

2-BENZOPYRYLIUM SALTS.XXXVII.<sup>1</sup> OXYGEN ANALOGS OF REISSERT COMPOUNDS :  
MOLECULAR STRUCTURE AND REACTIONS WITH SODIUM HYDROXIDE

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*Abstract.* The weak intensity of the CN stretching band in IR spectra for 1-cyanoisochromenes is obviously determined by the steric position of the CN group in the molecule, as it was established by X-ray structural analysis for the cyanide addition product (2d) of 1-isopropyl-3-methyl-2-benzopyrylium salts. Depending on the other substituent in position 1, 1-cyanoisochromenes in aqueous solutions of sodium hydroxide eliminate hydrogen cyanide (2a,b,e), undergo inter-(2a,b) or intra-molecular (2c,d) recyclisation, or hydrolysis of the cyano group in 2f; reaction products include  $\alpha$ -naphthol (2c,e), 8-naphthol (2d), acylchrysenes 5a,b, or the isochromene-amide 11f; a stable 1-alkylideneisochromene 3e was obtained, and the intermediacy of 3-hydroxy-1-alkylideneisochromene was proved by their isolation in the case of 10c,d.

#### INTRODUCTION

Recently we have described<sup>2</sup> the nucleophilic addition of a cyanide anion to 2-benzopyrylium salts leading to 1-cyanoisochromenes, which are oxygen analogs of Reissert compounds. The absence of a C≡N stretching band in routinely recorded IR spectra has been noted as the first similarity between the newly prepared 1-cyanoisochromenes and the Reissert compounds. The second common feature has been the ability to be alkylated under conditions of phase-transfer catalysis. In this connection it seemed interesting to explain the strange behaviour of the cyano group in IR spectra for 1-cyanoisochromenes and to investigate conversions of these compounds as stable C-adducts of 2-benzopyrylium salts on one hand, and analogs of Reissert compounds on the other hand, in the presence of alkali hydroxides.

#### IR SPECTRA

We have noticed<sup>2a</sup> that a sharp CN stretching band can be detected in the IR spectra for 1-cyanoisochromenes. It appears with weak intensity at 2226 cm<sup>-1</sup> for compounds 2a,c and at 2246 cm<sup>-1</sup> for 2d. The spectra have been recorded in KBr with 100-fold scanning, 4-fold smoothing and expanding the ordinate by a factor of 50. Under these conditions the signal-to-noise ratio is approximately equal to 100 and remains unchanged in comparison with standard technical data for a Shimadzu instrument. The different values for the CN band are obviously due to the steric influence of the bulky isopropyl group in the cyanoisochromene 2d.

The poor detection of the CN stretching band is clearly determined by the small change in dipole moment for the C≡N bond in comparison with the change in the average dipole moment for the whole molecule and may be associated with the steric position of the CN group in 1-cyanoisochromenes as well as in Reissert compounds.

We reasoned that a suitable way to corroborate such conclusions could be the X-ray structure determination for one cyanoisochromene, namely for 2d. So far no report on the use of X-ray crystal structure analysis has appeared for Reissert compounds.<sup>3</sup>

#### X-RAY STRUCTURAL ANALYSIS

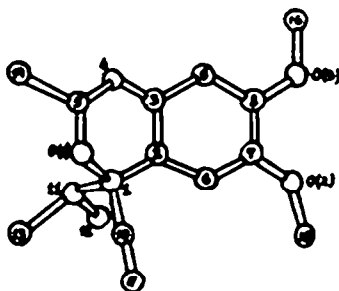


Figure 1. Molecular structure of 2d with the crystallographic numbering scheme.

The molecular structure depicted in Fig. 1 determined by X-ray crystallography corresponds to the chemical constitution of 1-cyano-1-isopropyl-6,7-dimethoxy-3-methyl-isochromene 2d. Bond lengths and bond angles have usual values both for heterocyclic<sup>4</sup> and aromatic fragments. The C(1)-C(10) bond is a normal covalent bond. The C(4)-C(5) double bond is localized with almost standard bond length<sup>5</sup> and determines the conformation of heterocycle. The torsion angle C(3)C(4)C(5)O(1) is equal to  $-2.3^\circ$  and these four atoms are in the same plane with an accuracy of  $0.01 \text{ \AA}$ . Atoms C(1) and C(2) are out of this plane by  $-0.70$  and  $-0.22 \text{ \AA}$ , respectively, and the six-membered heterocycle has a conformation of a partly strained twist half-boat. Some strain is associated with the torsion angle C(1)C(2)C(3)C(4), which is not equal to zero but has a value of  $-9.3^\circ$ . This skewing displaces the normally tetrahedral atom C(1) by  $0.18 \text{ \AA}$  from the plane of the aromatic ring. As a consequence, the quasi-axial isopropyl group is located at an angle of  $73.4^\circ$  relatively to the plane of C(2)C(3)C(6)C(9) and the CN group makes an angle of  $23.7^\circ$  with the same plane.

