Syntheses of Fluorescent Dyes. IX. New 4-Hydroxycoumarins, 4-Hydroxy-2-quinolones, 2*H*,5*H*-Pyrano[3,2-*c*]benzopyran-2,5-diones and 2*H*,5*H*-Pyrano[3,2-*c*]quinoline-2,5-diones (1)

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7-Substituted 4-hydroxycoumarins (**2a-e**) and 4-hydroxy-2-quinolones (**2f-i**) have been synthesized from the appropriate phenols or anilines and were converted to the enamines **3** using triethoxymethane and aniline. Condensation of **3** with nitriles **4a-h** gave substituted 2*H*,5*H*-pyrano[3,2-*c*]benzopyran-2,5-diones (**5a-r**) or 2*H*,5*H*-pyrano[3,2-*c*]quinoline-2,5-diones (**5s-x**), which exhibit both spontaneous and stimulated fluorescence with maxima between 418 and 549 nm. The marked influence of an electron withdrawing 3-substituent in **5** is demonstrated by the fluorescence spectra of **7a,b** (synthesized from **2d,e** and ethyl 3-oxobutyrate), whose maxima are sharply shifted to the blue as compared with compounds **2l-r**.

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Pyrano[3,2-*c*][1]benzopyrans and pyrano[3,2-*c*]quinolines are of interest as possible optical brighteners and laser dyes because of their high fluorescence efficiency (2). In previous papers we have presented new synthetic routes to annelated α-pyrones (1,3) and now wish to report their application to properly substituted coumarines and 2-quinolones to yield the strongly fluorescent pyrones **5**. Because of the substantial influence of substituents in the 3- and 8-position on the fluorescence behaviour of **5** [analogous to simple coumarines (4)], a number of 7-substituted **2** were used as starting materials. Variation of R^2 in **5** was conveniently effected in the last step of the reaction sequence by using different nitriles **4**.

The most strongly fluorescent 4-hydroxycoumarins and -2-quinolones are those with an electron donating 7-substituent (5). The syntheses of **2a-e** and of **2g-i** were accomplished using the corresponding phenols **1c-e** or anilines **1a-i**. (The preparation of **1a** has been improved substantially).

Method A involves thermal cyclisation of the phenol or aniline with diethyl malonate at 180-200° (6), method B involves condensation in the presence of phosphorus oxide trichloride (7), and method C involves condensation with bis-2,4-dichlorophenyl or bis-2,4,6-trichlorophenyl malonate (8). The 2-quinolones **2g-i** were obtained by all three methods, but coumarins **2c-e** were only obtained in acceptable yields using method B and C. Compounds **2a** and **2f** are commercially available; **2b** was prepared from resorcin and ethyl cyanoacetate by the method of Sonn (9). This method, however, fails with other phenoles with the exception of 3-methoxyphenol.

Conversion of **2** into their 3-anilinomethylene derivatives **3** was effected by heating **2** with an equimolar amount of aniline and a 1.5 molar excess of triethoxymethane in glacial acetic acid or DMF. Insoluble **2** were reacted without solvent. Quinolinones **2f-i** required stronger conditions than coumarins **2a-e**, which could be converted to **3a-e** even at room temperature provided that the reaction time was extended to several days.

The resulting enamines **3** were obtained as pale to deep yellow solids in good yield and excellent purity. Their pmr spectra showed CH and NH double doublets in the δ 8.5-9.0 and δ 11-14 regions, indicating the enamine structure and the presence of *E/Z* isomers. Dudek and coworkers (10) have shown the enamine structure to be prefered over the tautomeric iminoenol structure.

2-Aminomethylene-1,3-diones are synthetic equivalents to the less readily available and less stable 2-formylated 1,3-diketones. Thus, when the enamine **3** is reacted with equimolar amounts of a nitrile **4** in the presence of strong base in DMF (11), aniline is replaced by the nitrile anion. Subsequent acidification affords the corresponding pyrones **5**.

