
NITRILES IN HETEROCYCLIC SYNTHESIS: A NOVEL ROUTE FOR THE SYNTHESIS OF NAPHTHODIPYRANS, PYRIDINES, 2H- AND 4H-PYRANS

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Naphtho[2,1-*b*: 3,4-*b'*]dipyrans, naphtho[1,2-*b*: 5,6-*b'*]dipyrans and naphtho[1,2-*b*: 6,5-*b'*]dipyrans were synthesized by the reaction of cinnamonnitriles with 2,3-, 1,5-, 1,6-naphthalenediols, respectively. Polysubstituted pyridines, 2H-pyrans and 4H-pyrans were also synthesized from cinnamonnitriles, 2-hydroxyacetophenone and 3-acetyl-4-hydroxy-1-methylcarbostyryl, respectively.

The reaction of cinnamonnitriles with active hydrogen reagents has been utilized extensively in the synthesis of 4H-pyrans¹⁻³ and fused pyrans^{4,5}. Recently⁶, we have shown that phenols, 1-naphthol and 2-naphthol also react readily with cinnamonnitriles to yield 4H-benzopyrans and 4H-naphthopyrans, respectively.

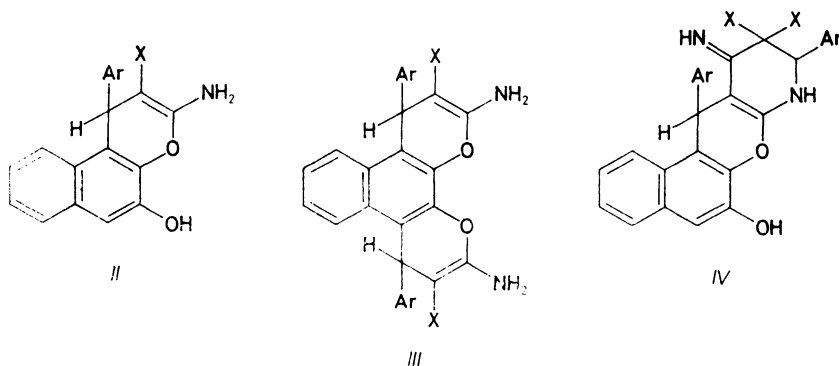
The behaviour of several substituted naphthols and phenols was investigated in the framework of this work. It has been found that *Ia*, *Ib*, *Id*, and *Ie* react with 2,3-naphthalenediol in ethanolic piperidine to yield either 1 : 1 adducts or 2 : 1 adducts depending on the applied reaction conditions. For the 1 : 1 adducts structure *II* could be suggested, based on analytical and ¹H NMR data, whereas two isomeric structures (*III* and *IV*) seemed possible for the 2 : 1 adducts. The structure *IV*, similar to that observed⁷ recently during the reaction of adjacent NH₂ and CN groups in pyrans, was suggested on the basis of ¹H NMR spectra which revealed only one signal for pyran H-4. If the reaction product was *IV*, one would expect two magnetically non-equivalent protons for 4H-pyran and pyridine H-2. Thus structure *III* was suggested for the reaction of *Ia*, *Ib*, *Id*, and *Ie* with 2,3-naphthalenediol in a molar ratio 2 : 1. *Iia*–*Iid* were converted into the 1 : 2 diadducts *IIIa*–*IIId* after further treatment with *Ia*, *Ib*, *Id*, and *Ie*, respectively.

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In formulae *1a, d* Ar = C₆H₅ ; *1b, e* Ar = 4-CH₃O-C₆H₄ ;
1c, f Ar = 4-Cl-C₆H₄

When *IIc* reacted with *Ia*, the 1 : 2 diadduct *Va* was formed. ¹H NMR of *Va* revealed two magnetically non-equivalent protons (at δ 5.45 and 5.75 ppm) for two protons linked to two sp³ carbons; both appeared at fields very similar to those of *IIIa* and *IIIc*. Also, the compound *IIId* reacted with *Ib* to yield *Vc*.



