Amine Exchange and Unexpected Ring-Opening Reactions of Pyranone Derivatives: Synthesis of 3-Amino-Substituted Oxonaphthopyran-carbaldehydes and Tetrahydropyrimidinethanones as New Potential Oligonucleotide Stabilization Agents

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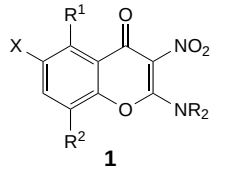
3-[(3-Aminopropyl)amino]-1-oxo-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde (**10**) was synthesized by nucleophilic substitution reaction of 2-(3-dimethylamino)-1-oxo-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde (**9**) and the monoprotected propane-1,3-diamine. The reaction with the unprotected reagent led to the unexpected 1-(2-hydroxynaphthalen-1-yl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (**6**). Extension of this reaction to chromone **16** gave 1-(2-hydroxy-3-isopropyl-6-methylphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (**7**). The X-ray crystal structures of **6** and **7** were also determined.

Introduction. – While developing new strategies to synthesize chromone derivatives, which can be linked to oligonucleotides to form conjugates with enhanced stabilization ability [1], we exploited the peculiar behavior of 3-nitrochromones, which can be summarized as follows: *a*) 2-(dialkylamino)chromones **1** undergo amine exchange when treated with mono- or diamines if position 2 is activated from a suitable substituent in position 3 [2]; *b*) the nitro group in position 3 can be displaced by an amino group (**2** and **3**) or, unexpectedly, by a cyano group (see **4**) [2].



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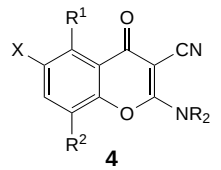

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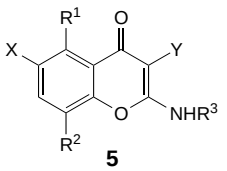

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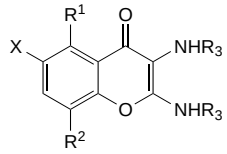

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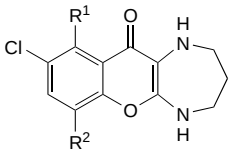

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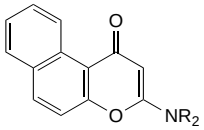

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X = H, Cl, NO_2 Y= NO_2, CHO R^1= Me R^2= i-Pr R^3= $(CH_2)_nNH_2$, $(CH_2)_nMe$

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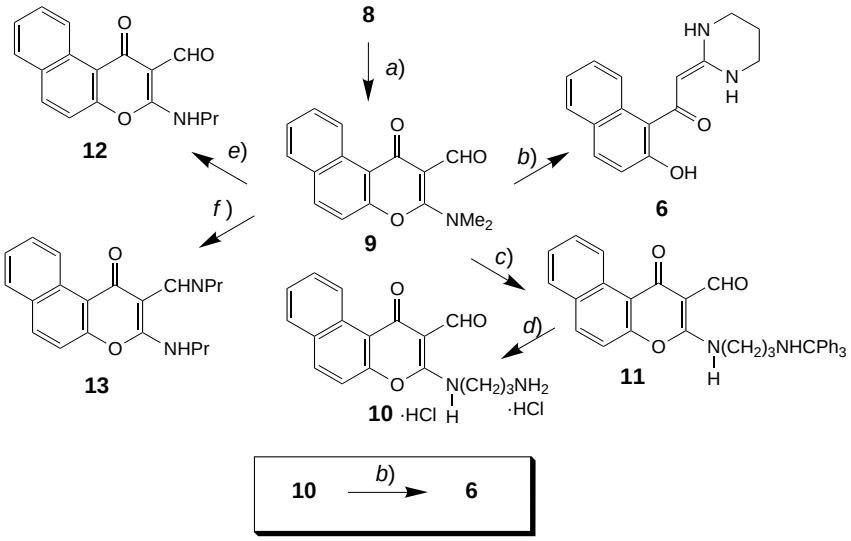
We took advantage of the above behavior by developing, *inter alia*, simple synthetic pathways to 2-[(3-aminoalkyl)amino][1]benzopyran-4(4*H*)-one derivatives **5**. These compounds, which are able to stabilize the complementary oligonucleotide complexes [3], have also demonstrated the ability to interact and inhibit HIV-1 reverse transcriptase (RT) [4][5]. Since these studies pointed out the primary role of formylchromone derivatives that interact with the RT site involved with tRNA [5], we focused our efforts on synthesizing new derivatives with a pyran carbaldehyde structure as a fixed moiety. The present report describes the synthesis of the carbaldehyde derivatives and the serendipitous preparation of the tetrahydropyrimidines **6** and **7** that have been characterized also by X-ray analysis.