The base chosen must be strong enough to generate the anion of **4** but not so strong as to lead to reaction with the enamine **3**. Dry potassium hydroxide (potassium *t*-butoxide for the less reactive **4a,b**) was found to be a suitable reagent. Since the methylene hydrogens in **4a,b** exhibit only weak acidity, their anions are increasingly reactive, causing side reactions which lower the yield of the corresponding **5**. On the contrary, the pyrones formed by cyclisation with the strongly acidic **4f-h** were obtained in high yields. Compounds **4c-d** were of medium reactivity.

The structures of **5** have been confirmed by ir and pmr data. The annellated α-pyrones showed characteristic carbonyl absorption bands within the 1800-1780 cm^{-1} region when R^2 was an ester group. Otherwise the resonance frequency was shifted to 1760-1730 cm^{-1}, partially coinciding with the coumarine lactone absorption. The pmr spectra showed the olefinic proton as a sharp singlet between δ 8.1-8.6.

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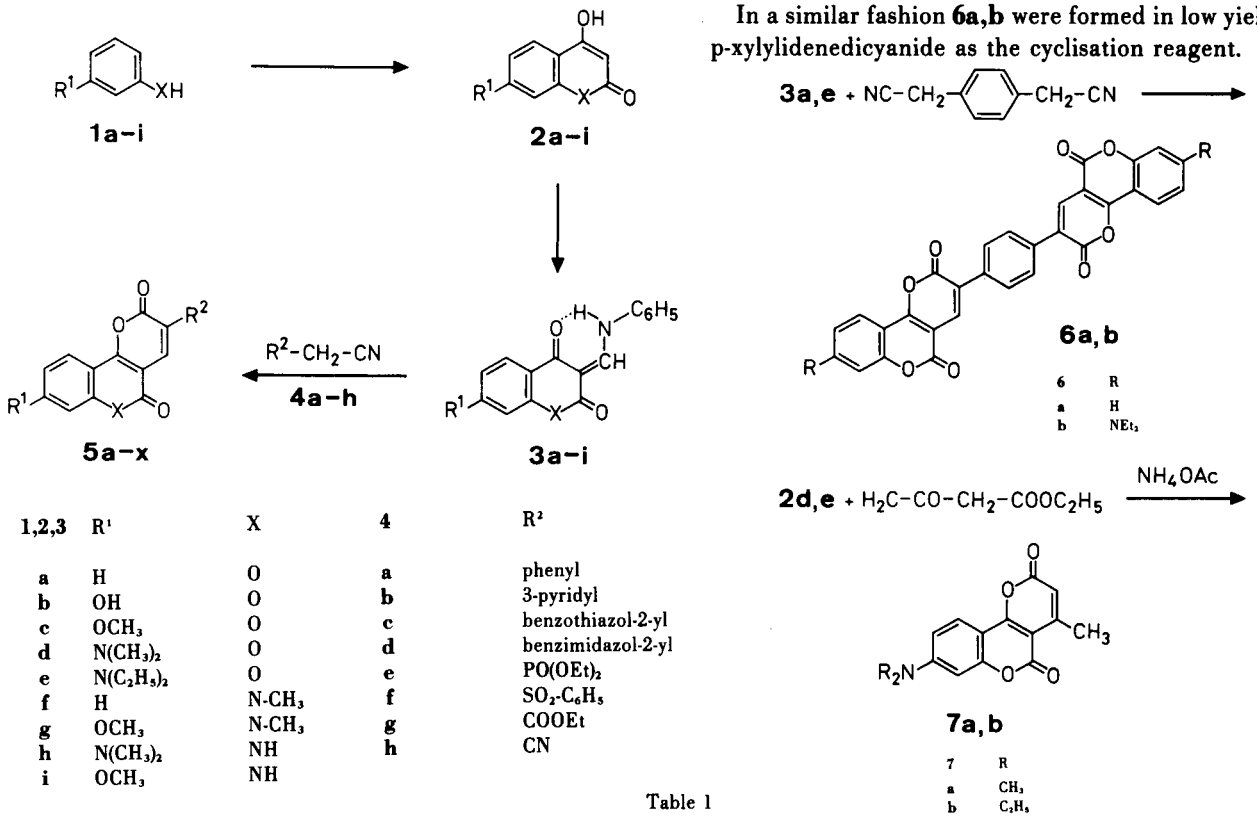