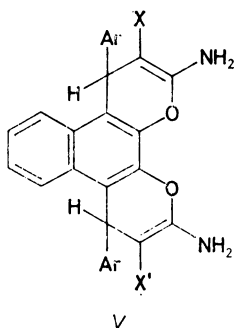
In formulae II-IV: *a*, Ar = C₆H₅; X = CN *b*, Ar = 4-CH₃O-C₆H₄; X = CN
c, Ar = C₆H₅; X = COOC₂H₅ *d*, Ar = 4-CH₃O-C₆H₄; X = COOC₂H₅

In the case of the formation of *Vb*, *Vd* by the reaction of *IIb* + *Ia* and *IIc* + *Ie* two non-equivalent protons appeared too; thus, the one appearing at higher field is attributed to the 4*H*-pyran proton linked to the aryl moiety carrying electron-donating substituents.

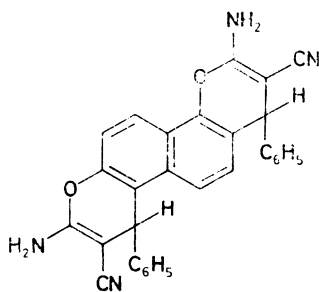
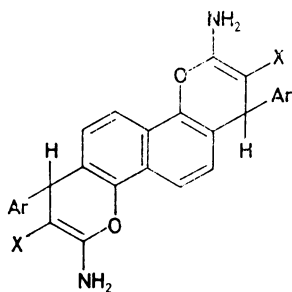
Reaction of *Ia* with 1,5-naphthalenediol or 1,6-naphthalenediol in a molar ratio 1 : 1 afforded products of molecular formulae C₃₀H₂₀N₄O₂ (M⁺ = 468) which correspond to naphtho[1,2-*b*:5,6-*b'*]dipyran *VIa* and naphtho[1,2-*b*:6,5-*b'*]dipyran *VII*, respectively. The same products could also be obtained in good yields by reacting of *Ia* with naphthalenediols in a molar ratio 2 : 1. Similarly, polysubstituted dipyrans *VIb*–*VIId* were also prepared from *Ib*, *d*, *e* and 1,5-naphthalenediol.

¹H NMR of *VII* revealed two pyran H-4 proton signals at δ 5.3 and δ 4.7 ppm. The pyran H-4 in *III*, *V* and *VII* is deshielded by about δ 0.5 ppm in comparison with that expected for 4*H*-pyran as a result of van der Waals deshielding effect of adjacent aryl protons.

1,7- or 2,7-Naphthalenediol failed to react with *I* in ethanolic piperidine or in dry pyridine. This may be attributed to the molecular overcrowding arising from the difficult formation of two pyran moieties located at 1,2- and 6,7-positions in the naphthalene ring.



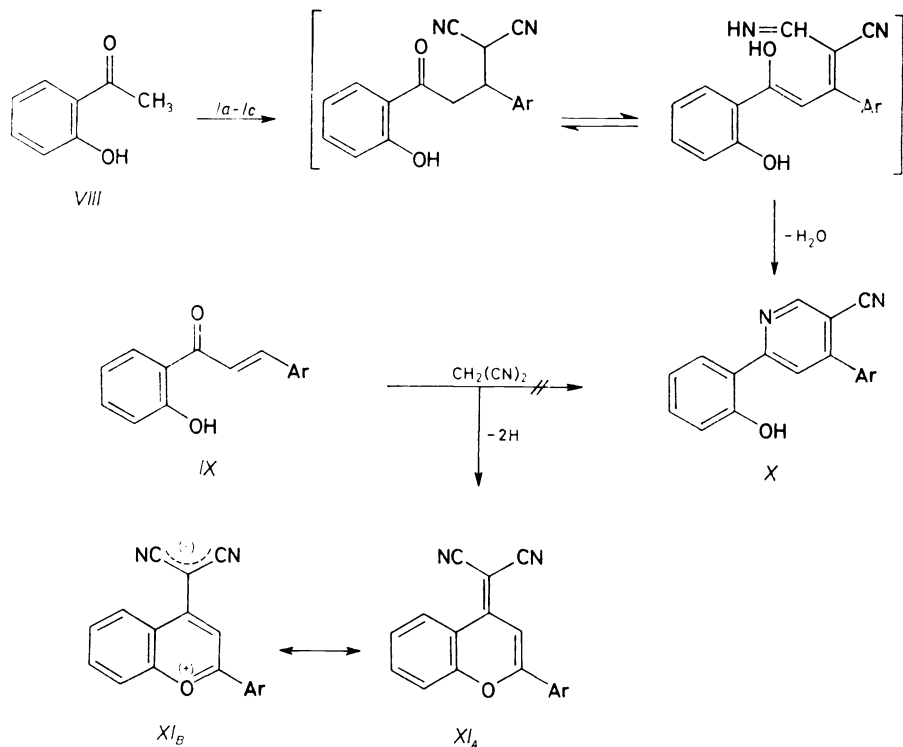
In formula V: *a*, Ar = Ar' = C₆H₅; X = CN; X' = COOC₂H₅ *b*, Ar = 4-CH₃O-C₆H₄; Ar' = C₆H₅; X = X' = CN *c*, Ar = Ar' = 4-CH₃O-C₆H₄; X = CN; X' = COOC₂H₅ *d*, Ar = C₆H₅; Ar' = 4-CH₂O-C₆H₄; X = X' = COOC₂H₅.