The only example of X-ray structural analysis for anthra-tetrahydrodicyanopyran derivatives,<sup>6</sup> which are condensed oxygen analogs of Reissert compounds, reveals also a quasi-axial position for a cyano group.

Thus one can conclude that the weak intensity of the nitrile band in IR spectra of 1-cyanoisochromenes is actually due to the vectorial changes in dipole moments for the C≡N bond which occur in a quasi-perpendicular direction to the rest of the molecule.

## CNDO/2 CALCULATIONS OF CHARGE DENSITIES

In a recent communication<sup>2</sup> we have used quantum chemical calculations by the CNDO/2 method with standard geometry for a model compound of 2a and received a good correlation with the <sup>1</sup>H- and <sup>13</sup>C-NMR data.

Application of X-ray analysis gives us experimental data providing an opportunity to refine earlier calculations and at the same time to check the ability of the CNDO/2 method<sup>6</sup> for 1-cyanoisochromenes.

The selected charge densities in 2a-e for standard geometry and in 2d for experimental X-ray geometry are presented in Table 1.

Table 1. Selected charges in 2a-e calculated with CNDO/2 method for standard geometry and in 2d also for experimental X-ray geometry.



Atom	<u>2a</u> (R <sup>1</sup> =Me, R <sup>2</sup> =R <sup>3</sup> =H)	<u>2b</u> (R <sup>1</sup> =Ph, R <sup>2</sup> =R <sup>3</sup> =H)	<u>2c</u> (R <sup>1</sup> =R <sup>3</sup> =Me, R <sup>2</sup> =H)	<u>2d</u> (R <sup>1</sup> =R <sup>2</sup> =R <sup>3</sup> =Me)		<u>2e</u> (R <sup>1</sup> =Me, R <sup>2</sup> =H, R <sup>3</sup> =Ph)
Geometry	Standard	Standard	Standard	Standard	Exptl.	Standard
C-1	.305	.302	.301	.290	.171	.237
C-3	.192	.167	.187	.209	.171	.190
C-4	-.135	-.120	-.131	-.144	-.087	-.136
C-5	-.030	-	-.037	-.029	-.040	-.031
C-6	-.028	-.027	.016	.039	.041	-.010
H-7 <sup>†</sup>	.032	.033	.002	-.023	-.016	.010
R <sup>2</sup> -8	.017	.016	-.011	-.066	-.027	.000
R <sup>3</sup> -9	.002	.001	-.035	-.030	-.017	-
C-10	-.028	-.026	-.028	-.030	.094	-.003
N-11	-.112	-.113	-.112	-.122	-.178	-.381

<sup>†</sup>The most mobile hydrogen atom.

One may see that the difference in charge density values for positions 1 and 3 of compound 2d (standard geometry) vanishes on using X-ray data. At same time the common tendency in charge distribution remains practically unchanged, providing evidence for the good applicability of the CNDO/2 method for 1-cyanoisochromenes.