In a similar fashion **6a,b** were formed in low yield using p-xylylidenedicyanide as the cyclisation reagent.

1,2,3	R^1	X	4	R^2
a	H	O	a	phenyl
b	OH	O	b	3-pyridyl
c	OCH_3	O	c	benzothiazol-2-yl
d	$N(CH_3)_2$	O	d	benzimidazol-2-yl
e	$N(C_2H_5)_2$	O	e	$PO(OEt)_2$
f	H	N-CH_3	f	SO_2-C_6H_5
g	OCH_3	N-CH_3	g	COOEt
h	$N(CH_3)_2$	NH	h	CN
i	OCH_3	NH		

6	R
a	H
b	NEt_2

7	R
a	CH_3
b	C_2H_5

Table 1

Substituted Coumarins and 2-Quinolinones **2,3**

Compound	R^1	X	Method	M.p. °C (a) Recrystallization solvent	Yield	Formula molmass	Calcd. Found	C	H	N	Fluorescence, max. in 95% ethanol (nm) (b)
2c	OCH_3	O	B	256 (c)	54	$C_{10}H_8O_4$		62.50	4.20		
			C	ethanol	61	192.17		62.60	4.11		349, 365 (sh)
2d	$N(CH_3)_2$	O	B (d)	260-262 dec.	62	$C_{11}H_{11}NO_3$		64.38	5.40	6.83	
			C	Acetic acid	79	205.21		64.20	5.50	6.85	407
2e	$N(C_2H_5)_2$	O	C	238 dec.	74	$C_{15}H_{15}NO_3$		66.94	6.48	6.00	
				Acetic acid		233.27		66.81	6.40	6.08	407
2g	OCH_3	NCH_3	A	285-287 dec.	56	$C_{11}H_{11}NO_3$		64.38	5.40	6.38	338 (sh), 348
			B	Acetic acid	71	205.21		64.24	5.37	6.84	365 (sh)
2h	$N(CH_3)_2$	NH	B	343-344 dec. (e)	80	$C_{11}H_{12}N_2O_2$		64.69	5.92	13.72	
			C	DMF	79	203.22		64.52	5.99	13.79	390
2i	OCH_3	NH	A	332 dec.	63	$C_{10}H_9NO_3$		62.82	4.75	7.33	332 (sh), 344
			C	DMF	72	191.19		62.90	4.80	7.46	360 (sh)
3c	OCH_3	O	D	200-202	64	$C_{17}H_{13}NO_4$		69.14	4.44	4.74	
				dioxane		295.30		69.18	4.50	4.81	
3d	$N(CH_3)_2$	O	D	234	76	$C_{18}H_{16}N_2O_3$		70.12	5.23	9.08	
				dioxane		308.34		70.18	5.08	9.14	
3e	$N(C_2H_5)_2$	O	D	153	61	$C_{20}H_{20}N_2O_3$		71.41	5.90	8.33	
				ethanol		336.39		71.51	5.82	8.38	
3g	OCH_3	NCH_3	D	163	68	$C_{18}H_{16}N_2O_3$		70.12	5.23	9.08	
				2-propanol		308.24		69.98	5.23	9.01	
3h	$N(CH_3)_2$	NH	E	297-300	59	$C_{18}H_{17}N_3O_2$		70.34	5.58	13.67	
				DMF		307.35		70.28	5.60	13.44	
3i	OCH_3	NH	E	301 dec.	62	$C_{17}H_{14}N_2O_3$		69.38	4.79	9.52	
				DMF		294.31		69.21	4.89	9.59.	