In formula VI: *a*, Ar = C₆H₅; X = CN *b*, Ar = 4-CH₃O-C₆H₄; X = CN
c, Ar = C₆H₅; X = COOC₂H₅ *d*, Ar = 4-CH₃O-C₆H₄; X = COOC₂H₅

Although compounds containing a cyanoacetyl group⁸⁻¹⁰ are highly reactive reagents in heterocyclic synthesis, no attention was paid to the possible utilization of the acetyl function in aromatic or heteroaromatic systems for reactions of this type. In the present paper we report the results of our investigations on the reaction of cinnamionitriles *Ia*–*If* with 2-hydroxyacetophenone (*VIII*) and 3-acetyl-4-hydroxy-1-methylcarbostyryl (*IX*). The nature of the end products was found to be dependent on the nature of the utilized reactants and the time of reaction until complete precipitation, which ranges from 6 h for *VIII* to 10 min for *IX*.

Thus, *Ia–Ic* reacted with *VIII* to yield condensation products via water elimination. Structure *X* was suggested for these products on the basis of ^1H NMR spectra which revealed a low field signals at δ 8.6 for pyridine H-2. The absence of a methyl function in ^1H NMR spectra is also considered as an evidence for involvement of the acetyl group in the reaction. Formation of *X* from *Ia–Ic* and *VIII* is assumed to proceed via the sequence demonstrated in Scheme 1. Similar mechanism was sug-

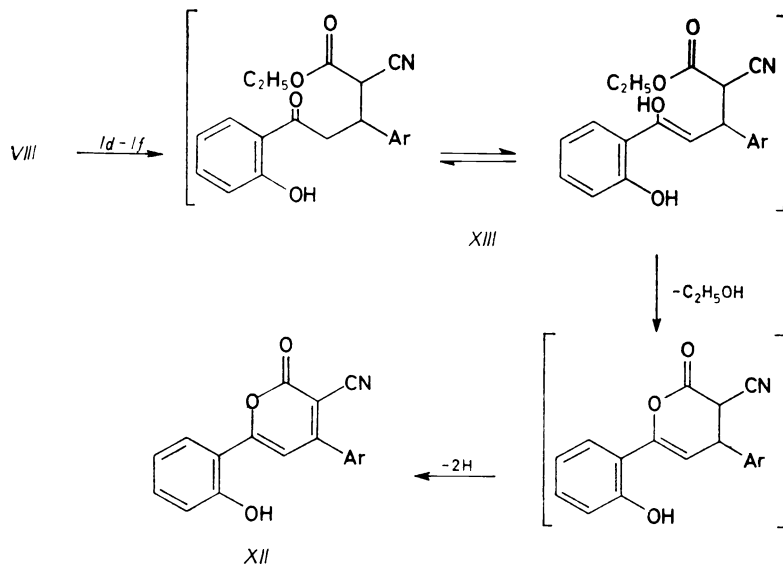


In formulae IX, XI: a, Ar = C_6H_5 b, Ar = 4-Cl- C_6H_4

SCHEME 1

gested previously for the formation of isoquinoline¹¹. Trials to obtain *X* by the reaction of chalcones¹² with malononitrile under the same reaction conditions (cf. Experimental) have resulted in the formation of a flavone which exists, most likely, as an mesomeric hybrid of $\text{XI}_A \leftrightarrow \text{XI}_B$. Compound *XI* was found to be inert towards bromination and action of other electrophilic reagents.