## CONVERSIONS IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS

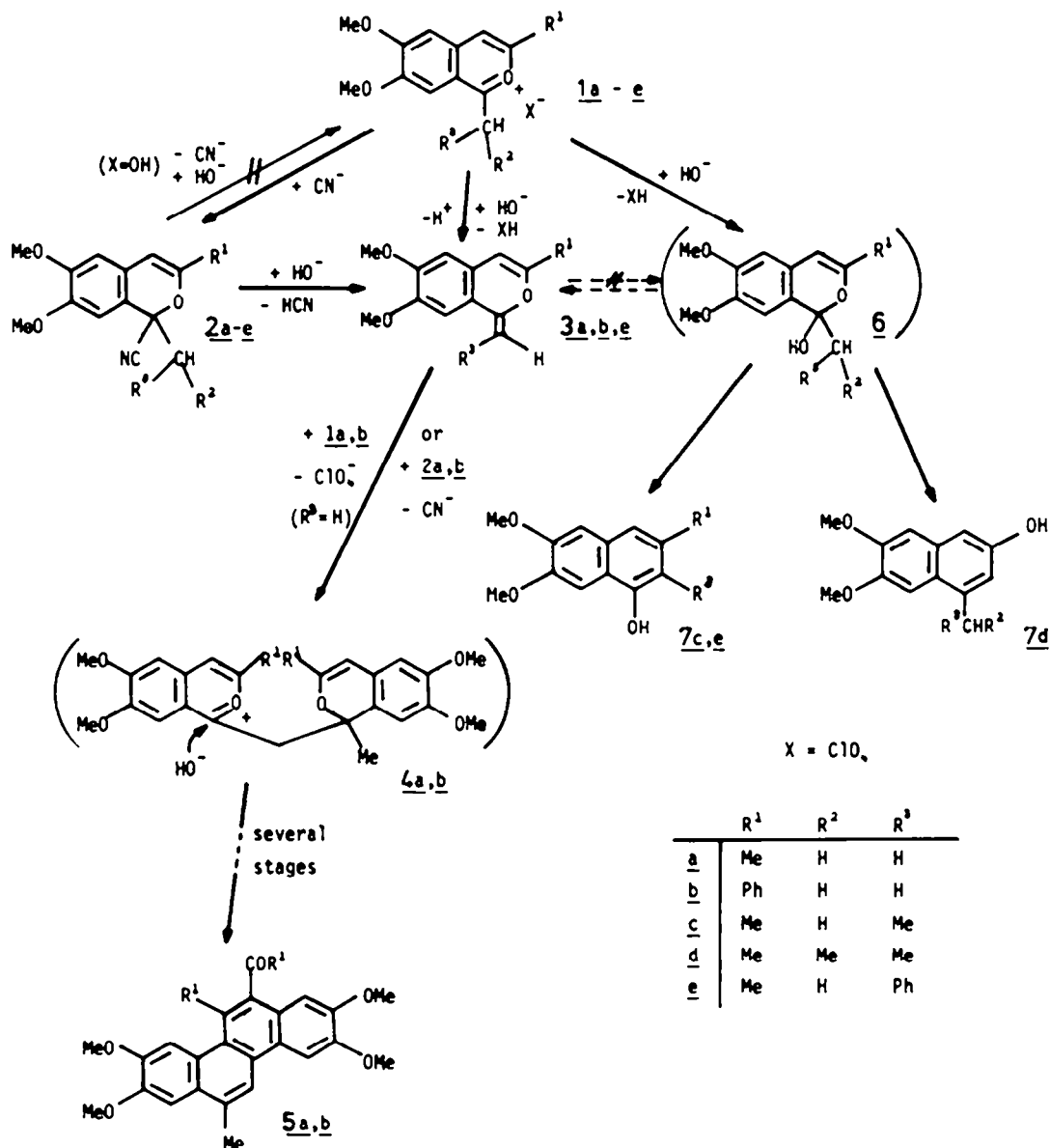
We found that the course of reaction between 2-benzopyrylium salts 1a-c,e and alkali hydroxides depends on the substituent in position 1: when R<sup>2</sup>=R<sup>3</sup>=H (as in 1a,b), intermolecular interaction takes place leading to chrysenes 5a,b as major products,<sup>7,8</sup> whereas when R<sup>3</sup>≠H (as in 1c,e), intramolecular recyclization leads to α-(7e)<sup>9</sup> or β-naphthols (7d)<sup>10</sup> (Scheme 1). The poor yields for α- and β-naphthols in the latter case may be explained by a competition in the formation of anhydrobases (3c,d) and pseudobases (6). The only stable anhydrobase which is unchanged in aqueous alkali hydroxide solutions is 3e,<sup>9</sup> because the R<sup>3</sup>≠H group stabilizes the vinyl ether structure more than in compounds 3a-d. Probably the shielding effect of R<sup>3</sup> in 3c,e prevents interaction of these compounds with such a bulky electrophile as the 2-benzopyrylium cation by contrast to 3a,b which lead to dimers 4a,b, and hence to chrysenes derivatives 5a,b.

The other substituent in position 1 of 1-cyanoisochromenes 2a-f also determines inter-

or intramolecular pathways for conversions of these compounds in 3%, 15% or 50% aqueous sodium hydroxide solutions on heating.

