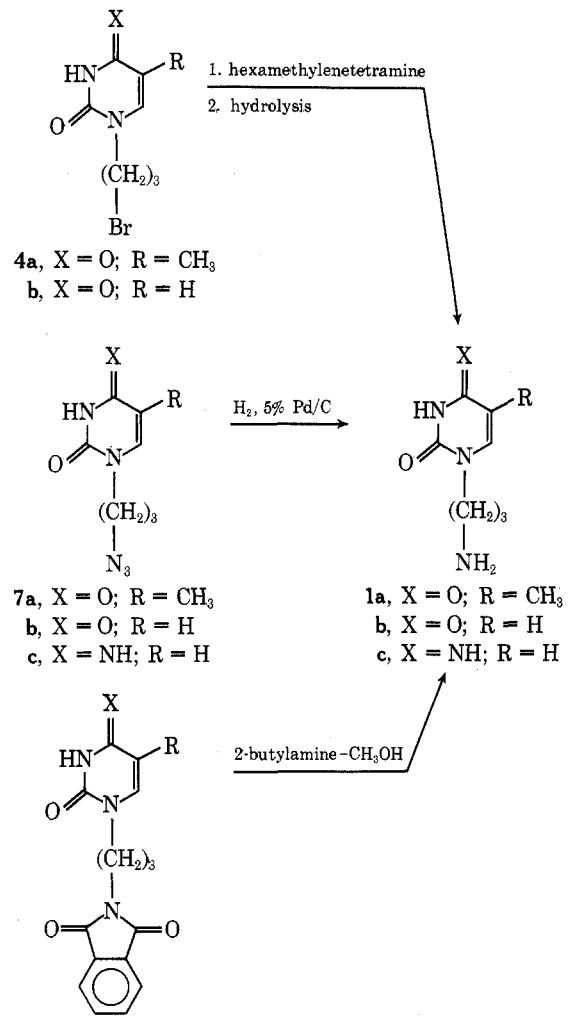
3a, R = CH_3
b, R = H

these compounds and their photochemistry are reported elsewhere.[3] The pertinence of this work to the photochemistry and photobiology of these pyrimidine bases has been established by other work, from this laboratory[4–7] and in the laboratories of others.[8,9]

Recently,[10] Brown, Eisinger, and Leonard reported the preparation of 1,3-(bispyrimidinyl)propanes and 1-pyrimidinyl-3-purinylpropanes from 1-(3-aminopropyl)pyrimidines. Our synthetic scheme is based on their procedures, but we report several alternate procedures for preparing the amines.

We chose two readily available fluorogenic reagents, 5-dimethylaminonaphthalenesulfonyl chloride (dansyl chloride, DNS Cl) and 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD Cl), and converted 3-aminopropylthymine, -uracil, and -cytosine into their corresponding fluorescent derivatives. Attempts to prepare a third type of compound, 1-[3-(α-naphthylamino)propyl]thymine, though successful synthetically, afforded a product which underwent rapid discoloration on standing. This instability, it was felt, would preclude later spectroscopic studies and thus further elaboration of the series was suspended.

In the course of our experimental work three routes were investigated for the preparation of the aminopropylpyrimidines: (1) Delepin (Sommelet) reaction,[11] (2) aminolysis of phthalimidopropylpyrimidines, and (3) catalytic reduction of azidopropylpyrimidines.[12] All afforded good yields of amine with the exceptions that preparation of the uracil



4a, X = O; R = CH_3
b, X = O; R = H

7a, X = O; R = CH_3
b, X = O; R = H
c, X = NH; R = H

1a, X = O; R = CH_3
b, X = O; R = H
c, X = NH; R = H

6a, X = O; R = CH_3
b, X = O; R = H
c, X = NAc; R = H

derivative by method 1 produced only minor quantities of desired amine, and aminolysis of the phthalimidopropyl derivatives was successful only with refluxing 2-butylamine–methanol.

