REACTION OF 4-DIETHYLAMINOSALICYLALDEHYDE WITH MALONONITRILE

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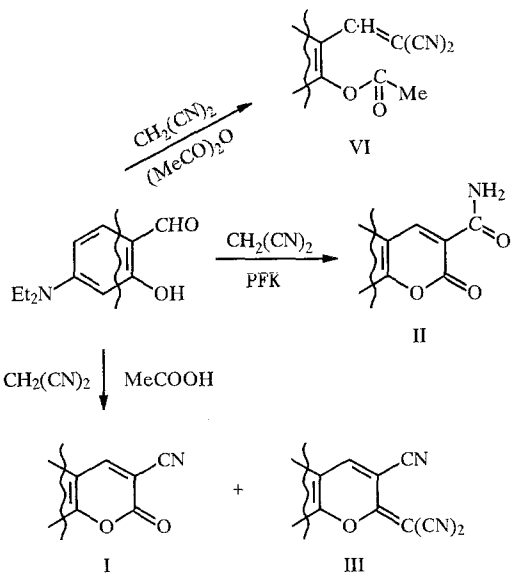
The composition of the products from the reaction of 4-diethylaminosalicylaldehyde with malononitrile depends on the reaction conditions. A suitable method for the preparation of 2-dicyanomethylene-2H-1-benzopyrans is proposed. The dissociative ionization under electron impact of coumarin analogs has been studied. The relation between the polarity of the exocyclic double bond at C_2 of coumarin, the position of the ^1H NMR signal, and the position of the long-wavelength absorption band in the electronic spectrum is established.

Coumarin derivatives with electron—acceptor substituents at position 3 are obtained by Knoevenagel consideration of aromatic o-hydroxycarbonyl compounds with active methylene compounds accompanied by ring closure of the heterocycle [1]. When substituted acetonitriles are used as the active methylene compounds, derivatives of iminobenzopyran are formed, the spectroluminescent properties of which, like those of coumarin derivatives [2], are of considerable practical interest [3, 4]. For example, when malononitrile condensed with salicylaldehydes the products were 2-imino-3-cyano-2H-1-benzopyrans, which in most cases underwent hydrolysis to 3-cyanocoumarins under the reaction conditions [5-9]. Compounds of more complex structure were also isolated which were formed either by reaction of the carbonyl with self-condensation products from malononitrile (dimer, trimer) or as a result of further addition of malononitrile to the cyanocoumarin intermediate [10-13]. It is known that malononitrile and its dimer can add to coumarins with a free position 4 (Michael addition) [12-16].

To examine the preparative possibilities of condensations of this type to give organic luminophores the reaction of 4-diethylaminosalicylaldehyde with malononitrile has been studied. The product composition was found to depend on the reaction conditions. In acid media the principal product is either 3-cyano-7-diethylamino-2H-1-benzopyran-2-one (I) (acetic, butyric, or trifluoroacetic acid, or a solution of HCl in ethanol), or its hydrolysis product, 7-diethylaminocoumarin-3-carbonamide (II) (polyphosphoric acid).

Compound II, coumarin-3-carboxylic acid (IV), and 7-diethylaminocoumarin (V) were obtained by the hydrolysis of 3-cyanocoumarin (I) in sulfuric acid. Similarly, hydrolysis of the amide II gave coumarins IV and V, depending on the conditions.



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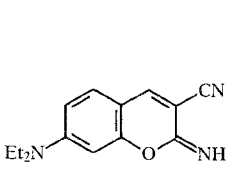
When the reaction was carried out in acetic and butyric acids 2-dicyanomethylene-3-cyano-7-diethylaminobenzopyran (III) was formed along with compound I with molar ratios of aldehyde from 1:1-3, with a maximum yield of compound III at a ratio of 1:2.2 [17].

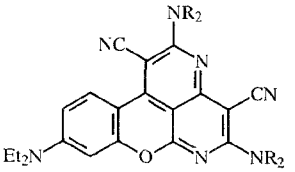
When the reaction was carried out in a mixture of acetic acid and acetic anhydride the product was 2-cyano-3-(4-diethylamino-2-acetoxyphenyl)acrylonitrile (V) with compounds I and III as impurities (based on TLC). Compound VI is readily converted to coumarin I by acid hydrolysis.