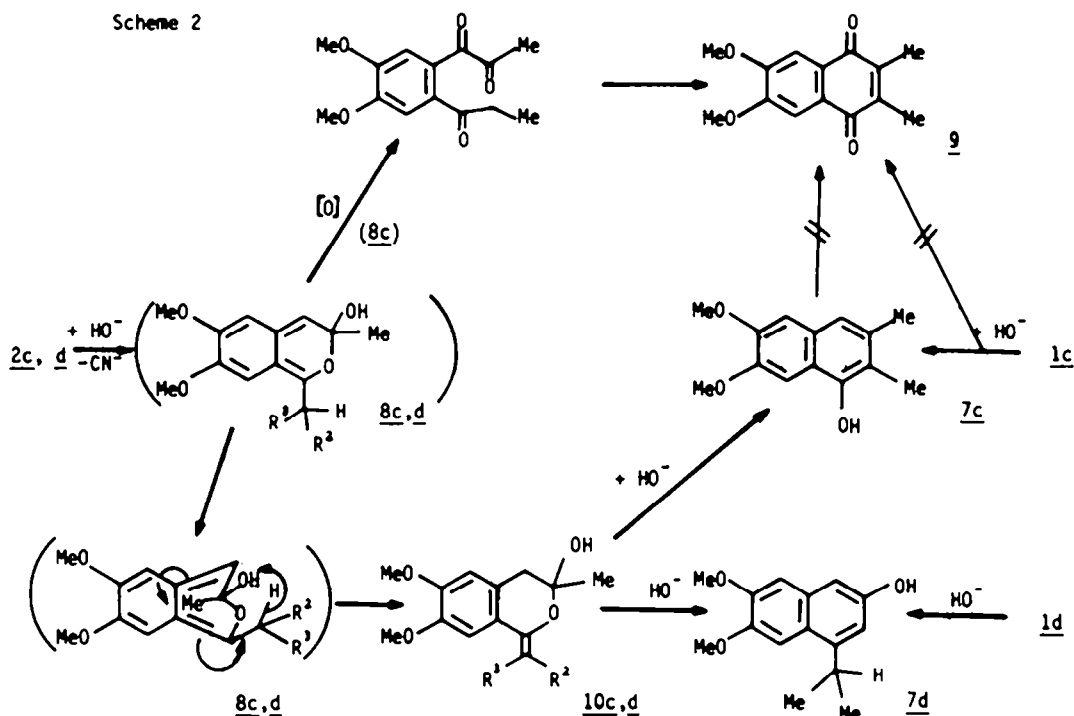
From quantum chemical calculations one could expect an easier elimination of hydrogen cyanide from 2e as well as from 2a,b in comparison with 2c,d (the most mobile hydrogen atom is marked with an asterisk in Table 1). Actually, compound 2e gives the stable anhydrobase 3e in all cases. The theoretical correlation is also confirmed by formation of chrysenes 5a,b in high yield from 1-cyanoisochromenes 2a,b. Obviously, the first step of reaction includes elimination of hydrogen cyanide, leading to 3a,b. Then anhydrobases 3a,b act as nucleophiles and expel a CN anion from cyanoisochromenes 2a,b giving products of intermolecular interaction 4a,b (Scheme 1), which are converted into chrysenes 5a,b as was described for 2-benzopyrylium salts.<sup>9</sup>

Scheme 1



The intramolecular cyclizations of 2-benzopyrylium salts 1c,d and 1-cyanoisochromenes 2c,d yielding naphthols also exhibit some differences. Thus, heating of compound 2d for two hours in 50% aqueous sodium hydroxide solution leads to the  $\beta$ -naphthol 7d with yield 80%, whereas on using the same conditions 2-benzopyrylium salt 1d gives 7d in a yield of only 40% (Scheme 2).

At the same time or heating in alkali hydroxide solutions at any concentration, cyanoisochromene 2c is converted into the orange coloured naphthoquinone 9 in good yield, whereas salt 1c gives only traces of 9 (TLC control) with the  $\alpha$ -naphthol 7c as a major product, which itself is not oxidized into quinone 9 under these conditions.