Catalytic reduction of the appropriate azide also afforded the amine and, in our hands, was a simpler reaction to run than that previously described using Raney nickel.[10] Reduction in alcoholic or aqueous alcoholic solutions over 5% Pd on carbon proceeded rapidly with a minimum of work-up necessary.

The insensitivity of dansyl chloride toward hydrolysis in aqueous solutions[6] permitted the use of aqueous systems for the preparation of the fluorescent derivatives. Dimethylformamide, dimethyl sulfoxide, and pyridine were found to be unsatisfactory solvents, since the percent conversion of amine to fluorescent derivative was low. When

Table I
Absorption and Emission Properties of the Fluorescent Derivatives of Aminopropylpyrimidines

Compd	Absorption maxima, nm (ε)[a]	Emission maximum,[b] nm
2a	258.5 (18,300)	517
	335 (4800)	
2b	258 (20,000)	517
	334 (4960)	
2c	286 (19,100)	517
	320 (1800)	
N-Propyl-5-dimethylamino-naphthalene-1-sulfonamide	251 (12,600)	517
	334 (4800)	
3a	270 (9400)	523
	340 (7100)	
	475 (23,000)	
3b	261 (10,100)	523
	340 (7000)	
	476 (22,900)	
4-Propylamino-7-nitro-benzo-1,3-diazole	342 (7140)	523
	478 (21,400)	

[a] l. M^{-1} cm^{-1} in alcohol or 50% aqueous alcohol. [b] Data obtained on a Perkin-Elmer Model MPF-3L in 30% aqueous ethanol.

aqueous acetonitrile (pH 8) was used, the yields of fluorescent derivative became quantitative and the work-up simpler. All the dansyl derivatives crystallized from the reaction mixture and were readily purified by silica chromatography. The compounds are soluble in most organic solvents and slightly soluble in water. Use of preparative TLC is not recommended for purification of these materials, since we observed some decomposition on the plate during and after development. Some decomposition was also noted after prolonged periods in water.

NBD chloride is more susceptible to hydrolysis in aqueous systems and initial studies indicated that hydrolysis may be competitive with the amination, particularly at high pH. The preparation of the NBD derivatives could be accomplished in refluxing ethanol with anhydrous potassium carbonate as a base. The NBD derivatives were crystalline solids with low solubility in most solvents.

The ultraviolet spectra of all the derivatives exhibit maxima characteristic of both chromophores with about 2.4% hypochromism at the pyrimidine absorption maximum for **3a** and no new absorption bands. Table I lists the absorption and emission data for the fluorescent derivatives prepared.

Experimental Section

1-(3-Aminopropylthymine) hydrochloride (**1a** HCl), 1-(3-bromopropyl)uracil (**4b**), and (3-bromopropyl)-N^4-acetylcytosine were prepared by previously reported procedures.[10] Dansyl chloride, NBD chloride (Pierce Chemical Co.), and *N*-(3-bromopropyl)phthalimide (Aldrich Chemical Co.) were used without further purification. Infrared spectra were recorded on a Beckman IR 18A, ultraviolet spectra on an Hitachi Perkin-Elmer 124, NMR spectra on a Varian T-60, and mass spectra on a Hitachi Perkin-Elmer REM-5E. Melting points were observed on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and all samples were dried at 92° (3 Torr) over P_2O_5 prior to analysis.