Results and Discussion. – For the synthesis of the carbaldehyde derivatives, we used the tricyclic 3-(dimethylamino)-1*H*-naphtho[2,1-*b*]pyran **8** as a starting molecule. The reason for selecting a naphthopyran instead of a chromone derivative was that the naphtho better than the benzo moiety might improve lipophilicity and cell penetration [6].

Vilsmeier formylation of **8** gave the 2-formyl derivatives **9** [7], which, by exploiting our amine-exchange method [2], should have given the desired aminoalkylamino derivatives **10**. However, in this case, we obtained tetrahydropyrimidine derivative **6** as a main product instead of the expected compound **10** (*Scheme 1*).

The synthesis of the 3-aminonaphtho derivative **10** was then accomplished *via* the protected derivative **11**, which was easily obtained from **9** by amine exchange with *N*-

Scheme 1

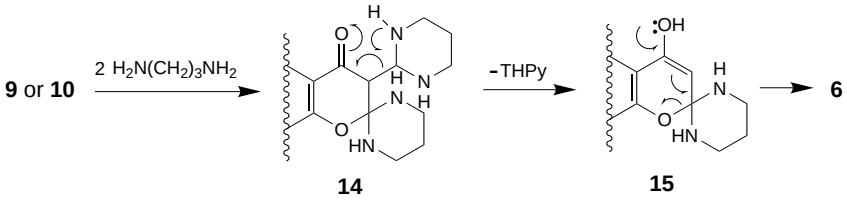


a) *Vilsmeier* formylation. *b*) **9** (0.75 mmol), propane-1,3-diamine (7.5 mmol), toluene, 110°. *c*) **9** (1.5 mmol), *N*-(triphenylmethyl)-1,3-propanediamine (1.5 mmol), toluene, r.t. *d*) Aq. HCl, 60°, 2 h. *e*) **9** (1.5 mmol), propanamine (1.5 mmol), toluene, reflux, 2 h. *f*) **9** (1.5 mmol), propanamine (15 mmol), toluene, reflux, 2 h.

(triphenylmethyl)propane-1,3-diamine at room temperature. Detritylation with HCl gave **10**, which was isolated and purified as the hydrochloric acid salt.

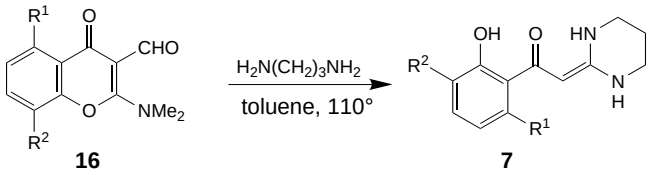
The concomitant presence of the carbaldehyde substituent and the diamine reagent is the most plausible explanation for the formation of the pyrimidine derivative **6**. In fact, reactions involving **9** and 1 mol of propanamine essentially gave the 1-oxo-3-(propylamino)-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde (**12**), while 2 mol of propanamine gave the 3-(propylamino)-2-[(propylimino)methyl]naphtho[2,1-*b*]pyran-1(1*H*)-one (**13**). Furthermore, **10** was converted to **6** by treatment with propane-1,3-diamine under the same conditions used to convert **9** to **6** (*Scheme 1*). The highly hindered monoprotected diamine cannot yield compound **14** due to the obvious steric impediment; consequently, it gives compound **11**. On the contrary, the propane-1,3-diamine could form **14**, which is the key intermediate of the reaction. After elimination of 1,4,5,6-tetrahydropyrimidine, **14** is then converted to **15**, which is the source of **6**. Moreover, the reaction seems to be generally applicable; in fact, the extension to chromone **16** succeeded, and tetrahydropyrimidine **7** was then obtained.