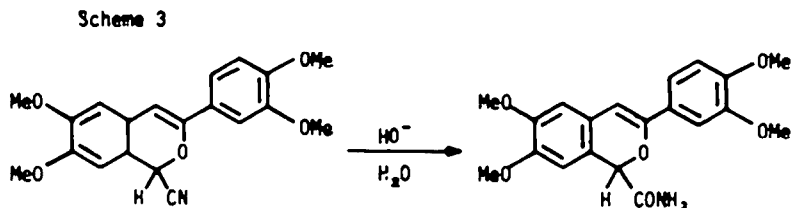
Yield : 30% (1c + 7c) ; 70% (2c → 9) ; 40% (1d → 7d) ; 80% (2d → 7d)

These results indicate an attack by the hydroxyl ion to position 3 of cyanoisochromenes 2c,d, which have bulky substituents in position 1, with simultaneous elimination of a CN<sup>-</sup> anion (a kind of tele-substitution<sup>3</sup>) that leads to the formation of *ortho*-quinonoid structures (8c,d). This suggestion is in good agreement with quantum chemical calculations which revealed both a low mobility of hydrogen atoms at C-6 and approximately equal charge densities in positions 1 and 3 for 2c,d (Table 1). In this case the formation of quinone 9 from 2c could be easily explained by oxidation of the unstable *ortho*-quinonoid compound 8c. On the other hand, compounds 8c,d can undergo a thermally allowed 1,5-hydrogen transfer leading to alkylideneisochromenes 10c,d as the result. Indeed, we have captured the stable colorless 10d on heating 2d for one hour in 50% aqueous sodium hydroxide solution or for two hours in solution at 15% concentration. Also, on keeping 2c for one hour at room temperature in NaOH solution at 15% concentration, isochromene 10c has been obtained instead of quinone 9 formed only in boiling solutions.

Compounds 10c,d are converted with perchloric acid into salts 1c,d and with hot aqueous sodium hydroxide solutions for two hours into corresponding naphthols 7c,d. The latter conversion proceeds obviously by rupture of the C(3)-O bond with subsequent intramolecular condensation of the intermediately formed 1,5-diketones.<sup>7</sup>

In the case of 1-H-1-cyanoisochromene 2f, amide 11 has been isolated as the result of

hydrolysis of a nitrile group under alkaline conditions as it was described for Reissert compounds (Scheme 3).<sup>12</sup>



#### STRUCTURE PROOF OF THE NEW COMPOUNDS

The identification of compounds 7c,d, 9 and 12 posed no difficulties. Some of their characteristics are given in the experimental part.

however, it is necessary to mention a double OH stretching band in the IR spectrum of  $\beta$ -naphthol 7d at 3527 and 3420  $\text{cm}^{-1}$ . The second band is obviously due to associates easily formed by hydrogen bonds in 7d by contrast to  $\alpha$ -naphthols 7c,e,<sup>9,13</sup> whose steric hindrance prevents such behaviour.

The evidence for key compounds 10c,d required a rigorous proof. Thus, their IR spectra show characteristic stretching bands at 3460 and 3540  $\text{cm}^{-1}$  (O-H) and at 1647 and 1660  $\text{cm}^{-1}$  (exocyclic C=C bond) for 10c and 10d respectively. The <sup>1</sup>H-NMR spectra of 10c,d confirm precisely their structure as 1-alkylidene-3-hydroxyisochromanes. The 3-methyl signal in 10d is found at  $\delta=1.24$  and the methylene peak at  $\delta=3.00$ . The signal at  $\delta=1.98$  belongs to the hydroxyl group and disappears on deuteration. The two methyl groups at exocyclic C=C bond are non-equivalent and have chemical shifts at  $\delta=1.10$  and 1.19; the two singlets of aromatic protons appear at  $\delta=6.56$  and 7.45.

The <sup>1</sup>H-NMR spectrum and assignments of 10c are to be seen in Fig. 2.

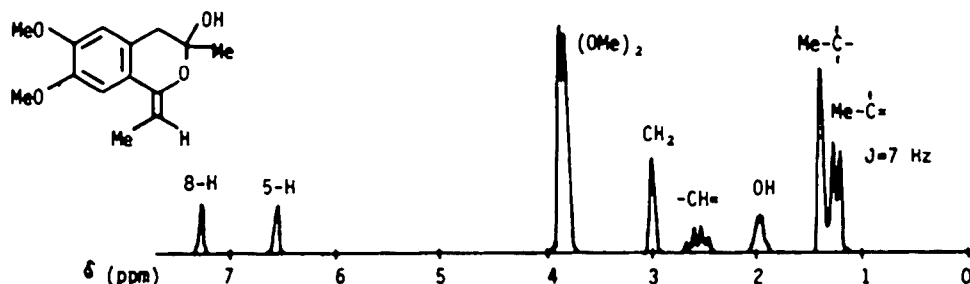


Figure 2. <sup>1</sup>H-NMR spectrum of 10c in  $\text{CDCl}_3$ .