1-[*N*-(3-Phthalimidopropyl)]thymine (6a). Thymine (5.0 g, 39.0 mmol) was dissolved in DMSO (100 ml) and then treated with potassium carbonate (5.5 g, 40 mmol) and *N*-(3-bromopropyl)phthalimide (5.35 g, 20.0 mmol) for 11 hr at room temperature. After the precipitate was filtered, the filtrate was vacuum concentrated to a viscous, yellowish liquid. This liquid was diluted with water (1:1) and the suspension was extracted with chloroform (5 × 100 ml). The chloroform fractions were combined and concentrated at reduced pressure. The resulting oil was dissolved in a small volume of ethyl acetate and induced to crystallize with ether. A total of 3.89 g was isolated (66% based on alkylating agent): mp 197–198°; ir 3.17, 3.3, 3.52, 5.62, 5.82, 5.90, 7.20, 9.4, 11.2, 13.7 μ; uv max (MeOH) 267 nm (ε 19,100); NMR ($CDCl_3$) δ 1.88 (d, 3 H, 5-CH_3), 2.1 (m, 4 H), 3.7 (m, broad, 2 H), 7.1 (d, 1 H, thymine 6-H), 7.5 (m, 4 H). Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.33; H, 4.83; N, 13.41. Found: C, 61.29; H, 4.83; N, 13.29.

1-[*N*-(3-Phthalimidopropyl)]uracil (6b). Uracil (5.0 g, 45 mmol) was alkylated in a manner similar to thymine with *N*-(3-bromopropyl)phthalimide (5.35 g, 19 mmol). A total of 2.99 g was isolated representing 53% yield, mp 188–189°. The NMR and ir spectra were characteristic, uv max (MeOH) 264 nm (ε 20,100). Anal. Calcd for $C_{15}H_{13}N_3O_4$: C, 60.12; H, 4.39; N, 14.04. Found: C, 59.98; H, 4.78; N, 13.94.

1-[*N*-(3-Phthalimidopropyl)]-N^4-acetylcytosine (6c). N^4-Acetylcytosine (5.0 g, 38.2 mmol) was alkylated in a similar fashion with *N*-(3-bromopropyl)phthalimide (11.0 g, 38.1 mmol). A total of 9.82 g of a white, crystalline (EtOAc) solid was isolated (75%): mp 208–210°; ir 3.12, 5.65, 5.9, 6.0, 6.65, 7.2, 7.6, 9.5, 11.3, 13.7 μ; uv max (MeOH) 272 (ε 16,400), 250 nm (s); NMR ($CDCl_3$) δ 2.28 (s, 3 H, acetyl CH_3), 3.5 (m, 2 H), 3.8 (m, 2 H), 3.97 (m, 2 H), 7.5 (d, 1 H), 7.8 (d, 2 H), 7.87 (d, 2 H), 7.95 (d, 1 H). Anal. Calcd for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46. Found: C, 60.01; H, 5.01; N, 16.28.

1-(3-Azidopropyl)thymine (7a). 1-(3-Bromopropyl)thymine (**4a**, 614 mg, 2.5 mmol) and sodium azide (195 mg, 3.00 mmol) were refluxed in acetonitrile for 18 hr. Afterward the solid was filtered and the solution was concentrated to a gum, which slowly crystallized. The material was recrystallized from water and afforded 399.1 mg (76%): mp 98–100°; ir 4.89 μ; uv max (MeOH) 271 nm (ε 9200); NMR ($CDCl_3$) δ 1.93 (s, 3 H), 2.26 (m, 2 H), 3.42 (m, 2 H), 3.88 (m, 2 H), and 7.1 (s, 1 H). Anal. Calcd for $C_8H_{11}N_5O_2$: C, 45.91; H, 5.30; N, 33.49. Found: C, 45.45; H, 5.01; N, 33.45.

1-(3-Azidopropyl)uracil (7b). 1-(3-Bromopropyl)uracil (**4b**, 1.167 g, 5.0 mmol) and sodium azide (330 mg, 5.0 mmol) were used to prepare 642 mg (55%) of azido derivative, in the manner described above: mp 74.5–76°; ir 4.75 μ; uv max (MeOH) 266 nm (ε 10,400); NMR ($CDCl_3$) δ 2.14 (m, 2 H), 3.44 (t, 2 H), 3.90 (m, 2 H), 5.24 (d, 1 H, J = 4 Hz), and 7.23 (m, 1 H). Anal. Calcd for $C_7H_9N_5O_2 \cdot 2H_2O$: C, 40.75; H, 4.89; N, 33.97. Found: C, 40.29; H, 4.47; N, 33.77.