In contrast to *Ia–Ic*, *Id–If* reacted with *VIII* in ethanolic piperidine to yield condensation products for which 2*H*-pyrone structure *XII* was suggested, on the basis of IR and ¹H NMR spectra. IR spectra revealed absorption bands characteristic for OH, CN, and CO groups. ¹H NMR revealed signals characteristic for aromatic proton multiplet and a low field proton at δ 8.35 for the pyrone H-5. Also a broad D₂O exchangeable signal for phenolic OH appeared at δ 7.8. The formation of *XII* is assumed to proceed via Michael type addition of the methyl function in *VIII* to the activated double bond to yield the acyclic adduct *XIII* which then cyclized into *XII* via the ethanol and hydrogen elimination. Elimination of H₂ in similar systems was observed previously^{13–15} (Scheme 2).



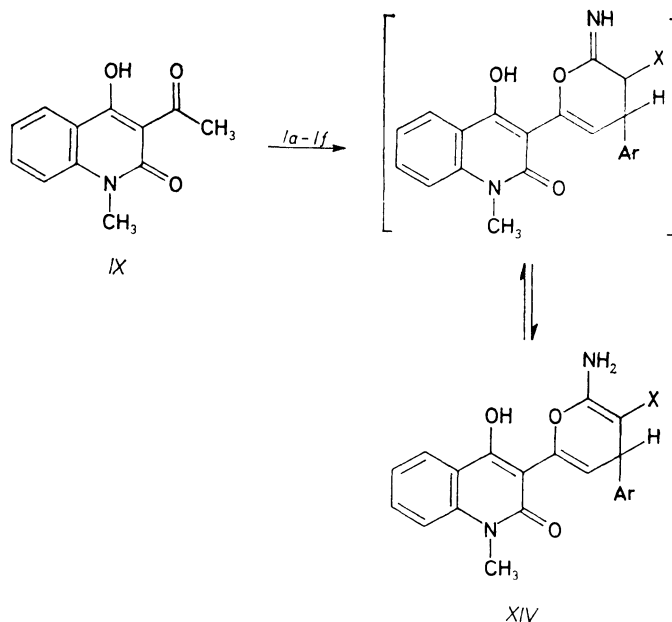
In formulae X, XII: a, Ar = C₆H₅ b, Ar = 4-OCH₃-C₆H₄ c, Ar = 4-Cl-C₆H₄

SCHEME 2

Ia–If reacted with 3-acetyl-4-hydroxy-1-methylcarbostyryl (*IX*) to form 1:1 adducts (Scheme 3). Although several isomeric structures seemed possible, structure *XIV* was suggested, as ¹H NMR spectra revealed a signal at δ 4.6 ~ 4.8 for 4*H*-pyran protons and at δ 3.3 for the amino group.

It is necessary to mention that the aromatic OH function in *VIII* and *IX* was not involved in the reactions, in contrast to the observed⁶ high reactivity of phenolic OH towards *I* (cf. structures *II–VII*). This may be attributed to involvement of the hydroxy function in *VIII* and *IX* in hydrogen bonding. However, deactivation of the

carbon adjacent to the hydroxyl group in compound VIII by electron-withdrawal effect of acetyl function cannot be overlooked.



In formula XIV: *a*, Ar = C₆H₅; X = CN *b*, Ar = 4-OCH₃-C₆H₄; X = CN
c, Ar = 4-Cl-C₆H₄; X = CN *d*, Ar = C₆H₅; X = COOC₂H₅
e, Ar = 4-OCH₃-C₆H₄; X = COOC₂H₅ *f*, Ar = 4-Cl-C₆H₄;
 X = COOC₂H₅

SCHEME 3

EXPERIMENTAL

All melting points are uncorrected. Recorded yields correspond to pure products. IR spectra were recorded (KBr) on a Pye Unicam SP-1100 spectrophotometer. ¹H NMR spectra were measured on a Varian EM-360 Spectrophotometer (60 MHz) in CD₃SOCD₃ solutions using tetramethylsilane as an internal standard, and chemical shifts are expressed as δ values. Micro-analytical data were obtained from the microanalytical Data Unit at Cairo University.

2-Amino-4-aryl-3-cyano (or ethoxycarbonyl)-10-hydroxy-4H-naphtho[2,1-b]pyrans (IIa–II*d*)

A solution of 1.6 g (0.01 mol) of 2,3-naphthalenediol in absolute ethanol (30 ml) was treated with the appropriate cinnamionitrile I (0.01 mol) and piperidine (0.1 ml). The reaction mixture was heated for 15 min and the solid product formed was collected by filtration and recrystallized from a suitable solvent yielding colourless products (cf. Table I).