The shielding of the methine hydrogen atom at the exocyclic C=C bond is manifested by its chemical shift, due to the configuration of 10c as it is presented in Fig. 2.

The mass spectrum for 10c gives a molecular ion at  $m/x=264$  (78%) and a base peak at  $m/x=246$  ( $\text{M}-\text{H}_2\text{O}$ )<sup>+</sup> together with main fragment peaks at  $m/x=247$  ( $\text{M}-\text{OH}$ )<sup>+</sup> (42%), 231 [ $(\text{M}-\text{H}_2\text{O})-\text{CH}_3$ ]<sup>+</sup> (96%), 222 ( $\text{M}-\text{CH}_2\text{COH}$ )<sup>+</sup> (23%) and 221 ( $\text{M}-\text{CH}_2\text{CO}$ )<sup>+</sup> (94%).

All these facts constitute structural proofs for 10c,d.

#### CONCLUSION

The transformations of 1-cyanoisochromenes under alkaline conditions with elimination of a CN group by analogy with 1-substituted Reissert compounds<sup>14,15</sup> probably include the formation of a 2-benzopyrylium cation in the transition state. The higher reactivity of this cation than of isoquinolinium is the source of the more varied conversions of 1-cyanoisochromenes in comparison with Reissert compounds.<sup>3</sup>

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## EXPERIMENTAL PART

IR spectra were determined with a Shimadzu IR-435 instrument in KBr for 2a,c,d and with a Specord 75-IR instrument in chloroform solutions or in nujol for other compounds.  $^1\text{H-NMR}$  spectra were recorded on a Tesla BS-467 spectrometer at 80 MHz in  $\text{CDCl}_3$  solutions. Mass spectra were obtained on a Finnigan 4021 instrument using direct insertion at 70 eV.

X-Ray crystal structure determination of 2d.

Crystal data: 2d  $\text{C}_{18}\text{H}_{15}\text{O}_3$ ,  $M = 273$ , monoclinic from a solution of isopropanol-ethyl ether,  $a = 15.113(2)$ ,  $b = 8.723(1)$ ,  $c = 10.785(1)$  Å,  $\beta = 104.06(2)^\circ$ ,  $U = 1470.5(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.23$  g·cm<sup>-3</sup>, space group  $P2_1/c$ . Intensities of 3007 unique reflections were collected on an Enraf-Nonius CAD-4, computer controlled, Kappa-axis diffractometer ( $\lambda\text{MoK}_\alpha$ , scan speed ratio  $\omega : \theta = 1.2 : 1$ ,  $\theta < 28^\circ$ ). The crystal structure was determined by the direct method based on MULTAN program and refined by least-squares method of 1746 reflections ( $F^2 > 5\sigma$ ) with isotropic temperature factors for hydrogen atoms and anisotropic temperature factors for all other atoms. Final  $R = 0.032$ ,  $R_w = 0.042$ . All calculations were performed on a PDP 11/23 PLUS computer using SDP-PLUS program.<sup>14</sup> A list of positional co-ordinates is given in Table 2, and Tables 3 and 4 list bond lengths and bond angles in 2d.