Aminopropylthymine (1a) from the Amine Hydrochloride. A. 1-(3-Aminopropyl)thymine hydrochloride[10] was dissolved in a minimum volume of water and then made basic with aqueous ammonia or saturated potassium carbonate. This aqueous solution was then continuously extracted with chloroform. In a typical case 11.5 g of the amine hydrochloride afforded after extraction 4.3 g of free amine: mp 119–120°; ir 2.95 (broad), 5.58, 5.98, 7.4, 8.5, and 12.65 μ; uv max (EtOH–H_2O) 270 nm (ε 9400). Anal. Calcd for $C_8H_{11}N_3O_2$: C, 52.45; H, 7.10; N, 22.95. Found: C, 52.19; H, 6.89; N, 22.74.

B. The alternative approach was to reflux the amine salt in absolute ethanol in the presence of anhydrous potassium carbonate for 18 hr. The insoluble salt was filtered and the filtrate was concentrated and chilled to induce crystallization. A typical experiment converted 1.4 g of salt (in ethanol with 1.5 g of potassium carbonate) to 900 mg of free amine, mp 120–121°. This sample was identical with the analyzed sample and homogeneous in four TLC systems.

1-(3-Aminopropyl)uracil (1b). 1-[*N*-(3-Phthalimidopropyl)]-uracil (**6b**, 2.0 g, 6.5 mmol) was treated with a solution of 2-butylamine–methanol (1:4 v/v) at reflux for 2 days. The reaction mixture was concentrated to dryness and then partitioned between ethyl acetate and water. The aqueous phase was neutralized with ammonium bicarbonate and then applied in large volume to a C-244 column in NH_4^+ form and eluted with a linear concentration gradient of ammonium bicarbonate (1 l. of 1 M NH_4HCO_3 to 1 l. of water). A total of 140 fractions were collected and the product was distributed from fractions 87 to 110. These were pooled and freeze-dried, and the resulting white powder was dried at 3 Torr over P_2O_5 for 24 hr at 92°, affording 485 mg of an off-white powder. The product was very hygroscopic and tended to gum on exposure to air. It was homogeneous in four TLC systems and electrophoresis: NMR (TFA/TMS) δ 2.42 (t, 2 H), 3.53 (m, 2 H), 4.18 (t, 2 H), 6.15 (d, 1 H, J = 7.8 Hz), 7.07 (s, 2 H), 7.75 (d, 1 H, J = 7.8 Hz); uv max (a bicarbonate salt, H_2O) 261 nm (ε 10,400).

1-(3-Aminopropyl)cytosine (1c). 1-(3-Bromopropyl)-N^4-acetylcytosine (**4c**, 1.506 g, 5.5 mmol) was refluxed for 24 hr in 100 ml of acetonitrile with sodium azide (379 mg, 5.75 mmol). After the solid was filtered, the filtrate was concentrated and applied to a silica gel column in chloroform. Elution with chloroform and then

chloroform–methanol (195:5) afforded 888 mg of a white, crystalline solid (mp 110–112°, remelt, 136–137°). This material was treated with a solution of aqueous ammonia (27%) and pyridine (3:1) for 72 hr. After the solvents were removed a white, crystalline solid was obtained (435 mg, mp 193.5–196°). This material, 1-(3-azidopropyl)cytosine, (400 mg), was dissolved in ethanol–water (1:1) and submitted to catalytic reduction with 5% Pd on carbon at 1 atm. After 10 hr no azide remained. The catalyst was filtered and the reaction mixture was concentrated to a gum. The gum was carefully dissolved in 95% ethanol (small volume). Dilution with 1:1 isopropyl alcohol–ethyl acetate rendered the solution cloudy, and on standing crystallization occurred, affording, after filtering and drying, 314 mg of a white solid, mp 159–162°. Anal. Calcd for $C_7H_{12}N_4O$: C, 49.99; H, 7.19. Found: C, 49.93; H, 7.00. The material was homogeneous in four TLC systems and electrophoresis.