The reaction of 4-diethylaminosalicylaldehyde with malononitrile under neutral and basic conditions was also studied. When the reagents were fused in equimolar quantities (at 60-70°C), or when the reaction was carried out in neutral (benzene, DMF, ethanol) or basic conditions (benzene or ethanol with addition of pyridine, piperidine, alkali metal alkoxides, etc.; benzene in the presence of triethylbenzylammonium chloride and aqueous NaOH solution; DMF in the presence of ammonium or piperidinium acetate) mixtures of the same substances were obtained: 2-imino-3-cyano-7-diethylamino-2H-1-benzopyran (VII) and products of its further reaction with malononitrile (or products of the addition of malononitrile oligomers [18] with the aldehyde). However, the ratio of the products depends on the reaction conditions when equimolar amounts of the reactants are used. For example, the yield of the iminocoumarin VII is maximal (48%) in strongly basic conditions (benzene in the presence of triethylbenzylammonium chloride and aqueous NaOH solution, ethanolic potassium *tert*-butoxide).

Under these conditions a series of other compounds are formed, apart from the iminocoumarin VII, with interesting spectroluminescent properties. The only compound isolated was VIII, as a result of its poor solubility in organic solvents. Compound VIII and the remaining components of the mixture may be products of further reactions of the iminocoumarin VII, as shown by TLC comparison of products from the reactions of 4-diethylaminosalicylaldehyde and the iminocoumarin VII with malononitrile under identical conditions (in the molten state, or in ethanol with basic reagents listed above).



VII



VIII, IX

VIII R=H; IX R=Et

Only 3-cyanocoumarin I (42% yield) was isolated when the reaction was carried out in aqueous ethanol in the presence of diethylamine with subsequent addition of hydrochloric acid to the reaction mixture.

Compound VIII was also obtained from the reaction of various 3-R-7-diethylaminocoumarins (R = cyano, carboxy, acetyl, benzimidazoyl, amino) with malononitrile in DMF in the presence of 15% aqueous KOH solution.

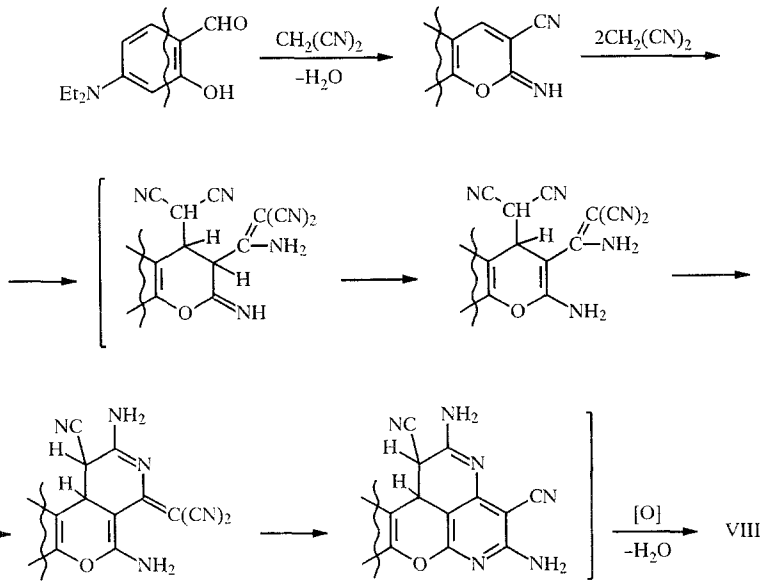
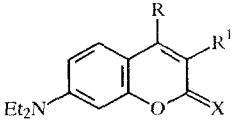


TABLE 1. Characteristic Peaks of Ions of Compounds III, VII, XII, XIV, and XV with the General Formula



Compound	X	M (Φ_0)	M − CH_3 (Φ_1)	M − CX (Φ_4)	M − CH_3 − C_2H_4 (Φ_2)	M − CH_3 − CX (Φ_5)	M − CH_3 − C_2H_4 − $HN{=}CH_2$ (Φ_3)	M − CH_3 − C_2H_4 − CX (Φ_6)
III	$C(CN)_2$	290 (43)	275 (100)	—	247 (37)	—	218 (7)	—
VII	NH	241 (43)	226 (100)	—	198 (24)	—	—	—
XII	NCH_3	255 (66)	240 (100)	—	212 (18)	199 (6)	183 (8)	171 (15)
XIV	$C(CN)_2$	279 (73)	264 (100)	—	236 (24)	—	207 (4)	—
XV	S	247 (87)	232 (100)	203 (14)	204 (22)	188 (13)	175 (3)	160 (6)