TABLE I
Analytical data for compounds *Ila*–*Ild* and *IIla*–*IIId*

Compound	M.p., °C (Yield, %)	Formula (M.w.)	Calculated/Found			$\tilde{\nu}$ (KBr), cm ⁻¹ (Selected bands)
			% C	% H	% N	
<i>Ila</i> ^a	281–283 (90)	C ₂₀ H ₁₄ N ₂ O ₂ (314.3) ^c	76.42 76.35	4.50 4.72	8.91 8.85	3 630, 3 510, 3 400–3 200 (NH ₂ , OH); 2 200 (CN)
<i>Ilb</i> ^b	295–297 (95)	C ₂₁ H ₁₆ N ₂ O ₃ (344.4)	73.24 72.96	4.68 4.82	8.13 8.27	3 630, 3 530, 3 410 (NH ₂ , OH); 2 210 (CN)
<i>Ilc</i> ^a	235–237 (85)	C ₂₂ H ₁₉ NO ₄ (361.4)	73.12 73.38	5.30 5.42	3.88 3.72	3 510, 3 450, 3 320 (NH ₂ , OH); 1 700 (C=O)
<i>Ild</i> ^a	260–262 (80)	C ₂₃ H ₂₁ NO ₅ (391.4)	70.58 70.63	5.41 5.65	3.58 3.72	3 500, 3 450, 3 350 (NH ₂ , OH); 1 700 (C=O)
<i>IIla</i> ^a	> 300 (85)	C ₃₀ H ₂₀ N ₄ O ₂ (468.5) ^d	76.91 76.82	4.30 4.40	11.96 12.15	3 650, 3 500–3 300 (NH ₂), 2 200 (CN); 1 650 (δ NH ₂)
<i>IIlb</i> ^b	> 300 (85)	C ₃₂ H ₂₄ N ₄ O ₄ (528.6)	72.72 72.98	4.58 4.51	10.60 10.68	3 510, 3 400, 3 220 (NH ₂); 2 200 (CN); 1 660 (δ NH ₂)
<i>IIlc</i> ^b	264–266 (90)	C ₃₄ H ₃₀ N ₂ O ₆ (562.6)	72.58 72.66	5.37 5.41	4.98 5.22	3 530, 3 400, 3 220 (NH ₂); 1 690 (CO); 1 660 (δ NH ₂)
<i>IIId</i> ^b	282–284 (75)	C ₃₆ H ₃₄ N ₂ O ₈ (622.7)	69.44 69.62	5.50 5.38	4.50 4.37	3 550, 3 430–3 200 (NH ₂); 1 690 (CO)

Compounds *Ila*–*Ild* and *IIla*–*IIId* were obtained as colourless products. Crystallized from ^a ethanol-dimethylformamide, ^b dioxane. M⁺ is ^c 314 and ^d 468.

TABLE II
Analytical data for compounds *Va*–*Vd*

Compounds ^a	M.p., °C	Utilized reagents	Yield ^b	Formula (M.w.)	Calculated/Found		
					% C	% H	% N
<i>Va</i>	> 300	(i) <i>Ila</i> + <i>Id</i>	75	C ₃₂ H ₂₅ N ₃ O ₄ (515.6)	74.55	4.89	8.15
		(ii) <i>Ilc</i> + <i>Ia</i>			74.68	5.11	8.38
<i>Vb</i>	> 300	(i) <i>Ila</i> + <i>Ib</i>	65	C ₃₁ H ₂₂ N ₄ O ₃ (498.5)	74.69	4.45	11.24
		(ii) <i>Ilb</i> + <i>Ia</i>			74.38	4.43	11.54
<i>Vc</i>	> 300	(i) <i>Ilb</i> + <i>Ie</i>	60	C ₃₄ H ₂₉ N ₃ O ₆ (575.6)	70.94	5.08	7.30
		(ii) <i>Ild</i> + <i>Ib</i>			70.83	5.23	7.45
<i>Vd</i>	273–275	(i) <i>Ilc</i> + <i>Ie</i>	65	C ₃₅ H ₃₂ N ₂ O ₇ (592.7)	70.93	5.44	4.73
		(ii) <i>Ild</i> + <i>Id</i>			70.77	5.31	4.81

^a Compounds *Va*–*Vd* were obtained as colourless crystals from ethanol-dioxane; ^b yields obtained by method (i) or (ii) are nearly the same.