The preparation of aminopropylthymine (**1a**) and aminopropyluracil (**1b**) from the corresponding azides followed the same procedure as above.

***N*-Propyl-5-dimethylaminonaphthalene-1-sulfonamide.** DNS Cl (270 mg, 1 mmol) was dissolved in 25 ml of acetonitrile and the dark yellow solution was treated with propylamine (1 ml). After 30 min no dansyl chloride remained by TLC. The solution was concentrated and partitioned between chloroform and water. The organic phase was filtered over 10 g of silica gel. The filtrate was concentrated to a gum, which was dissolved in 5–10 ml of 95% ethanol. The solution was then rapidly diluted with 10 ml of water and immediately chilled. The cloudy solution afforded, after 18 hr, 280 mg of a white, crystalline solid, representing 96% yield: mp 86–88°; ir 3.02, 7.55, 8.57, 8.70, 8.75, and 12.7 μ; uv max (MeOH) 251 nm (ϵ 12,600), 334 (4800); NMR (pyridine-d_5) δ 0.75 (t, 3 H), 2.74 (s, 6 H), 3.02 (q, 2 H), 4.8 (broad s, 1 H), 7.0 (m, 4 H), and 7.65 (m, 2 H); MS (70 eV) *m/e* (rel intensity) 292 (100, M^+), 171 (130, $M^+ - C_3H_8NSO_2$), 154 (20). Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.60; H, 6.89; N, 9.58; S, 10.97. Found: C, 61.85; H, 6.93; N, 9.29; S, 10.85.

***N*-3-[1-(5-Methyl-2,4-dihydroxypyrimidinyl)]propyl-5-dimethylaminonaphthalene-1-sulfonamide (2a).** 1-(3-aminopropyl)thymine (**1a**, 230 mg, 1.25 mmol) was dissolved in 25 ml of acetonitrile, 5 ml of water, and 5 ml of saturated aqueous sodium bicarbonate. To this mixture was added dansyl chloride (340 mg, 1.26 mmol). The reaction mixture was stirred for 60 min, at which time TLC revealed that no free amine nor amine salt were present. The reaction mixture was concentrated to small volume and recrystallization began. The slurry was chilled at 0° for 12 hr and filtered. After drying in air, 421.4 mg was recovered. The white solid was homogeneous in five TLC systems: mp 194–195°; ir 5.9 (broad), 7.56, 8.05, 8.2, 8.62, 8.75, and 13.9 μ; uv max (MeOH) 258.5 nm (ϵ 18,300), 335 (4800); NMR (pyridine-d_5) δ 1.88 (s, 3 H), 2.78 (s, 6 H), 3.14 (d, 2 H, J = 7 Hz), 3.75 (m, 2 H), 4.84 (s, 1 H, broad), 7.0 (d, 2 H), 7.2 (s, 1 H), 7.26 (m, 2 H), and 7.55 (m, 2 H); MS (70 eV) *m/e* (rel intensity) 416 (100, M^+), 235 (10, M^+ – PrTh), 171 (75, M^+ – APT-SO_2). Anal. Calcd for $C_{20}H_{24}N_4O_4S$: C, 57.67; H, 5.81; N, 13.45; S, 7.69. Found: C, 58.05; H, 5.97; N, 13.31; S, 7.49.