TABLE 2. ^1H NMR Spectra of Compounds I, III, VII and XII-XV in $CDCl_3$

Compound	Chemical shifts, δ, ppm								Spin–spin coupling constants, J, Hz		
	3-H (d)	4-H (d)	5-H (d)	6-H (d, d)	8-H (d)	N $(CH_2CH_3)_2$ (t)	N $(CH_2CH_3)_2$ (q)	other protons	J_{56}	J_{68}	$J_{3,CH3}$
XII	—	7,44	7,08	6,43	6,30	1,21	3,41	=N–CH_3 3,20 (1H s)	9,5	2,5	—
VII	—	7,57	7,12	6,45	6,32	1,22	3,41	=N–H not observed	9,0	2,2	—
I	—	7,96	7,33	6,64	6,46	1,25	3,45	—	9,5	2,0	—
III	—	7,76	7,34	6,70	6,55	1,28	3,53	—	9,2	2,0	—
XIII	5,91	—	7,37	6,59	6,47	1,22	3,41	4-CH_3 2,32 (3H, d)	9,0	2,5	1
XV	6,92	—	7,45	6,71	6,66	1,25	3,45	4-CH_3 2,31 (3H, d)	9,8	2,6	1
XIV	6,51	—	7,47	6,75	6,60	1,28	3,50	4-CH_3 2,43 (3H, d)	9,0	2,5	1

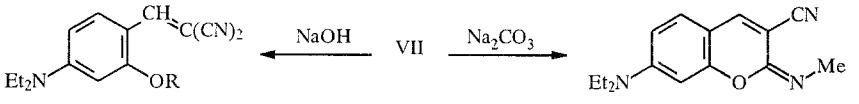
TABLE 3. Mass Spectra of Compounds VI and VIII-XI

Compound	Characteristic peaks of the ions (relative intensity, %)
VI	$[M]^+$ 283 (31), $[M - CH_3]^+$ 268 (16), $[M - CH_2CO]^+$ 241 (38), $[M - CH_3 - CH_2CO]^+$ 226 (100), $[M - CH_3 - CH_2CO - C_2H_4]^+$ 198 (28)
VIII	$[M]^+$ 371 (59), $[M - CH_3]^+$ 356 (100), $[M - CH_3 - C_2H_4]$+ 328 (35), $[M - CH_3 - C_2H_4 - HN{=}CH_2]^+$ 299 (9)
IX	$[M]^+$ 483 (52), $[M - CH_3]^+$ 468 (6), $[M - C_2H_4]^+$ 455 (100), $[M - C_2H_4 - CH_2]^+$ 441 (58)
X	$[M]^+$ 269 (28), $[M - CH_3]^+$ 254 (100), $[M - CH_3 - C_2H_4]^+$ 226 (10), $[M - CH_3 - C_2H_4 - C_2H_4]^+$ 198 (20)
XI	$[M]^+$ 255 (50), $[M - CH_3]^+$ 240 (100), $[M - CH_3 - C_2H_4]^+$ 212 (13)

When compound VIII was heated in triethyl phosphate in the presence of potassium carbonate compound IX, which has excellent solubility in organic solvent, was formed. Molecular formulas were established from mass spectrometric data (VIII, M^+ 371; IX, M^+ 483) and elemental analysis: VIII is $C_{20}H_{17}N_7O$ while IX is $C_{28}H_{33}N_7O$. Compound IX was identified as 1,4-dicyano-2,5,9-tris(diethylamino)-3,6-diazabenzo[h,*a'*]xanthene with the help of ^1H, ^{13}C, and ^{15}N NMR spectroscopy (Bruker AM-360, working frequency 360 Hz for protons) on the basis of ^1H, ^{13}C, and ^{15}N chemical shifts, $J_{H,H}$, $J_{C,H}$ (proton-coupled ^{13}C NMR spectra), and $J_{C,C}$ coupling constants (1D—INADEQUATE), tracking the sequence of carbon—carbon bonds (2D—INADEQUATE), and calculation of the ^{13}C chemical shifts by an additive scheme.*

Consequently, compound VIII is 1,4-dicyano-2,5-diamino-9-diethylamino-3,6-diazabenzo[h,*a'*]xanthene. One possible route for its formation is given above.