(a) Sealed tube. (b) 4-Hydroxycoumarin has a fluorescence maximum at 359 nm (in ethanol). (c) Reference (9) gives m.p. 256°; A. Ermili, M. Mazzei, G. Roma and C. Cacciatore, *Il Farmaco, Ed. Sci.*, **32**, 375 (1977) give m.p. 258°. (d) Also prepared from Meldrum's acid and 3-dimethylaminophenol in 35% yield: O. S. Wolfbeis, *Monatsh. Chem.*, **108**, 499 (1977). (e) Reference (6) gives m.p. 338-340°.

Table 2

Substituted Pyrano[3,2-c][1]benzopyran-2,5-diones and Pyrano[3,2-c]quinoline-2,5-diones 5

5	R^1	R_2	X	m.p. (°C) Recryst. solvent	yield (%)	Formula Molecular mass	Calcd. C Found C	H H	N N	S	Fluorescence max. in ethanol (nm)
a	H	C_6H_5	O	247	37	$C_{16}H_{10}O_7$	74.48	3.47			447, 421 (sh)
				1-butanol		290.28	74.58	3.65			470 (sh)
b	H	3-Pyridyl	O	272	28	$C_{17}H_9NO_4$	70.10	3.11	4.81		
				1-butanol		291.27	70.15	3.13	4.96		440, 417 (sh)
c	H	Benzthiazol-2-yl	O	311 dec.	65	$C_{19}H_9NO_4S$	65.70	2.61	4.03	9.23	
				DMF		347.35	65.79	2.63	3.88	9.39	494
d	H	Benzimidazol-2-yl	O	349-351	59	$C_{19}H_{10}N_2O_4$	69.09	3.05	8.48		
				DMF/Water		330.30	69.28	3.20	8.55		510
e	H	$SO_3C_6H_5$	O	324 dec.	79	$C_{24}H_{15}NO_8S$	67.12	3.52	3.26	7.47	
				DMF		429.44	67.08	3.59	3.30	7.54	427
f	H	$PO(OEt)_2$	O	152	46	$C_{16}H_{15}O_7P$	54.86	4.32			
				EtOH		350.26	55.07	4.20			418
g	OH	C_6H_5	O	dec. > 280	44	$C_{19}H_{10}O_5$	70.59	3.29			
				1-butanol		306.28	70.89	3.42			459 (a)
h	OH	Benzthiazol-2-yl	O	dec. > 375	61	$C_{19}H_9NO_5S$	62.81	2.50	3.86	8.82	
				DMF	61	363.35	62.98	2.64	3.90	8.71	547 (b)
i	OH	Benzimidazol-2-yl	O	> 350	60	$C_{19}H_{10}N_2O_5$	65.90	2.91	8.09		
				DMF		346.30	66.22	2.92	7.94		532 (b)
j	OH	$SO_2C_6H_5$	O	271	78	$C_{24}H_{15}NO_6S$	64.71	3.39	3.14	7.20	
				DMF		445.44	64.77	3.45	3.22	7.10	522 (b)
k	H_3CO	$COOC_2H_5$	O	206-208	6a	$C_{16}H_{12}O_7$	60.76	3.82			
				dioxane		316.27	60.87	3.85			442
l	$(CH_3)_2N$	C_6H_5	O	249	33	$C_{20}H_{15}NO_4$	72.06	4.54	4.20		
				1-butanol		333.35	71.97	4.55	4.37		503
m	$(C_2H_5)_2N$	Benzothiazol-2-yl	O	275 dec.	56	$C_{23}H_{16}N_2O_4S$	66.02	4.34	6.69	7.66	
				DMF		418.47	65.83	4.42	6.67	7.90	549
n	$(C_2H_5)_2N$	Benzimidazol-2-yl	O	dec. > 270	47	$C_{23}H_{19}N_3O_4$	68.82	4.77	10.47		
				DMF		401.42	68.59	4.64	10.36		535
o	$(CH_3)_2N$	$SO_2C_6H_5$	O	dec. > 275	72	$C_{20}H_{15}NO_6S$	60.45	3.80	3.52	8.07	
				DMF		397.40	60.50	3.85	3.38	8.06	531
p	$(H_3C)_2N$	$COOC_2H_5$	O	228	83	$C_{17}H_{15}NO_6$	62.00	4.59	4.25		
				ethanol		329.31	62.10	4.62	4.19		521
q	$(H_5C_2)_2N$	$COOC_2H_5$	O	193	82	$C_{19}H_{19}NO_6$	63.86	5.36	3.92		
				DMF		357.37	63.74	5.38	3.90		522
r	$(H_3C)_2N$	CN	O	286	47	$C_{15}H_{10}N_2O_4$	63.83	3.57	9.93		
				DMF		282.26	63.67	3.60	9.90		528
s	H	C_6H_5	NCH_3	201	34	$C_{19}H_{13}NO_5$	75.24	4.32	4.62		
				1-butanol		303.32	75.31	4.42	4.60		450
t	H	Benzthiazol-2-yl	NCH_3	dec. > 285	52	$C_{20}H_{12}N_2O_5S$	66.66	3.36	7.77	8.90	
				DMF		360.39	66.45	3.43	8.05	9.03	496
u	H	Benzimidazol-2-yl	NCH_3	328-330	56	$C_{20}H_{13}N_3O_5$	69.97	3.82	12.24		
				DMF		343.34	69.81	3.90	12.40		504
v	H	$SO_2C_6H_5$	NCH_3	281-282	75	$C_{19}H_{15}NO_5S$	62.12	3.57	3.81	8.73	
				Acetic acid		367.38	61.97	3.65	4.15	8.91	496
w	H_3CO	$COOC_2H_5$	NCH_3	228	72	$C_{17}H_{15}NO_6$	62.00	4.59	4.25		
				DMF		329.31	61.85	4.44	4.31		462
x	$(H_3C)_2N$	$COOC_2H_5$	NH	296	43	$C_{17}H_{16}N_2O_5$	62.19	4.91	8.53		
				DMF		328.33	62.24	5.06	8.80		524