***N*-3-[1-(2,4-Dihyroxypyrimidinyl)]propyl-5-methylaminonaphthalene-1-sulfonamide (2b).** 1-(3-Aminopropyl)uracil (**1b**, 330 mg, 1.95 mmol) was converted in the manner described above into the fluorescent dansyl derivative. The crude product was chromatographed on silica gel with $CHCl_3$ and afforded 423.2 mg (55%) of crystalline solid from $CHCl_3$–CCl_4 (2:1): mp 142–143°; ir 5.9 (broad), 7.56, 8.06, 8.2, 8.62, 8.75, and 13.9 μ; uv max (MeOH) 334 nm (ϵ 4960), 258 (20,000); NMR (pyridine-d_5) δ 1.8 (m, 2 H), 2.8 (s, 6 H), 3.4 (m, 2 H), 3.7 (m, 2 H), 5.50 (d, 1 H, J = 7.0 Hz), 6.95 (d, 1 H, J = 7.0 Hz), 7.0 (d, 2 H), 7.26 (m, 2 H), and 7.55 (m, 2 H). Anal. Calcd for $C_{19}H_{22}N_4O_4S$: C, 56.70; H, 5.51; N, 13.92; S, 7.97. Found: C, 56.68; H, 5.43; N, 13.70; S, 7.68.

***N*-3-[1-(2-Hydroxy-4-aminopyrimidinyl)]propyl-5-dimethylaminonaphthalene-1-sulfonamide (2c).** 1-(3-Aminopropyl)cytosine (**1c**, 168 mg, 1 mmol) was converted by the above-described procedure to the fluorescent dansyl derivative. The crude product was purified by column chromatography on silica gel. The product was eluted with $CHCl_3$–MeOH (19:1). After fractions were pooled and concentrated to a greenish oil, the product was obtained crystalline by diluting a hot EtOH solution with ten volumes of cold water. The greenish, translucent solution was then concentrated on a rotary evaporator at reduced pressure. A greenish-yellow solid crystallized from the solution: 183.3 mg (46%); mg 133–136°; ir 2.82, 2.9, 5.9 (s), 6.65, 7.65, 8.8, and 12.7 μ; uv max (MeOH) 320 nm (ϵ 1800), 286 (19,000); NMR (pyridine-d_5) δ 1.93 (m, 2 H), 2.7 (s, 6 H), 3.12 (m, 2 H), 3.83 (m, 2 H), 5.75 (d, H, J = 7.0 Hz), 7.15 (d, 1 H, J = 7.0 Hz). Anal. Calcd for $C_{19}H_{23}N_5O_3S$: C, 56.84; H, 5.77; N, 17.44; S, 7.99. Found: C, 56.86; H, 6.26; N, 16.62; S, 8.34.

4-Propylamino-7-nitrobenzo-2-oxa-1,3-diazole. To a solution of propylamine (200 mg, 3.4 mmol) in ethyl acetate was added NBD chloride (190 mg, 0.9 mmol). The solution was maintained at 60° under reflux for 2 hr. After evaporation of the solvent, the residue was triturated with chloroform and then water. The brown solid remaining was chromatographed on silica gel in ethyl acetate. The material isolated from the column was crystallized in carbon tetrachloride–chloroform (2:1), affording 120 mg of red-brown crystals (55%): mp 110–112°; ir 3.02, 3.25, 6.16, 6.45, 6.64, 8.35, 10.8, 11.7 μ; uv max (50% MeOH–H_2O) 342 nm (ϵ 7140), 478 (21,400); NMR (TFA) δ 1.1 (t, 3 H), 1.8 (m, 2 H), 3.62 (t, 2 H), 6.5 (d, 1 H, J = 10 Hz), and 8.7 (d, 1 H, J = 10 Hz); MS (70 eV) *m/e* (rel intensity) 222 (95, M^+), 193 (100), 117 (85), 103 (23). Anal. Calcd for $C_9H_{10}N_4O_3$: C, 48.65; H, 4.51; N, 25.23. Found: C, 48.56; H, 4.63; N, 24.95.