We have also studied some reactions of the iminocoumarin VII. For example, alkylation with diethyl sulfate, dimethyl sulfate, and methyl iodide in the presence of aqueous NaOH gave 2-cyano-3-(4-diethylamino-2-alkoxyphenyl)acrylonitrile (X, XI) as a result of opening of the lactone ring. Alkylation with dimethyl sulfate in dioxane in the presence of aqueous sodium carbonate gave 2-N-methylimino-3-cyano-7-diethylamino-2H-1-benzopyran (XII) with retention of that ring.

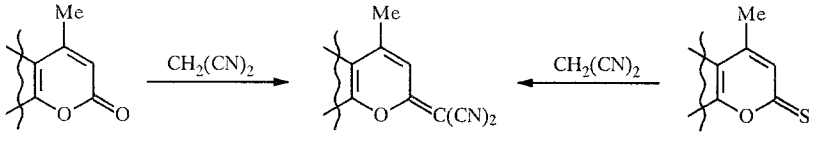


X, XI XII

X R=Et; XI R=Me

In contrast to the result in neutral or basic media, reaction of the iminocoumarin VII with malononitrile in acetic acid gave the dicyanomethylene derivative III in approximately the same yield as in the reaction of 4-diethylaminosalicylaldehyde with malononitrile, plus other products.

Unlike the iminocoumarin VII, coumarin I does not react with malononitrile to give a dicyanomethylene derivative either in acid conditions or even in the presence of a dehydrating agent ($POCl_3$), whereas 4-methyl-7-diethylaminocoumarin (XIII) with malononitrile in $POCl_3$ formed 2-dicyanomethylene-7-diethylamino-2H-1-benzopyran (XIV) in 8% yield. Compound XIV can also be obtained, but in 66% yield, by condensation of 2-thio-4-methyl-7-diethylamino-2H-1-benzopyran (XV) with malononitrile in strongly basic conditions.



XIII XIV XV

We have studied some physicochemical properties of the compounds prepared.

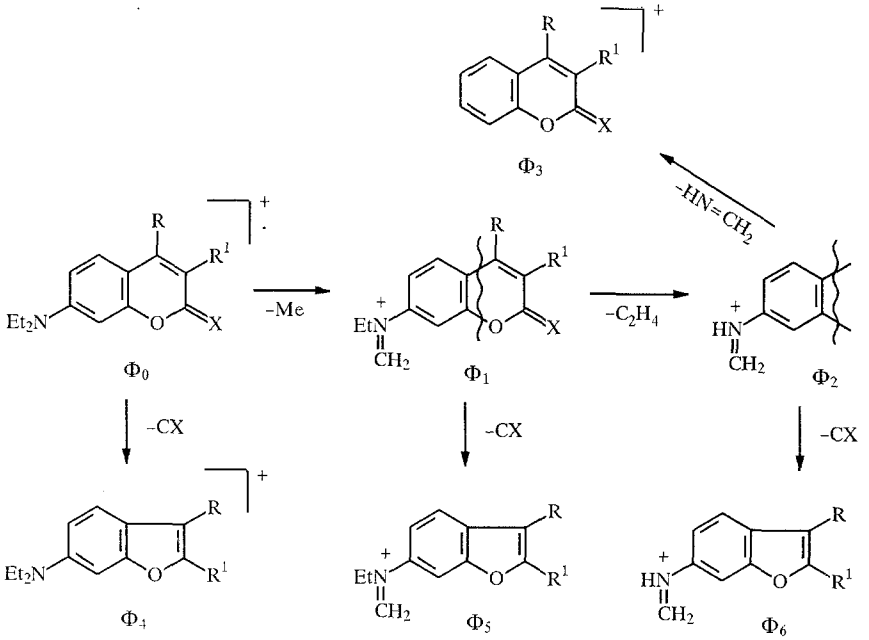
*A. V. Buevich, N. D. Sergeeva, and N. M. Sergeev recorded and interpreted the NMR spectra.