(a) Neutral molecule; fluor. max. of the anion 520 nm (in aqueous *p*H 9 buffer solution.) (b) Anion fluorescence in protic solvents due to photodissociation (17).

Table 3

Ir and ^{1}H-nmr Data for Representative Examples of Compounds **2,3,5**

Compound	ir [cm^{-1}]	^{1}H-nmr (solvent, δ units, TMS = 0)
2c	3100 (broad), 1615, 1610	(DMSO-d_6): 3.88 (s, 3H); 5.50 (s, 1H); 6.8-7.0 (m, 2H); 7.75 (d, J = 10 Hz, 1H); 12.2 (br., s, 1H)
2g	3040, 2980, 2560 (br.) 1650, 1625, 1609	(DMSO-d_6): 3.51 (s, 3H); 3.83 (s, 3H); 5.78 (s, 1H); 6.7-7.0 (m, 2H); 7.69 (d, J = 9 Hz, 1H); 11.18 (br., 1H)
3c	1714, 1613, 1592	(Deuteriotrifluoroacetic acid): 3.92 (s, 3H); 6.77-7.37 (m, 3H); 7.48 (s, 5H); 8.05 (d, J = 9 Hz, 1H); 9.17 (d, J = 9 Hz, 1H)
3g	2970, 1658, 1611, 1590	(Deuteriotrifluoroacetic acid): 3.69 (s, 3H); 3.93 (s, 3H); 6.90-7.22 (m, 3H); 7.43 (s, 5H); 8.25 (d, J = 9 Hz, 1H)
5a	2980, 1739, 1649, 1622	(Deuteriochloroform): 7.18-7.88 (m, 9H); 8.12 (s, 1H)
5f	3020, 1743, 1639, 1613	(Deuteriochloroform): 1.40 (t, J = 7 Hz, 6 H); 4.23 (q, J = 7 Hz, 2H); 4.33 (q, J = 7 Hz, 2H); 7.27-8.23 (m, 4H); 8.67 (d, J = 17 Hz, 1H)
5k	3080, 2938, 1777, 1746, 1621	