2,11-Diamino-3,10-dicyano-(or diethoxycarbonyl)-4,9-diaryl-4,9-dihydronaphtho[2,1-*b*:3,4-*b'*]dipyrans *IIIa*—*III d*

From 2,3-naphthalenediol and two moles of I: A suspension of 1.6 g (0.01 mol) of 2,3-naphthalenediol and 0.02 mol of *Ia*, *Ib* or *Id*, *Ie* in ethanol (30 ml) was refluxed in the presence of piperidine (0.1 ml) for 30 min. The obtained solid products were collected by filtration and recrystallized yielding colourless products (cf. Table I).

TABLE III
Infrared spectra (selected bands) of compounds *Va*—*Vd*

Compound	$\tilde{\nu}$, cm^{-1}
<i>Va</i>	3 580, 3 280, 3 170 (NH_2), 2 190 (CN), 1 670 (CO)
<i>Vb</i>	3 500, 3 395, 3 300, 3 190 (NH_2), 2 190 (CN)
<i>Vc</i>	3 450, 3 390, 3 280, 3 170 (NH_2), 2 190 (CN), 1 660 (CO)
<i>Vd</i>	3 450, 3 400, 3 300 (NH_2), 1 690 (CO), 1 640 (δNH_2)

TABLE IV
Analytical data for the synthesized compounds *VIa*—*VI d* and *VII*

Compound (Colour)	M.p., °C (Yield, %)	Formula (M.w.)	Calculated/Found			$\tilde{\nu}$, cm^{-1} (Selected bands)
			% C	% H	% N	
<i>VIa</i> ^a (yellow)	>300 (85)	$\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_2$ (468.5) ^c	76.91 77.15	4.30 4.50	11.96 11.71	3 460, 3 350— —3 250(NH_2), 2 210(CN), 1 660(δNH_2)
<i>VIb</i> ^a (yellow)	>300 (80)	$\text{C}_{32}\text{H}_{24}\text{N}_4\text{O}_4$ (528.6)	72.72 72.57	4.58 4.81	10.60 10.92	3 450, 3 330, 3 210(NH_2) 2 200(CN), 1 660(δNH_2)
<i>VIc</i> ^a (colourless)	285—287 (75)	$\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_6$ (562.6)	72.58 72.82	5.37 5.25	4.98 5.24	3 400, 3 300 (NH_2) 1 690 (C=O)
<i>VI d</i> ^b (colourless)	292—294 (73)	$\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_8$ (622.7)	69.44 69.35	5.50 5.43	4.50 4.33	3 430, 3 320 (NH_2) 1 700 (C=O)
<i>VII</i> ^a (yellow)	>300 (90)	$\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_2$ (468.5) ^c	76.91 76.73	4.30 4.55	11.96 11.89	3 500, 3 200(NH_2), 2 220 (CN), 1 650(δNH_2)

Crystallized from ^a dimethylformamide, ^b ethanol; ^c M^+ is 468.

From II and I: A suspension of equimolecular amounts (0.01 mol) of *Ila*–*Ild* and *Ia*, *Ib*, *Id*, *Ie* in ethanol (30 ml) and piperidine (0.1 ml) was refluxed for 15 min. The products obtained in this manner were collected by filtration, crystallized and identified as *IIIa*–*IIId*. Compound *Va* can be also obtained from the reaction of *Ila* with *Id* or from *Iic* with *Ia*, following the procedure