Analysis of the mass spectra of the analogous coumarins III, VII, XII, XIV, and XV (Table 1) shows that the basic dissociative ionization of these compounds under electron impact is decomposition at the 7-diethylamino group ($\Phi_1 \rightarrow \Phi_3$), which is characteristic for 7-dialkylaminocoumarins [19, 20].

However, in the case of the N-methyliminocoumarin XII, the concurrent process of pyrone ring destruction with formation of fragments Φ_5 and Φ_6 has a considerable influence, and this is even stronger with the thiocoumarin XV (fragments Φ_4-Φ_6).

Fragmentation of the substituent in position 2 was also observed for the N-methyliminocoumarin XII: the fragments $[M-CH_2]^+$ 241 (20.4%) and $[M-CH_2-CH_3]^+$ 226 (4.5%) were observed. Loss of the cyano group at position 3 was not observed for the coumarin derivatives III, VII, and XII.

Fragmentation of the diazabenzoxanthene VIII (Table 2) occurs analogously at the diethylamino group, whereas loss of the CH_3 group from compound IX occurs to a smaller extent and is based on the fragments $[M-C_2H_4]^+$ and $[M-C_2H_4-CH_2]^+$.



Fragmentation of the benzene derivatives VI, X, and XI occurs at both the diethylamino group and the substituent in position 2 (see Table 2).

Analysis of the ^1H NMR spectra of compounds I, III, VII, and XII-XIV shows that the proton signals for these compounds are in regions typical for coumarins [21] and the chemical shifts of protons H_5, H_6, and H_8 in the series of analogs XII—VII—I—III and XIII—XV—XIV increase in parallel with the increase in polarity of the exocyclic double bond at C_2 of the pyran system (Table 3). Protons H_8 in compounds XIV and XV are exceptions. The proton signals for the ethyl radicals of the 7-diethylamino group also undergo weak field shifts with increased polarity of the exocyclic double bond in the same series, which indicates an increase in charge transfer from the 7-diethylamino group into the ring. The long-wavelength absorption bands in the electronic spectra of the same compounds also shift bathochromically in parallel with this increase in charge transfer (Table 4). For example, replacement of the carbonyl oxygen of the lactone group by the dicyanomethylene fragment caused a bathochromic shift of the long-wavelength maximum by about 100 nm. This is evidently connected with a considerable charge transfer from the amino group to the dicyanomethylene unit in the ground state. The small Stokes shift and the low quantum yield for luminescence observed for compounds III and XIV may be explained in the same way. The decrease in quantum yield on going from compound XIII to its thio-analog XV is evidently explained by the "heavy atom effect," the increase in the spin-orbital coupling constant, and the consequent increase in the probability of intercombination conversion.

EXPERIMENTAL

Absorption spectra were recorded with a Specord UV-VIS spectrophotometer. Fluorescence spectra were recorded with an SLM 4800S phase spectrofluorimeter. IR spectra of KBr disks were obtained with a Zeiss UR-20 spectrometer. Mass spectra were measured with an MX-1320 apparatus with an ionizing voltage of 50 eV. ^1H NMR spectra were recorded with a Bruker WP-80 at 80 MHz and with TMS as internal standard. Silufol UV-25 strips were used for TLC.

The purity of compounds was monitored by TLC. Elemental analyses found for C, H, N, and S corresponded to the calculated values. Physical constants for the compounds are cited in Tables 1-4.