Scheme 2



THPy = 1,4,5,6-tetrahydropyrimidine

Scheme 3



R^1 = Me; R^2 = i-Pr

All new compounds gave satisfactory combustion-analysis and spectroscopic data, in accordance with the given structures (see *Exper. Part*).

X-Ray Structures of **6** *and* **7**. *Fig. 1* shows an ORTEP [8] view of **6** with the atom-numbering scheme, while selected bond distances and angles for both **6** and **7** are reported in *Table 1*.

The molecular structure of **6** is characterized by the presence of intramolecular H-bonds between the carbonyl O(1)-atom as acceptor and the adjacent H-atom belonging to the pyrimidine N-atom and the H-atom of the OH-group of the naphthalene moiety. The length of the latter H-bond O(1)···H–O(2) is 1.67(4) Å with an O(1)···O(2) distance of 2.549(3) Å and an O(1)···H–O(2) angle of 151(4)°, the first one,

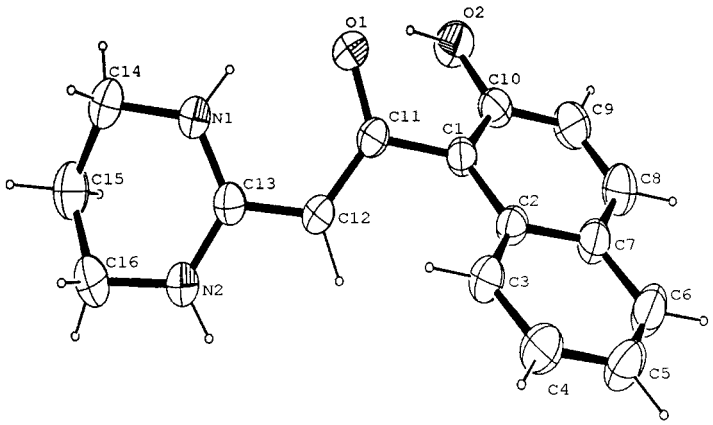


Fig. 1. *ORTEP* [8] *Drawing of the crystal structure of* **6** (ellipsoids at 50% probability)

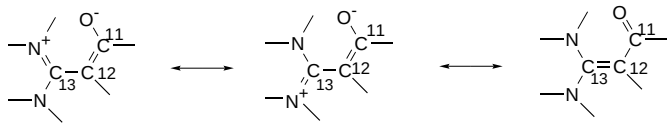
Table 1. *Significant Bond Distances* [Å] *and Angles* [°] *for* **6** *and* **7**

	6	**7**
N(1)–C(13)	1.326(3)	1.332(3)
N(2)–C(13)	1.338(3)	1.325(3)
N(1)–C(14)	1.468(3)	1.452(4)
N(2)–C(16)	1.464(3)	1.452(4)
C(14)–C(15)	1.509(5)	1.512(5)
C(15)–C(16)	1.501(5)	1.499(5)
C(12)–C(13)	1.429(3)	1.427(4)
C(12)–C(11)	1.383(3)	1.369(3)
C(11)–O(1)	1.292(3)	1.305(3)
C(1)–C(11)	1.502(3)	1.500(3)
N(1)–C(13)–N(2)	119.5(2)	119.7(2)
C(13)–N(1)–C(14)	123.5(2)	123.7(2)
C(13)–N(2)–C(16)	122.8(2)	123.3(2)
C(13)–C(12)–C(11)	123.6(2)	124.7(2)
C(12)–C(11)–C(1)	120.0(2)	120.3(2)

N(1)–H···O(1), is 1.97(3) Å with an N(1)···O(1) distance of 2.695(3) Å and an N(1)–H···O(1) angle of 138(3)° (*Fig. 1*). In addition, an intermolecular contact involving the H-atom of N(2) points to the direction of O(1)′ of an adjacent molecule (′at $1/2+x$, $1/2-y$, $1/2+z$) with an N(2)···O(1)′ distance of 2.996(3) Å, N(2)–H···O(2)′ distance of 2.14(3) Å and an N(2)–H···O(2)′ angle of 172(3)°. The tetrahydropyrimidine moiety deserves some comment. The protonation of both N-atoms, N(1)–C(13) and N(2)–C(13) bond distances of 1.326(3) and 1.328(3) Å, respectively, associated with the values of C(13)–C(12) 1.429(4) Å, C(12)–C(11) 1.382(2) Å and C(11)–O(1) 1.292(3) Å, could be justified by the presence of the resonance forms shown in *Scheme 4*.