TABLE V
Analytical data for compounds *X*, *XI*, *XII* and *XIV*

Compound (Colour)	M.p., °C (Yield, %)	Formula (M.w.)	Calculated/Found			$\tilde{\nu}$, cm ⁻¹ (Selected bands)
			% C	% H	% N	
<i>Xa</i> ^a (orange)	> 300 (60)	C ₁₈ H ₁₂ N ₂ O (272.3)	79.39 79.63	4.44 4.52	10.29 10.18	3 500–3 300 (OH), 2 220 (CN)
<i>Xb</i> ^a (orange)	> 300 (55)	C ₁₉ H ₁₄ N ₂ O ₂ (302.3)	75.48 75.31	4.67 4.52	9.27 9.05	3 500–3 350 (OH), 2 220 (CN)
<i>Xc</i> ^a (orange)	> 300 (52)	C ₁₈ H ₁₁ ClN ₂ O (306.8)	70.48 70.45	3.61 3.43	9.13 8.75	3 550–3 300 (OH), 2 220 (CN)
<i>XIa</i> ^b (colourless)	215–217 (72)	C ₁₈ H ₁₀ N ₂ O (270.3)	79.99 79.89	3.72 3.83	10.36 10.54	2 220 (CN)
<i>XIb</i> ^b (yellow)	275–277 (70)	C ₁₈ H ₉ ClN ₂ O (304.7)	70.95 70.72	2.98 3.19	9.19 9.37	2 200 (CN)
<i>XIIa</i> ^a (yellow)	248–250 (75)	C ₁₈ H ₁₁ NO ₃ (289.3)	74.73 75.00	3.83 4.15	4.84 4.60	3 500–3 350 (OH), 2 210 (CN), 1 700 (CO)
<i>XIIb</i> ^a (yellow)	230–232 (75)	C ₁₉ H ₁₃ NO ₄ (319.3)	71.47 71.18	4.10 4.32	4.39 4.37	3 550, 3 350 (OH), 2 210 (CN), 1 710 (CO)
<i>XIIc</i> ^a (yellow)	265–267 (75)	C ₁₈ H ₁₀ ClNO ₃ (323.7)	66.78 66.52	3.11 3.19	4.32 4.21	3 450, 3 350 (OH), 2 210 (CN), 1 710 (CO)
<i>XIVa</i> ^b (yellow)	302–304 (95)	C ₂₂ H ₁₇ N ₃ O ₂ (371.4)	71.15 71.22	4.61 4.54	11.31 11.42	3 400–3 300 (OH, NH ₂), 2 200 (CN), 1 670 (CO)
<i>XIVb</i> ^b (orange)	260–262 (95)	C ₂₃ H ₁₉ N ₄ O ₃ (401.4)	68.82 68.70	4.77 4.65	10.47 10.43	3 400–3 300 (OH, NH ₂), 2 200 (CN), 1 680 (CO)
<i>XIVc</i> ^b (orange)	234–236 (92)	C ₂₂ H ₁₆ ClN ₃ O ₂ (405.8)	65.11 64.90	3.97 4.10	10.35 10.12	3 520–2 890 (OH, NH ₂), 2 190 (CN), 1 670 (CO)
<i>XIVd</i> ^a (colourless)	> 300 (95)	C ₂₄ H ₂₂ N ₂ O ₅ (418.5)	68.89 69.11	6.69 5.41	6.69 6.72	3 400–3 300 (OH, NH ₂), 1 690, 1 660 (CO)
<i>XIVe</i> ^b (colourless)	258–260 (90)	C ₂₅ H ₂₄ N ₂ O ₆ (448.5)	66.95 67.00	5.39 5.60	6.25 6.29	3 400, 3 280 (OH, NH ₂), 1 690, 1 650 (CO)
<i>XIVf</i> ^a (colourless)	275–277 (95)	C ₂₄ H ₂₁ ClN ₂ O ₅ (452.9)	63.65 63.50	4.67 4.90	6.19 6.41	3 400–3 280 (OH, NH ₂), 1 690, 1 660 (CO)

Crystallized from ^aethanol–dimethylformamide, ^b dioxane.

mentioned above. For reactants utilized for the preparation of *Vb*–*Vd*, see Table II. IR spectra are summarized in Table III.

2,8-Diamino-3,9-dicyano-(or diethoxycarbonyl)-4,10-diaryl-4,10-dihydronaphtho[1,2-*b*:5,6-*b'*]dipyrans *VIa*–*VIId*

A mixture of 1.6 g (0.01 mol) of 1,5-naphthalenediol, 0.01 mol of *Ia*, *Ib* or *Id*, *Ie* and piperidine (0.2 ml) in ethanol (50 ml) was refluxed for 1 h. The mixture was then concentrated and the remaining solid was collected by filtration, crystallized and identified as *VIa*–*VIId* (cf. Table IV).