TABLE 4. Characteristics of the Compounds Synthesized

Compound	Molecular formula	mp, °C	IR spectrum, ν, cm^{-1}, in KBr	Spectro-luminescent properties (in ethanol)		
				λ_{max}^{abs}, nm (log ε)	λ_{max}^{lum}, nm	quantum yield, η
I	$C_{14}H_{14}N_2O_2$	229...230	2216 (C≡N), 1725 (C=O), 1636 (C=C)	215 (4,34), 258 (4,12), 428 (4,64)	474	0,13
III	$C_{17}H_{14}N_4O$	240...240,5	2226 (C≡N), 2218 (C≡N), 2208 (C≡N), 1650 (C=C)	267 (4,41), 295 (4,20), 330 (4,15), 490 (4,52), 516 (4,67)	546	0,08
VI	$C_{16}H_{17}N_3O_2$	96...97	2221 (C≡N), 1784 (C=O), 1617 (C=C)	263 (3,86), 440 (4,66)	—	—
VII	$C_{14}H_{15}N_3O$	125...126	3328 (N—H), 2216 (C≡N), 1645 и 1628 (C=N or C=C)	217 (4,44), 256 (4,11), 424 (4,59)	473	0,40
VIII	$C_{20}H_{17}N_7O$	> 350	3441 и 3350 (N—H), 2212 (C≡N), 1630 (C=C)	Low solubility		
IX	$C_{28}H_{33}N_7O$	177...178	2200 (C≡N), 1635 (C=C)	256 (4,46), 285 (4,60), 405 (4,60)	470	0,70
X	$C_{16}H_{19}N_3O$	132...133	2215 (C≡N), 1622 (C=C)	280 (3,95), 287 (3,97), 442 (4,87)	—	—
XI	$C_{15}H_{17}N_3O$	119...120	2215 (C≡N), 1620 (C=C)	280 (3,92), 286 (3,94), 441 (4,83)	—	—
XII	$C_{15}H_{17}N_3O$	139...140	2222 (C≡N), 1667 и 1625 (C=N и C=C)	254 (4,48), 330 (3,78), 413 (4,54)	470	0,20
XIII	$C_{14}H_{17}NO_2$	73...74	1710 (C=O), 1620 (C=C)	243 (4,16, 315 (3,54), 375 (4,38)	450	0,54
XIV	$C_{17}H_{17}N_3O$	196...197*	2217 (C≡N), 1639 (C=C)	252 (4,36), 276 (4,24), 452 (4,42), 477 (4,51)	522	0,09
XV	$C_{14}H_{17}NOS$	95...96	1633 (C=C)	250 (4,48), 310 (3,70), 460 (4,46)	515	0,05

*The literature [24] gives mp 201°C.

3-Cyano-7-diethylaminocoumarin (I). A. Dry hydrogen chloride was bubbled through a solution of 4-diethylaminosalicylaldehyde (5.79 g, 30 mmoles) in ethanol (70 ml). Malononitrile (3.96 g, 60 mmoles) was added and the mixture was boiled 1 h in a stream of HCl. Water (910 ml) was added, the mixture was cooled, and the precipitate filtered off, treated with sodium carbonate solution, washed with water, and dried. It was recrystallized from ethanol—ethyl acetate to give compound I (4.92 g, 68%), mp 229-230°C. The literature gives mp 229°C [22] and 234-235°C [8].

B. Diethylamine (2 ml) and water (6 ml) were added to a solution of 4-diethylaminosalicylaldehyde (3.86 g, 20 mmoles) and malononitrile (1.32 g, 20 mmoles) in ethanol (50 ml), the mixture was heated to 60°C and stirred for 5 min. Concentrated HCl (6 ml) was added to the suspension formed and the mixture was stirred for 5 min at 60°C. The precipitate was filtered off, washed, dried, and recrystallized to give compound I (2.02 g, 42%), mp 229-230°C.

C. Compound VI (2.83 g, 10 mmoles) was boiled in a mixture of ethanol (15 ml) and 15% HCl (4 ml) for 20 min; the mixture was cooled, poured into water (35 ml), and neutralized with 15% NaOH. The precipitate was filtered off, dried, and crystallized from ethanol—ethyl acetate to give coumarin I (2.03 g, 84%).

7-Diethylaminocoumarin-3-carboxamide (II). A. A solution of 4-diethylaminosalicylaldehyde (3.86 g, 20 mmoles) and malononitrile (1.32 g, 20 mmoles) in polyphosphoric acid (30 g) was stirred over a boiling water bath for 2 h. The mixture was poured into water (150 ml) and neutralized with 10% NaOH solution. The precipitate was filtered off, dried, and recrystallized twice from ethyl acetate to give the amide II (2.76 g, 53%), mp 229-230°C [22].

B. Coumarin I (1.21 g, 5 mmoles) was heated in 90% H_2SO_4 (10 ml) at 90-95°C for 20 min; the mixture was cooled, poured into water (50 ml), and neutralized with 20% NaOH solution. The precipitate was filtered off, dried, and crystallized from ethanol to give amide II (1.07 g, 82%).