4-[3-[1-(5-methyl-2,4-dihydroxypyrimidinyl)]propylamino]-7-nitrobenzo-2-oxa-1,3-diazole (3a). 1-(3-Aminopropyl)thymine (**1a**, 280 mg, 1.5 mmol) was dissolved in 8 ml of absolute ethanol and then added to the amine solution. This mixture was refluxed for 3.5 hr. Afterward the ethanol was evaporated to dryness at reduced pressure. The resulting brown slurry was triturated first with chloroform and then with water. A brown solid (250 mg, 76%) was obtained by filtration. This material was crystallized from 1:1 ethanol–dimethylformamide to afford a red-brown solid: 205 mg (62%); mp 246–250°; ir 3.08, 3.13, 6.04, 6.38, 7.8, 8.0, 12.7, and 12.9 μ; uv max (50% EtOH–H_2O) 270 nm (ϵ 9300), 340 (7100), and 475 (23,000); NMR (TFA) δ 2.0 (s, 3 H), 2.4 (m, 2 H), 3.8 (t, 2 H, J = 5 Hz), 4.2 (t, 2 H, J = 5 Hz), 6.5 (d, 1 H, J = 10 Hz), 7.57 (s, 1 H), 8.7 (d, 1 H, J = 10 Hz); MS (70 eV) *m/e* (rel intensity) 346 (5, M^+), 310 (10), 204 (40), 180 (100). Anal. Calcd for $C_{14}H_{14}N_6O_5$: C, 48.56; H, 4.05; N, 24.28. Found: C, 48.56; H, 4.27; N, 24.12.

4-[3-[1-(2,4-Dihydroxypyrimidinyl)]propylamino]-7-nitrobenzo-2-oxa-1,3-diazole (3b). 1-(3-Aminopropyl)uracil (**1b**) bicarbonate salt (217 mg, 1 mmol) and NBD Cl (220 mg, 1.1 mmol) were combined by the procedure described above to afford 230 mg of a black-brown solid, which was then repeatedly extracted with 2-propanol (5 × 50 ml). All the alcohol extracts were pooled and concentrated to small volume and then chilled. The solid was filtered and air dried: 158 mg; mp 297–301°; ir similar to that of **3a**; uv max (50% EtOH–H_2O) 261 nm (ϵ 10,000), 340 (7000), 476 (22,900); NMR (pyridine-d_5) δ 2.3 (t, 2 H), 3.8 (m, 2 H), 4.21 (t, 2 H), 6.15 (d, 1 H, J = 7.8 Hz), 6.45 (d, 1 H, J = 10 Hz), 7.75 (d, 1 H, J = 7.8 Hz), and 8.65 (d, 1 H, J = 10 Hz). An analytical sample was recrystallized from hot 2-propanol (mp 298–301°). Anal. Calcd for $C_{13}H_{12}N_6O_5$: C, 46.97; H, 3.64; N, 25.30. Found: C, 47.04; H, 3.54; N, 24.15.

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Registry No.—**1a**, 46187-50-2; **1a** HCl, 54517-89-4; **1b**, 54494-30-3; **1c**, 22919-47-7; **2a**, 54494-27-8; **2b**, 54517-90-7; **2c**, 54517-91-8; **3a**, 54494-28-9; **3b**, 54494-29-0; **4a**, 22919-50-2; **4b**, 22917-77-7; **4c**, 22917-95-9; **6a**, 54517-92-9; **6b**, 54517-93-0; **6c**, 38718-31-9; **7a**, 54517-94-1; **7b**, 54517-95-2; **7c**, 54517-96-3; thymine, 65-71-4; uracil, 66-22-8; N^4-acetylcytosine, 14631-20-0; *N*-(3-bromopropyl)-phthalimide, 5460-29-7; *N*-propyl-5-dimethylaminonaphthalene-1-sulfonamide, 54517-97-4; dansyl chloride, 605-65-2; 4-propylamino-7-nitrobenzo-2-oxa-1,3-diazole, 54517-98-5; propylamine, 107-10-8; 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole, 10199-89-0.

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