Table 2. Atomic co-ordinates for 2d ( $\times 10^4$  for the non-hydrogen atoms and  $\times 10^3$  for the hydrogen atoms).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
O(1)	3195(1)	-548(1)	760(1)	C(10)	2883(1)	-2600(2)	1912(2)	H(123)	377(1)	-226(2)	429(2)
O(2)	777(1)	-73(1)	4265(1)	C(11)	3978(1)	-749(2)	3000(1)	H(131)	471(1)	-134(2)	170(2)
O(3)	714(1)	2787(1)	3657(1)	C(12)	3938(1)	-1216(2)	4333(2)	H(132)	525(1)	-134(2)	317(2)
N	2715(1)	-3865(2)	1847(2)	C(13)	4694(1)	-1596(3)	2577(2)	H(133)	458(1)	-281(3)	258(2)
C(1)	3105(1)	-952(2)	2022(1)	C(14)	3726(1)	1315(2)	-445(2)	H(141)	365(1)	239(2)	-67(2)
C(2)	2397(1)	-23(2)	2372(1)	C(15)	706(1)	-1673(2)	4492(2)	H(142)	350(1)	76(2)	-126(2)
C(3)	2334(1)	1503(2)	1981(1)	C(16)	802(1)	4402(2)	3621(2)	H(143)	433(1)	99(2)	-8(2)
C(4)	2846(1)	2016(2)	1122(2)	H(4)	288(1)	306(2)	93(1)	H(151)	125(1)	-212(2)	497(2)
C(5)	3238(1)	1014(2)	535(1)	H(6)	193(1)	-169(2)	339(1)	H(152)	28(1)	-173(2)	490(2)
C(6)	1873(1)	-596(2)	3112(2)	H(9)	170(1)	349(2)	216(1)	H(153)	50(1)	-228(2)	363(2)
C(7)	1309(1)	362(2)	3524(2)	H(11)	410(1)	31(2)	303(1)	H(161)	41(2)	483(2)	400(2)
C(8)	1272(1)	1922(2)	3180(2)	H(121)	452(1)	-103(2)	491(2)	H(162)	139(1)	474(2)	402(2)
C(9)	1764(1)	2465(2)	2398(2)	H(122)	349(1)	-52(2)	465(2)	H(163)	67(1)	478(2)	270(2)

Table 3. Bond lengths (Å) for bonds involving non-hydrogen atoms in 2d.

C(1)C(2)	1.520(2)	C(3)C(9)	1.397(2)	C(8)C(9)	1.374(2)
C(1)C(10)	1.479(2)	C(4)C(5)	1.326(2)	C(8)O(3)	1.367(1)
C(1)C(11)	1.550(2)	C(5)C(14)	1.485(2)	C(10)N	1.134(2)
C(1)O(1)	1.447(1)	C(5)O(1)	1.389(1)	C(11)C(12)	1.511(2)
C(2)C(3)	1.392(2)	C(6)C(7)	1.385(2)	C(11)C(13)	1.529(2)
C(2)C(6)	1.388(2)	C(7)C(8)	1.408(2)	C(15)O(2)	1.427(2)
C(3)C(4)	1.453(2)	C(7)O(2)	1.360(1)	C(16)O(3)	1.417(2)

Table 4. Bond angles ( $^\circ$ ) for the non-hydrogen atoms for 2d.

C(1)O(1)C(3)	115.1(1)	C(1)C(2)C(6)	123.3(1)	O(2)C(7)C(6)	125.2(1)
C(7)O(2)C(15)	117.6(1)	C(3)C(2)C(6)	120.5(1)	O(2)C(7)C(8)	115.6(1)
C(8)O(3)C(16)	117.3(1)	C(2)C(3)C(4)	118.5(1)	C(6)C(7)C(8)	119.2(1)
O(1)C(1)C(2)	110.8(1)	C(2)C(3)C(9)	118.9(1)	O(3)C(8)C(7)	115.1(1)
O(1)C(1)C(10)	103.8(1)	C(4)C(3)C(9)	122.6(1)	O(3)C(8)C(9)	124.8(1)
O(1)C(1)C(11)	109.3(1)	C(3)C(4)C(5)	120.8(1)	C(7)C(8)C(9)	120.1(1)
C(2)C(1)C(10)	110.9(1)	O(1)C(5)C(4)	120.9(1)	C(3)C(9)C(8)	120.8(1)
C(2)C(1)C(11)	112.5(1)	O(1)C(5)C(14)	110.8(1)	NC(10)C(1)	178.9(2)
C(10)C(1)C(11)	109.1(1)	C(4)C(5)C(14)	128.3(1)	C(1)C(11)C(12)	112.0(1)
C(1)C(2)C(3)	116.0(1)	C(2)C(6)C(7)	120.4(1)	C(12)C(11)C(13)	111.3(1)
				C(1)C(11)C(13)	111.5(1)

Numbering of atoms in Tables 2-4 is given in Fig. 1.

General procedure for reaction with sodium hydroxide.