2-Dicyanomethylene-3-cyano-7-diethylamino-2H-1-benzopyran (III). A. A solution of 4-diethylaminosalicylaldehyde (2.90 g, 15 mmoles) and malononitrile (2.18 g, 33 moles) in acetic acid (20 ml) was boiled for 1.5 h. The acetic acid was evaporated in vacuum, water was added (25 ml), and the solution neutralized with sodium carbonate solution. The precipitate was filtered off, washed with water, and dried. Reddish needles of compound III (0.27 g, 6.2%) and compound I (0.98 g, 27%) were separated by column chromatography (silicagel 40/100, chloroform eluent) and recrystallized from ethanol—ethyl acetate.

B. A solution of the iminocoumarin VII (0.97 g, 4 mmoles) and malononitrile (0.27 g, 4 mmoles) in acetic acid (10 ml) was boiled for 1 h. The acetic acid was evaporated in vacuum, water (10 ml) added, and the solution neutralized with sodium carbonate solution. The precipitate was filtered off, washed with water, and dried. The dicyanomethylenebenzopyran III (0.10 g, 8.6%) and the cyanocoumarin I (0.21 g, 22%) were obtained after chromatography and recrystallization

7-Diethylaminocoumarin-3-carboxylic Acid (IV). A. The coumarin I (2.0 g, 8.3 mmoles) was heated in 70% H_2SO_4 (15 ml) at 90-95°C for 40 min; water (30 ml) was added, and the mixture boiled for 40 min, cooled and neutralized with 20% NaOH solution. The precipitate was filtered off and recrystallized from DMF to give the acid IV (1.31 g, 60%), mp 227-229°C [23].

B. The amide II (1.3 g, 5 mmoles) was boiled in 20% HCl for 2 h, cooled, neutralized with 20% NaOH solution, and recrystallized from DMF to give acid IV (0.98 g, 75%).

7-Diethylaminocoumarin (V). Coumarin I (1.0 g, 4.13 mmoles) was boiled in 35% H_2SO_4 (45 ml) for 8 h, the mixture was cooled, neutralized with 30% NaOH solution ($T \leq 30°C$), the precipitate filtered off, and dried to give compound V (0.84 g, 93%), mp 90-90.5°C (from heptane). The literature [19] gives mp 90°C.

Compound V was obtained from amide II and acid IV by an analogous method in yields of 90-94%.

2-Cyano-3-(4-diethylamino-2-acetoxyphenyl)acrylonitrile (VI). A solution of 4-diethylaminosalicylaldehyde (2.90 g, 15 mmoles) and malononitrile (2.18 g, 33 mmoles) in a mixture of acetic acid (16 ml) and acetic anhydride (4 ml) was boiled for 1 h. The mixture was cooled, neutralized with 15% NaOH solution, and extracted with ethyl acetate (3 × 40 ml). The combined extract was dried over $CaCl_2$ and partially evaporated. The product was purified by column chromatography (silicagel 40/100, eluent benzene—ethyl acetate) and recrystallized from benzene to give yellowish compound VI (2.08 g, 49%).

2-Imino-3-cyano-7-diethylamino-2H-1-benzopyran (VII). A solution of 4-diethylaminosalicylaldehyde (4.83 g, 25 mmoles) and malononitrile (1.65 g, 25 mmoles) in absolute ethanol (35 ml) was stirred at room temperature for 20 min with a catalytic amount of potassium *tert*-butoxide. The precipitate was filtered off and mixed with acetone (50 ml). The residue, insoluble in acetone, was separated and recrystallized from DMF to give compound VIII (0.30 g, 3.2%).The acetone solution was poured into heptane (400 ml). The precipitate was separated and reprecipitated several times from acetone—heptane mixtures, and dried at room temperature to give the iminocoumarin VII (2.90 g, 48%).

1,4-Dicyano-2,5-diamino-9-diethylamino-3,6-diazabenzo[h,*a*']xanthene (VIII). A. A solution of 4-diethylaminosalicylaldehyde (1.93 g, 10 mmoles) and malononitrile (3.90 g, 60 mmoles) in DMF (20 ml) was boiled for 30 min in the presence

of a catalytic amount of potassium *tert*-butoxide. The mixture was cooled, the precipitate filtered off, and recrystallized from DMF to give compound VIII (1.88 g, 51%).