In fact, the C–N bonds in the ring show some double-bond character, as well C(13)–C(12) and C(12)–C(11), while C(11)–O is longer than a usual C=O group, which is on the order of 1.24 Å, indicating a delocalized π-system.

Scheme 4



The conformation of the heterocycle is that of a half chair with the C(15)-atom 0.676(4) Å out of plane. The overall molecular conformation is characterized by the torsion angle O(1)–C(11)–C(1)–C(2) of 141.5° that avoids contact between H–C(12) and H–C(3). The molecular structure of **7** is reported in *Fig. 2*.

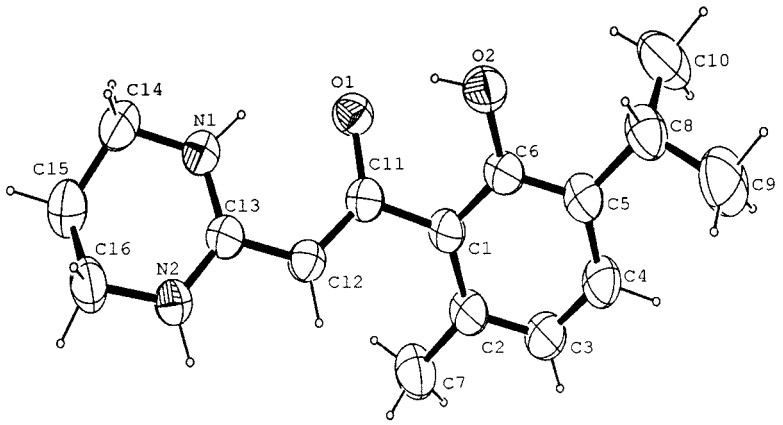


Fig. 2. *ORTEP* [8] *Drawing of the crystal structure of* **7** (ellipsoids at 50% probability)

The molecular skeleton is rather similar to that of **6**, apart from a missing benzene nucleus and the presence of Me and i-Pr groups at C(2) and at C(5), respectively. The values of the common bond distances are in agreement, as shown in *Table 1*. The two intramolecular contacts N(1)–H···O(2) (1.92(3) Å) and its angle (141(3)°; N(1)···O(1) 2.690(3) Å) and O(2)–H···O(1) (1.76(4) Å; O(1)···O(2) 2.603(3) Å) and its angle (150(3)°) are as in **6**. The crystal packing in this case is characterized by an intermolecular contact N(2)–H···O(1)′ (′at x, $1/2-y$, $1/2+z$; 1.87(3) Å; 171(3)°; N(2)···O(1) 2.771(3) Å) with the carbonyl O(1)-atom in addition to the two intramolecular contacts previously described. These results could account for the difference in the NMR spectra of the two compounds in the δ values for NH and OH. The half-chair conformation of the pyrimidine ring is again confirmed from the out-of-plane distance of C(15) of 0.630(4) Å as in **6**.

Conclusions. – The present study has highlighted the capability of our amine-exchange method [2] to be applied to naphthopyran derivatives. We were then able to obtain compound **10**, which can easily be linked to DNA (data not shown). This meets our particular requirements for ongoing studies on selective inhibitors of RT. This synthetic strategy could also be suitable in the preparation of pyran or naphthopyran

derivatives with amino side chains that are more complex and of different lengths. On the other hand, the addition-elimination stages, which give rise to the opening of the pyrone ring, thus giving the new tetrahydropyrimidines **6** and **7**, could open a new route in the preparation of not easily accessible derivatives. The formation of intramolecular H-bonds O(1)···H–O(2) and O(1)···H–N(1) could be important for the elucidation of the enzymatic reaction mechanisms in future applications of these products as stabilizing-intercalating agents.

Experimental Part

General. All commercially available reagents were used without further purification. The reactions were monitored by TLC. M.p.s: *Fisher-Johns* apparatus; uncorrected. IR Spectra: *Perkin-Elmer 398* spectrometer; ν in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AC-300* (300 MHz,^1H; 75 MHz, ^{13}C) or *Varian Gemini-200* (200 MHz,^1H; 50 MHz, ^{13}C) spectrometers; with Me_4Si as internal standard ($\delta = 0$ ppm). Elemental analyses were performed on a *Carlo-Erba 1106 Elemental Analyser* in the Microanalysis Laboratory in our department.