The mixture of 2-benzopyrylium salt 1c,d or cyanoisochromene 2 (10 mmol) and 20 ml 50% aqueous sodium hydroxide solution was refluxed for 2 hrs, then 20 ml of cold water were added and the residue was extracted into chloroform. Pure compounds 3e, 5a,b, 7c,d and 9 (TLC control) were obtained after evaporating the dried chloroform solutions.

Compound 11, insoluble in chloroform, was filtered off and recrystallized from n-propanol with hot filtration.

The aqueous sodium hydroxide solution was acidified with hydrochloric acid, and for the case of salts 1c,d and cyanoisochromene 2d, additional amounts of naphthols 7c,d were filtered off.

- 1-Benzylidene-6,7-dimethoxy-3-methylisochromene (3e), m.p. = 139° (98% yield).
- 12-Acetyl-2,3,8,9-tetramethoxy-6,11-dimethylchryseene (5a), m.p. = 197°<sup>17</sup> (70% yield).
- 12-Benzoyl-2,3,8,9-tetramethoxy-6-methyl-11-phenylchryseene (5b), m.p. = 250°<sup>7</sup> (70% yield).
- 6,7-Dimethoxy-2,3-dimethyl-1-naphthol (7c), m.p. = 149°<sup>18</sup> (30% yield from 1c and 50% yield from 10c).
- 4-Isopropyl-6,7-dimethoxy-2-naphthol (7d), m.p. = 87° (40% yield from 1d, 80% yield from 2d and 98% yield from 10d). Found: C, 73.02; H, 7.20. C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> requires: C, 73.17; H, 7.31%. <sup>1</sup>H-NMR spectrum, δ: 1.32 (3H, s, CH(CH<sub>3</sub>)<sub>2</sub>); 1.43 (3H, s, CH(CH<sub>3</sub>)<sub>2</sub>); 3.97 (7H, s and m, 2CH<sub>3</sub>O and CH(CH<sub>3</sub>)<sub>2</sub>); 6.97 (2H arom, s); 7.05 (1H arom, s) and 7.35 ppm (1H arom, s).
- 6,7-Dimethoxy-2,3-dimethyl-1,4-naphthoquinone (8), m.p. = 215° (70% yield). Found: C, 68.15; H, 5.75. C<sub>14</sub>H<sub>10</sub>O<sub>4</sub> requires: C, 68.29; H, 5.69%. IR spectrum (in CHCl<sub>3</sub>): 1650, 1500, 1320 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectrum: δ: 2.15 (6H, s, 2CH<sub>3</sub>); 4.00 (6H, s, 2CH<sub>3</sub>O); 7.43 ppm (2H arom, s).
- 1-Ethylidene-3-hydroxy-3-methyl-6,7-dimethoxyisochromene (10a), m.p. = 183° (50% yield). Mass spectrum, m/s = 250 (M<sup>+</sup>). Found: C, 67.42; H, 7.24; C<sub>14</sub>H<sub>14</sub>O<sub>4</sub> requires: C, 67.20; H, 7.20%.
- 1-Isopropylidene-3-hydroxy-3-methyl-6,7-dimethoxyisochromene (10d), m.p. = 128° (30% yield in solution at 50% concentration and 60% yield in solution at 15% concentration). Found: C, 68.24; H, 7.62; C<sub>15</sub>H<sub>20</sub>O<sub>4</sub> requires: C, 68.18; H, 7.58%.
- 1-B-1-Amido-6,7-dimethoxy-3-(3,4-dimethoxyphenyl)isochromene (11), m.p. = 218° (60% yield). Found: C, 64.75; H, 5.78; N, 3.82; C<sub>20</sub>H<sub>21</sub>NO<sub>6</sub> requires: C, 64.69; H, 5.66; N, 3.77%. IR spectrum: 3447, 3180, 1687, 1620, 1607, 1507, 1207, 1127 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectrum (in DMFA-D<sub>6</sub> at 100°): δ: 3.71 (3H, s, CH<sub>3</sub>O); 3.73 (3H, s, CH<sub>3</sub>O); 3.75 (3H, s, CH<sub>3</sub>O); 3.78 (3H, s, CH<sub>3</sub>O); 5.50 (H-1, s); 6.38 (H-4, s); 6.73 (1H arom, s); 7.00-7.35 ppm (6H, m, 4H arom and CONH<sub>2</sub>). Mass spectrum, m/s = 371 (M<sup>+</sup>, 18%), 327 ([M-CONH<sub>2</sub>]<sup>+</sup>, 100%).

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