B. An analogous experiment with absolute ethanol as solvent gave compound VIII (1.81 g, 49%).

C. A 15% solution of KOH was added to a solution of a 3-R-7-diethylaminocoumarin (R = cyano, carboxy, acetyl, benzimidazoyl, amino) (5 mmoles) and malononitrile (30 mmoles) in DMF (20 ml). The mixture was boiled for 1 h, cooled, the precipitate filtered off, and recrystallized from DMF to give compound VIII in 8-24% yield.

1,4-Dicyano-2,5,9-tris(diethylamino)-3,6-diazabenzo[h,*a*']xanthene (IX). Potassium carbonate (1.3 g) was added to a solution of compound VIII (0.74 g, 2 mmoles) in triethyl phosphate (15 ml) and the mixture was boiled for 8 h, cooled, poured into water (60 ml), and 15% NaOH (5 ml) added. The precipitate was filtered off and recrystallized from heptane to give compound IX (0.42 g, 50%).

2-Cyano-3-(4-diethylamino-2-alkoxyphenyl)acrylonitrile (X, XI). A. To a solution of the iminocoumarin VII (0.48 g, 2 mmoles) in dioxane (15 ml) was added a 20% solution of NaOH (9 ml). The solution was cooled to 12°C and diethyl sulfate (0.92 g, 6 mmoles) was added. The mixture was stirred at room temperature for 3 h, water (100 ml) was added, and stirring was continued for 1 h. The precipitate was filtered of, dried, and recrystallized from pentane to give compound X (0.33 g, 61%).

Compound XI was obtained in 58% yield by alkylation with dimethyl sulfate under analogous conditions.

B. A 20% solution of NaOH (9 ml) and methyl iodide (1.42 g, 10 mmoles) were added to a solution of the iminocoumarin VII (0.72 g, 3 mmoles) in dioxane (18 ml). The mixture was stirred at 35-40°C for 2 h, poured into water (100 ml), and stirred for 1 h. The precipitate was filtered off and recrystallized from heptane to give compound XI (0.26 g, 34%).

2-Methylimino-3-cyano-7-diethylamino-2H-1-benzopyran (XII). Dimethyl sulfate (0.76 g) and 10% sodium carbonate solution (10 ml) were added to a solution of the iminocoumarin VII (0.48 g, 2 mmoles) in dioxane (15 ml). The mixture was stirred for 5 h at room temperature, then poured into water (60 ml), and stirred for 1 h. The precipitate was filtered off, dried, and recrystallized from heptane to give the methyliminocoumarin XII (0.23 g, 45%).

2-Thio-7-diethylamino-4-methyl-2H-1-benzopyran (XV). P_2S_5 (8.88 g, 40 mmoles) was added to a hot solution of 7-diethylamino-4-methylcoumarin (XIII) (8.09 g, 35 mmoles) in toluene (50 ml) and boiled for 3 h. The toluene solution was decanted and the residue extracted with ethyl acetate. The solutions were combined and evaporated in vacuum. The product was separated by chromatography (silicagel 40/100, benzene—ethyl acetate eluent) and recrystallized from heptane to give the thiocoumarin XV (4.37 g, 51%).

2-Dicyanomethylene-7-diethylamino-4-methyl-2H-1-benzopyran (XIV). A. The coumarin XIII (4.62 g, 20 mmoles) and malononitrile (1.98 g, 30 mmoles) were boiled in $POCl_3$ (15 ml) for 3 h. Phosphorus oxychloride was evaporated in vacuum and the residue was dissolved in chloroform, washed with water (2 × 20 ml), and dried over $CaCl_2$. The product was purified by chromatography (silicagel, chloroform) and recrystallized from a benzene—heptane mixture to give compound XIV (0.45 g, 8%).

B. Malononitrile (0.26 g, 4 mmoles) and potassium *tert*-butoxide (0.22 g) were added to a solution of the thiocoumarin XV (0.50 g, 2 mmoles) in dry DMSO (7 ml), the mixture was stirred at room temperature for 10 h, poured into water (35 ml), and neutralized with acetic acid. The precipitate was filtered off, washed with water, dried and recrystallized from a benzene—heptane mixture to give compound XIV (0.37 g, 66%).

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