All **5** exhibit strong fluorescence in the visible region (12). The emission maxima are listed in Table 2. As expected, R^1 and R^2 (as opposed to X) have a marked influence on the position of the fluorescence maximum. Electron-withdrawing groups in the 3-position cause a red shift as compared to the unsubstituted molecule ($R^1 = R^2 = H$, X = O, λ max = 398 nm). Benzthiazolyl and benzimidazolyl substituents cause particularly noticeable red shifts (70-112 nm).

The influence of electron-accepting R^2 substituents is further demonstrated by the spectra of **7a,b**, which were synthesized from **2d,e** and ethyl 3-oxobutyrate in the presence of ammonium acetate in a modified Pechmann reaction (5b). Their fluorescence maxima are both located at 474 nm, which sharply contrasts with the long wave maxima of **5g** (522 nm) and **5m** (549 nm).

On the other hand, changing R^1 from H to a dialkylamino group causes a red shift of 50-100 nm, dependant upon the electron accepting properties of R^2.

EXPERIMENTAL

Melting points are uncorrected. Ir spectra were obtained using a Perkin Elmer 421, ^{1}H-nmr spectra were recorded on a Varian A 60 A. Chemical shifts and coupling constants are given on the δ scale and in Hz respectively. Fluorescence spectra were measured at room temperature with a Perkin Elmer Hitachi MPF 44.

N-Methyl-3-methoxyaniline (**1g**).

Thirty two g. (0.26 mole) of 3-methoxyaniline, 39 g. (0.36 mole) of trimethoxymethane and 1 g. of concentrated sulfuric acid were reacted following the method of Roberts and Vogt (13) to yield 31 g. (72%) of *N*-methyl-3-methoxyformamilide (b.p. 12, 170-174°).

Anal. Calcd. for $C_9H_{11}NO_2$ (165.2): C, 65.44; H, 6.71; N, 8.48. Found: C, 65.42; H, 6.75; N, 8.51.

The product was dissolved in 100 ml. of 10% hydrochloric acid and boiled for one hour, made alkaline with solid sodium hydroxide, extracted with ether, concentrated and distilled to give **1g** (20.5 g., 80%) b.p. 11, 126-127°, lit. b.p. 11, 125-126° (14); n_D^{22} 1.5690; ir (potassium bromide): 3480, 2980, 2880, 1620, 1605 cm^{-1}; pmr (carbon tetrachloride): δ 2.68 (s, 3H), 3.66 (s, 3H), 5.95-6.30 (m, 3H), 6.80-7.25 (m, 1H).

Anal. Calcd. for $C_8H_{11}NO$ (137.2): C, 70.04; H, 8.08; N, 10.21. Found: C, 70.12; H, 8.02; N, 10.20.

Method A. Thermal Cyclization of Anilines **1g-i** with Diethyl Malonate.

Sixteen g. (0.1 mole) of diethyl malonate and 0.1 mole of the appropriate aniline **1g-i** were heated together for 4 hours to 200°. The alcohol formed was distilled off through a short column. The solid residue was treated with 50 ml. of methanol, filtered and recrystallized (Table 1).

Method B. Condensations using Phosphorus Oxychloride.