N-*(Triphenylmethyl)propane-1,3-diamine*. Propane-1,3-diamine (25 g, 0.3 mmol) and Ph_3CCl (5.6 g, 0.02 mol) in $CHCl_3$ (150 ml) were kept at r.t. for 2 h. The reaction was quenched with H_2O (150 ml), the org. layer separated, dried ($MgSO_4$), and evaporated. The resulting solid was purified by CC (SiO_2, $CHCl_3$/EtOH/Et_3N 90:7:3) giving the title compound as a white solid (5 g, 79%): M.p. 59–61° ([9]: 59–61°).

*3-(Dimethylamino)-1-oxo-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde* (**9**). In a flask cooled in an ice bath and protected from moisture by a $CaCl_2$ trap, $POCl_3$ (0.92 g, 6 mmol) was added dropwise to 2 ml of DMF. The resulting soln. was stirred for 30 min at r.t. A suspension of 0.96 g (4 mmol) of 3-(dimethylamino) naphtho[2,1-*b*]pyran-1(1*H*)-one in DMF (10 ml) was added, and the mixture was heated at 95°. After 90 min, the mixture was cooled and poured onto crushed ice. The soln. was alkalinized (Na_2CO_3), and **9** precipitated immediately. The colorless solid was collected, washed with H_2O, dried, and crystallized from AcOEt, giving the title compound (0.9 g, 84%). M.p. 218–219° (EtOH) [10]: 218–219°. ^1H-NMR (200 MHz, $CDCl_3$): 3.37 (*s*, 2 Me); 7.34 (*d*, 1 arom. H); 7.56 (*m*, 1 arom. H); 7.66 (*m*, 1 arom. H); 7.75 (*d*, 1 arom. H); 8.05 (*d*, 1 arom. H); 10.02 (*d*, 1 arom. H); 10.31 (*d*, CHO).

*1-(2-Hydroxynaphthalen-1-yl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone* (**6**). A suspension of **9** (0.2 g, 0.75 mmol) and propane-1,3-diamine (0.63 ml, 7.5 mmol) in toluene (5 ml) was stirred at 110° for 2 h. The solvent was evaporated and the residue purified by CC (SiO_2, AcOEt/EtOH 8:2) to give 0.10 g (50%) of **6** as a brownish yellow oil, which solidified with Et_2O. M.p. 226–227° (AcOEt/EtOH 8:2) IR (KBr): 3320, 1620, 1580, 1510, 1460, 1380, 1370. ^1H-NMR (200 MHz, DMSO): 1.88 (*t*, CH_2); 3.33 (*d*, 2 CH_2N); 5.05 (*m*, CH); 7.03 (*m*, 1 arom. H); 7.27 (*m*, 1 arom. H); 7.45 (*m*, 1 arom. H); 7.76 (*m*, 2 arom. H); 8.30 (*d*, 1 arom. H); 9.25 (2 NH); 13.12 (OH). ^{13}C-NMR (50 MHz, (D_6)DMSO): 19.94 (CH_2); 37.72 (CH_2); 37.83 (CH_2); 85.36 (CH);118.10 (C); 119.15 (CH); 122.48 (CH); 124.70 (CH); 126.40 (CH); 128.31 (C); 128.63 (CH); 130.71 (CH); 131.00 (C); 157.24 (C); 159.36 (C); 179.58 (C). Anal. calc. for $C_{16}H_{16}N_2O_2$ (268.31): C 71.62, H 6.01, N 10.44; found: C 71.96, H 6.18, N 10.76.

By the above procedure, **6** was prepared from 3-[(3-aminopropyl)amino]-1-oxo-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde (**10**; 0.25 g, 0.75 mmol) and propane-1,3-diamine (0.63 ml, 7.5 mmol) in toluene (5 ml). After purification of the residue, 0.7 g (28%) of **6** were obtained.