TABLE VI

¹H NMR data of some prepared compounds

Compound	δ , ppm
<i>Iib</i>	3.7 s, 3 H (OCH ₃); 5.35 s, 1 H (pyran 4-H); 6.7 brs, 2 H (NH ₂ , D ₂ O exchangeable); 6.8–7.9 m, 10 H (ArH + OH)
<i>Iic</i>	1.3 t, 3 H (CH ₃ ester); 4.2 q, 2 H (CH ₂ ester); 5.6 s, 1 H (pyran 4-H); 7–8.1 m, 13 H (ArH + OH + NH ₂); 5.50 s, 2 H (two pyran 4-H); 6.7–7.8 m, 18 H (ArH + two NH ₂)
<i>IIIb</i>	3.8 s, 6 H (two equivalent OCH ₃); 5.45 s, 2 H (two equivalent pyran 4-H); 6.6–7.8 m, 16 H (ArH + two NH ₂)
<i>IIIc</i>	1.4 t, 6 H (two equivalent CH ₃ ester); 4.3 q, 4 H (two equivalent CH ₂ ester); 5.75 s, 2 H (two pyran 4-H); 7–8.2 m, 18 H (ArH + two NH ₂)
<i>Va</i>	1.4 t, 3 H (CH ₃ ester); 4.25 q, 2 H (CH ₂ ester); 5.45 s, 1 H (pyran 4-H); 5.75 s, 1 H (pyran 4-H); 6.9–8.2 m, 18 H (ArH + two NH ₂)
<i>Vb</i>	3.65 s, 3 H (OCH ₃); 5.25 s, 1 H (pyran 4-H); 5.35 s, 1 H (pyran 4-H); 6.7–7.8 m, 17 H (ArH + two NH ₂)
<i>Vd</i>	1.4 t, 6 H (two equivalent CH ₃ ester); 3.65 s, 3 H (OCH ₃); 4.2 q, 4 H (two equivalent CH ₂ ester); 5.5 s, 1 H (pyran 4-H); 5.6 s, 1 H (pyran 4-H); 6.7–8.1 m, 17 H (ArH + two NH ₂)
<i>VIa</i>	4.65 s, 2 H (two equivalent pyran 4-H); 7.1–7.95 m, 18 H (ArH + two NH ₂)
<i>VII</i>	4.7 s, 1 H (pyran 4-H); 5.35 s, 1 H (pyran 4-H); 6.9–8.3 m, 18 H (ArH + two NH ₂)
<i>Xa</i>	7.4–7.7 m, 8 H (ArH); 8.4 m, 3 H (ArH + OH); 8.6 d, 1 H (pyridine 2-H)
<i>XIa</i>	7.9–8.3 m, 10 H (ArH)
<i>XIIa</i>	7.3–7.7 m, 9 H (ArH); 7.75 brs, 1 H (OH); 8.35 d, 1 H (pyrone H-5)
<i>XIVb</i>	3.55 s, 3 H (CH ₃); 3.7 s, 3 H (CH ₃); 4.6 s, 1 H (pyran 4-H); 6.8–8.0 m, 12 H (ArH + OH + NH ₂)
<i>XIVe</i>	1.15 t, 3 H (CH ₃); 3.55 s, 3 H (CH ₃); 3.65 s, 3 H (CH ₃); 4.0 q, 2 H (CH ₂); 4.8 s, 1 H (pyran 4-H); 6.75–8.1 m, 12 H (ArH + OH + NH ₂)

2,9-Diamino-3,8-dicyano-4,7-diphenyl-4,7-dihydronaphtho[1,2-*b*:6,5-*b'*]dipyran *VII* can be also prepared from *Ia* and 1,6-naphthalenediol, following the procedure mentioned above for *VIa*–*VIId* (cf. Table IV).

Reaction of *Ia*–*If* with *VIII* and *IX*

A solution of *I* (0.01 mol) in ethanol (30 ml) was treated with *VIII* or *IX* (0.01 mol) and piperidine (0.1 ml). The reaction mixture was heated until the precipitation was completed (reaction time: 6 h for *VIII* and 10 min for *IX*). The solid product was collected by filtration and recrystallized from a suitable solvent (cf. Table V).

Preparation of *XI*

A suspension of chalcone (0.01 mol) and malononitrile 0.66 g (0.01 mol) in ethanol (50 ml) with a few drops of piperidine was heated for 20 min. The mixture was then concentrated and the remaining solid was collected by filtration, crystallized and identified as *XIa*, *XIb* (cf. Table V).

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