Malonic acid (10.4 g., 0.1 mole) 0.1 mole of the appropriate phenol or aniline and 10 ml. (16.7 g., 0.11 mole) of phosphorus oxychloride were mixed in an 500 ml. wide neck flask. On warming to 105°, a vigorous evolution of gas began and the mixture foamed strongly. After 4 hours at this temperature (exclusion of moisture!) the brown contents of the flask were pulverized, treated with ice water, dissolved in 200 ml. of 2 *N* sodium hydroxide filtered and precipitated with glacial acetic acid. The product may be recrystallized (Table 1), but is usually of sufficient purity to be used in the next step.

Method C. Cyclizations using Reactive Malonates.

Bis-2,4-dichlorophenyl malonate (15) (39.4 g., 0.1 mole) or 46.3 g. (0.1 mole) of bis-2,4,6-trichlorophenyl malonate (16) were dissolved with the phenol **1d-e** or the aniline **1g-i** in 100 ml. of dry toluene and heated under reflux for 2 hours. Compound **1c** reacted in boiling xylene for 2 hours. The mixture was cooled to room temperature, filtered, washed with hot ligroin to remove the chlorophenol and recrystallized (Table 1).

Preparation of 3-anilinomethylene-2,4-chromadiones and 3-anilinomethylene-1,2,3,4-tetrahydroquinoline-2,4-diones (**3a-i**) by three component condensation of **1a-i** with aniline and trithoxymethane was performed as described for **3a** (3) by refluxing in glacial acetic acid (method D) and **3b,f** (3,5) by melting together the components at 160° for 2 hours (method E).

2*H*,5*H*-Pyrano[3,2-*c*][1]benzopyran-2,5-diones and 2*H*,5*H*-Pyrano[3,2-*c*]-quinoline-2,5-diones (**5a,b,g,l,s**).

Five mmoles of the appropriate enamine **3** and 6 mmoles of the nitrile **4** were dissolved or suspended in 10 ml. of dry DMF. Potassium *t*-butoxide (1.68 g.,) 15 mmoles; if R^1 = OH, 30 mmoles are necessary) was added with vigorous stirring and the mixture heated to 110° for 5 hours. Most of the solvent was evaporated *in vacuo*, the residue taken up in benzene and stirred for one hour. The resulting brown solid product was removed by filtration, washed with benzene and dissolved in 20 ml. of water. The aqueous solution was filtered to remove insoluble material, concentrated to about 5 ml., diluted with alcohol, cooled in an ice bath and slowly acidified to *p*H < 1 with concentrated hydrochloric acid. The resulting crude precipitate was collected, washed neutral with 30% aqueous ethanol and purified by column chromatography. (Eluents: **5a,s**, chloroform; **5g**, dioxane; **5b**, chloroform-ethyl acetate 5/1; **5f** chloroform-

ethyl acetate 17/1). The desired product was detected by its fluorescence and, after evaporation of the eluent, recrystallized from the solvent given in Table 2.

2*H*,5*H*-Pyrano[3,2-*c*][1]benzopyran-2,5-diones and 2*H*,5*H*-Pyrano[3,2-*c*]-quinoline-2,5-dioines (**5c-e, f-k, m-r, t-x**).

Five mmoles of the appropriate enamine **3** and 6 mmoles of the nitrile **4** were dissolved or suspended in 10 ml. of dry DMF. Anhydrous potassium hydroxide (0.43 g., 7 mmoles; if R^1 = OH, 14 mmoles are necessary) in absolute ethanol (5 ml.) was added with vigorous stirring. The resulting clear solution was heated for 30 minutes at 80°. Alternatively the solution can be kept at room temperature until no more **3** can be detected by tlc (usually 5-7 days). After dilution with water the solution was cooled in an ice bath, slowly acidified to *p*H < 1 with concentrated hydrochloric acid and brought to *p*H 5 with sodium bicarbonate. The resulting precipitate was stirred for another hour at room temperature, collected, washed neutral with 50% aqueous ethanol and purified by recrystallization (Table 2).