*1-(2-Hydroxy-3-isopropyl-6-methylphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone* (**7**). Analogously to the preparation of **6**, 0.2 g (0.75 mmol) of 2-(dimethylamino)-8-isopropyl-5-methyl-4-oxo-4*H*-[1]benzopyran-3-carbaldehyde **16** and propane-1,3-diamine (0.63 ml, 7.5 mmol) in toluene (5 ml) was heated at 110° for 3 h. After cooling, the yellow precipitate was filtered off and crystallized from AcOEt (0.12 g, 58%). M.p. 240° (AcOEt). IR (KBr): 3320, 1620, 1580, 1510, 1460, 1380, 1370. ^1H-NMR (200 MHz, $CDCl_3$): 1.19 (*s*, Me); 1.22 (*s*, Me); 1.6 (2 NH); 2.00 (*m*, CH_2); 2.4 (*s*, Me); 3.38 (*m*, 2 CH_2, CH); 4.68 (*s*, CH); 6.62 (*d*, 1 arom. H); 7.02 (*d*, 1 arom. H); 11.25 (*s*, 1 OH). ^{13}C-NMR (50 MHz, (D_6)DMSO): 20.79 (CH_2); 22.56 (Me); 23.10 (2 Me); 26.91 (CH); 38.70 (2 CH_2); 86.01 (CH); 121.77 (CH); 125.91 (C); 126.41 (CH); 132.60 (C); 133.58 (C); 155.97 (C); 159.99 (C); 184.02 (C). Anal. calc. for $C_{16}H_{22}N_2O_2$ (274.36): C 70.04, H 8.08, N 10.21; found: C 69,63, H 8.31, N 10.35.

*3-[(3-Aminopropyl)amino]-1-oxo-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde Hydrochloride* (**10**·HCl). A soln. of **9** (0.4 g, 1.5 mmol) and 0.47 g (1.5 mmol) of *N*-(triphenylmethyl)propane-1,3-diamine in 15 ml of toluene was stirred at r.t. for 3 h. Evaporation of the solvent and purification of the residue by CC (SiO_2,

AcOEt) yielded 0.65 g of crude 1-oxo-3-{3-[(triphenylmethyl)amino]propylamino}-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde (**11**), which was hydrolyzed with diluted HCl at 60° for 2 h. H_2O was removed by co-evaporation with toluene and the residue crystallized with EtOH to give **10** · HCl (0.3 g, 60%) as colorless crystals. M.p. 210–213° (EtOH). IR (KBr): 3400, 2900, 2000, 1660, 1630, 1610, 1560, 1490. ^{1}H-NMR (200 MHz,(D_6)DMSO): 2.05 (*m*, CH_2); 2.90 (*m*, CH_2N); 3.72 (*m*, CH_2N); 7.73 (*m*, 3 arom. H); 8.07 (*d*, 1 arom. H); 8.20 (NH_3); 8.35 (*d*, 1 arom. H); 9.90 (*d*, 1 arom. H); 10.13 (*s*, CHO); 10.25 (NH). ^{13}C-NMR (50 MHz, (D_6)DMSO): 27.15 (CH_2); 36.46 (CH_2); 37.82 (CH_2); 100.67 (C); 114.48 (C); 117.46 (CH); 126.43 (CH); 126.54 (CH); 128.87 (CH); 129.26 (CH); 130.36 (C); 131.05 (C); 135.78 (CH); 154.36 (C); 163.05 (C);177.94 (C); 188.74 (CHO). Anal. calc. for $C_{17}H_{17}N_2O_3Cl$ (332.78): C 61.36, H 5.15, N 8.42, Cl 10.35; found: C 60.96, H 5.35, N 8.26, Cl 10.95.

*1-Oxo-3-(propylamino)-1*H*-naphtho[2,1-*b*]pyran-2-carbaldehyde* (**12**). A soln. of 0.4 g (1.5 mmol) of **9** and propanamine (0.12 ml, 1.5 mmol) in toluene (15 ml) was refluxed for 2 h. The mixture was allowed to cool to r.t., and the precipitate was collected by filtraton and purified by CC (SiO_2, AcOEt) to give 0.29 g (69%) of **12** as yellow crystals. M.p. 147–148° (EtOH; [11]: 147–148°). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.07 (*t*, Me); 1.79 (*m*, CH_2); 3.53 (*m*, CH_2); 7.35 (*d*, 1 arom. H); 7.57 (*m*, 1 arom. H); 7.68 (*m*, 1 arom. H); 7.75 (*d*, 1 arom. H); 8.02 (*d*, 1 arom. H); 10.00 (*d*, 1 arom. H); 10.30 (*d*, CHO); 10.40 (NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 11.85 (Me); 23.25 (CH_2); 42.95 (CH_2); 101.21 (C); 115.80 (C); 116.65 (CH); 126.92 (CH); 127.71 (CH); 128.66 (CH); 129.76 (CH); 131.45 (C); 131.60 (C); 134.79 (CH); 154.64 (C); 163.87 (C); 178.93 (C); 190.58 (CHO).