1,4-Bis[3-(2,5-dioxo-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyranyl)]benzene (**6a**).

Compound **3a** (0.81 g., 3 mmoles) and 0.47 g. (3 mmoles) of *p*-xylxidenedicyanide were suspended in 10 ml. of anhydrous DMF at 40°. Potassium *t*-butoxide (0.34 g., 5 mmoles) was added with vigorous stirring (the colour of the solution turned immediately from yellow to black). The mixture was kept at 40° for 20 hours, then cooled in an ice bath, acidified to *p*H < 1 with concentrated hydrochloric acid (colour turned orange) and diluted with 5 ml. of water. The crude precipitate was collected, washed neutral with 50% aqueous ethanol and recrystallized from nitrobenzene to give 0.35 g. (23%) of yellow needles, m.p. > 350°; ir (potassium bromide): 1727, 1636, 1608 cm^{-1}; me (m/e, relative intensity): 502 (10), 474 (7), 446 (6), 283 (11), 213 (60), 163 (33), 119 (100), 91 (77), 77 (38); fluorescence max (DMF): 460 and 487 nm.

Anal. Calcd. for $C_{30}H_{14}O_8$ (502.44): C, 71.72; H, 2.81. Found: C, 71.45; H, 2.95.

1,4-Bis[3-(8-dimethylamino-2,5-dioxo-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyranyl)]benzene (**6b**).

This compound was prepared from **3e** and *p*-xylyidenedicyanide by the method given for **6a**, but could not be obtained in analytical purity by recrystallization from DMSO, 0.29 g. (15%) of red crystals, m.p. > 350°; ir (potassium bromide): 2990, 1736, 1622 cm^{-1}; fluorescence max. (DMF): 539 nm.

8-Dimethylamino-4-methyl-2*H*,5*H*-pyrano[3,2-*c*]benzopyran-2,5-dione (**7a**).

Compound **2d**, (2.05 g., 10 mmoles), 2.60 g. (20 mmoles) of ethyl 3-oxobutyrate and 3 of ammonium acetate were mixed in a flask and heated to 170° for 30 minutes. The resulting mixture was poured into 100 ml. of water, the crystalline material thus obtained filtered off and recrystallized from DMF yielding 2.50 g. (92%) of **7a**, m.p. 260° ir (potassium bromide): 1755, 1735, 1643 cm^{-1}; pmr (deuteriotrifluoroacetic acid): δ 2.80 (s, 3H), 3.61 (s, 6H), 6.66 (d, J = 2 Hz, 1H), 790 (dd, J = 2 Hz, J′ = 9 Hz, 1H), 7.96 (s, 1H), 8.51 (d, J = 9 Hz, 1H); fluorescence max. (ethanol): 474 nm.

Anal. Calcd. for $C_{15}H_{13}NO_4$: (271.28): C, 66.42; H, 4.83; N, 5.16. Found: C, 66.46; H, 4.80; N, 5.20.

8-Dimethylamino-4-methyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-2,5-dione (**7b**).

Compound **7b** was prepared from **2e** by the method used for **7a**, yield 2.61 g. (87%), m.p. 194° (from dioxane); ir (potassium bromide): 3030, 1760 (sh), 1742, 1732, 1638 (sh), 1622 cm^{-1}; fluorescence max. (ethanol): 474 nm.

Anal. Calcd. for $C_{17}H_{17}NO_4$ (299.33): C, 68.11; H, 5.72; N, 4.68. Found: C, 68.20; H, 5.60; N, 4.59.

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(11) Replacement of DMF by other solvents results in reduced yields.

(12) The lasing properties of compounds **5** and **7** will be discussed in a subsequent publication.

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(17) Generally, this type of compound is a much stronger acid in its first excited singlet state than in its ground state and can undergo adiabatic photo-dissociation.