*3-(Propylamino)-2-[(propylimino)methyl]naphtho[2,1-*b*]pyran-1-(1*H*)-one* (**13**). A mixture of 0.48 g (1.5 mmol) of **9** and propanamine (1.23 ml, 15 mmol) in toluene (15 ml) was refluxed for 2 h. The solvent was evaporated, and the residue treated with petroleum ether. The resulting yellow solid, which was crystallized with EtOH, gave **13** (0.32 g, 66%). M.p. 76–77° (EtOH). IR (KBr): 3100, 2980, 2960, 2740, 1650, 1630, 1590, 1570. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.96 (*t*, Me); 1.05 (*t*, Me); 1.70 (*m*, 2 CH_2); 3.52 (*m*, 2 CH_2); 7.30 (*d*, 1 arom. H); 7.54 (*m*, 1 arom. H); 7.68 (*m*, 1 arom. H); 7.80 (*d*, 1 arom. H); 7.95 (*d*, 1 arom. H); 8.80 (*s*, CHN); 10.10 (*d*, 1 arom. H); 11.50 (NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 12.15 (Me); 12.26 (Me); 24.00 (CH_2); 25.00 $(CH)_2$); 44.38 (CH_2); 59.13 (CH_2); 97.50 (C); 114.93 (C); 117.19 (CH); 126.10 (CH); 127.80 (CH);

Table 2. *Crystal and Refinement Data for* **6** *and* **7**

	6	**7**
Formula	$C_{16}H_{16}N_2O_2$	$C_{16}H_{22}N_2O_2$
M_r	268.31	274.36
Crystal system	monoclinic	monoclinic
Space group	$P2_1$/n	$P2_1$/c
a [Å]	9.829(2)	11.721(2)
b [Å]	12.042(3)	11.024(3)
c [Å]	11.762(3)	11.965(3)
β [°]	102.65(2)	101.07(2)
V/[Å^3]	1358.4(6)	1517.3(6)
Z	4	4
D_c/[g cm^{-3}]	1.312	1.201
Temp./K	293	293
μ(MoK_α) [mm^{-1}]	0.088	0.080
Crystal size [mm]	0.11 × 0.13 × 0.08	0.10 × 0.12 × 0.10
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Data collected	(−12,0,0) to (12,15,15)	(−15, −2,0) to (15,14,15)
θ [°]	3.05–28.00	3.28–28.00
Refls. collected	2949	3232
Unique refls.	2819 (R_{int} = 0.011)	3098 (R_{int} = 0.016)
Data, restraints, parameters	2819,0,245	3098,0,269
Goodness-of-fit (F^2)	1.318	1.280
R ($I \geq 2\sigma(I)$[a])	0.069 (2722 refls.)	0.0790 (3000 refls.)
Rw_F[b])	0.1520	0.1625

[a]) $\Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b]) $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

128.51 (CH); 129.12 (CH); 131.18 (C); 131.89 (C); 134.78 (CH); 155.00 (C); 157.80 (CHN); 159.40 (C); 178.59 (C). Anal. calc. for $C_{20}H_{22}N_2O_2$ (332.40): C 74.51, H 6.88, N 8.69; found: C 74.10, H 6.78, N 8.77.

X-Ray Crystallography. The crystal data are given in *Table 2*. The intensity data were collected on a *CAD4* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71073 Å). The cell parameters were determined and refined by least-squares fit of 20 high-angle reflections. The structures were solved by direct methods using Sir-92 [12] and conventional *Fourier* synthesis [13]. The refinement of the structures was made by full-matrix least-squares on F^2. All non-H-atoms were refined anisotropically. The H-atom positions were detected in a difference *Fourier* synthesis and refined with isotropic thermal factors. The supplementary crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition Nos. CCDC-172504 and -172505). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44(1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

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