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KETOCOUMARINS

A NEW CLASS OF TRIPLET SENSITIZERS

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Abstract—Several derivatives of 3-ketocoumarins were prepared and are shown to have many of the photophysical criteria required for efficient triplet sensitizers. These compounds include 3-aroylcoumarins (**1**) and 3,3'-carbonyl-biscoumarins (**2**). The aryl groups in **1** are either phenyl and substituted phenyl derivatives or heterocyclic groups such as thienyl and benzofuryl. The substituents on the coumarin moiety in **1** and **2**, if any, are alkoxy or dialkylamino. These compounds, with absorption maxima between 330 and 450 nm, have extinction coefficients in the range of 10^4 to almost 10^5, which is an important criterion for efficient sensitization of thin films of polymers as those used in photoresists and lithography. The singlet–triplet intersystem crossing (isc) efficiencies of several derivatives approach unity. In others, however, a radiationless decay process competes with the isc. The decay process is particularly dominant in the asymmetrically substituted derivatives of **2**, but seems to be considerably suppressed in polymeric matrices. The triplet energies of these compounds range from *ca.* 48 to 60 kcal/mol. Some of these ketocoumarins show phosphorescence spectra that suggest the presence of "frozen-in" rotamers.

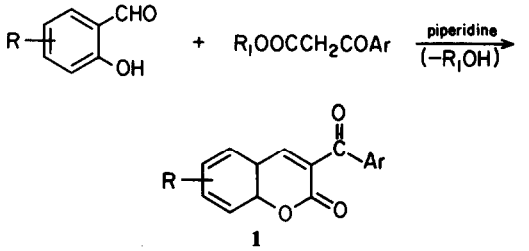
Sensitization via triplet–triplet energy transfer not only broadened the scope of organic photochemistry but is essential for some industrial applications. The triplet-sensitized photodimerization and the mixed addition of olefins have allowed easy access to numerous cyclobutane derivatives and are also the basis for crosslinking many polymers used for lithography and photoresist applications.

The photosensitization of crosslinking of poly(vinyl cinnamate) with several compounds, a process now recognized[1,2] to be predominantly if not entirely via cyclobutadimerization of the cinnamate moieties, was first reported by Minsk[3] in 1952. This technically important discovery, however, did not lead to the realization of its potential in organic photochemistry. Schenck and Steinmetz recognized the potential of the photosensitized cycloaddition reactions when they discovered that the cycloaddition of maleic anhydride to benzene can be sensitized by benzophenone.[4] The many examples of such reactions reported by Schenck *et al.*[5] and the countless related reactions studied by others[6,7] point to the importance of this discovery. Primarily through the work of Hammond *et al.* it is now accepted that the mechanism of most of these sensitized reactions involves triplet–triplet energy transfer from the sensitizer to the substrate.[7,8] This applies also for the sensitization of crosslinkable polymers.[1,2,9]

More efficient sensitizers have been needed for photoreactive systems. Also, systematic studies of energy transfer and related processes in fluid solutions as well as in polymeric matrices require the use of sensitizers with various triplet energies. Preferably these sensitizers should be selected from one class of compounds. This work deals with the preparation and pertinent photophysical properties of a new class of efficient triplet sensitizers ranging in triplet energy from *ca.* 48 to 60 kcal/mol with absorption maxima ranging from *ca.* 330 to 470 nm.

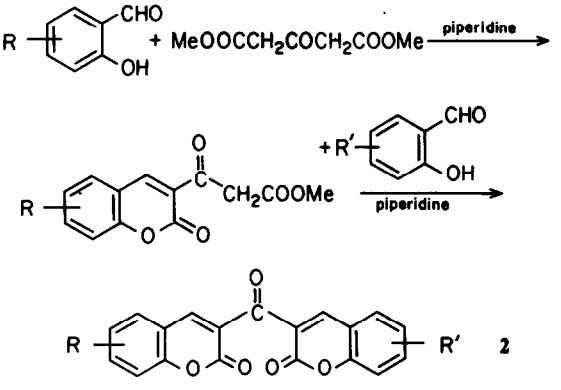
Synthesis

The ketocoumarin sensitizers are easily prepared by the condensation of salicylaldehyde derivatives with β-ketoesters[10] [eqn (1)].



1

The carbonylbiscoumarins (**2**) are analogously prepared from the ketodiester [eqn (2)]. The symmetrical compounds (**2**, R = R') are prepared in one step, whereas the asymmetrical derivatives (**2**, R ≠ R') are obtained in two-step reactions.



2

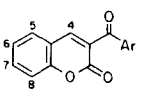
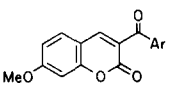
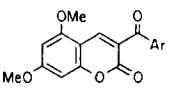
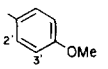
The aryl group Ar in **1** can be widely varied. Several derivatives have been prepared with Ar being phenyl, methoxyphenyl and cyanophenyl as well as heterocyclic groups such as thienyl and benzofuryl. The substituents, if any, on the coumarin nucleus in **1** and **2** are 7-alkoxy, 5,7-dialkoxy, or 7-dialkylamino groups.

Absorption spectra

As shown in Tables 1–4, the ketocoumarins have absorption maxima ranging from 330 to 470 nm in benzene.

The absorption spectra of several derivatives in EPA at 77K are considerably sharper than those at room

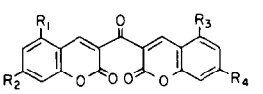
Table 1. Absorption data,[a] triplet energies,[b] and intersystem crossing quantum yields[a] of unsubstituted and alkoxy-substituted 3-aroylcoumarins

Ar	 λ_{max}, nm (ϵ, 10^3)	E_T[c]	ϕ_{isc}	 λ_{max}, nm (ϵ, 10^3)	E_T[c]	ϕ_{isc}	 λ_{max}, nm (ϵ, 10^3)	E_T[c]	ϕ_{isc}
	Ig ~330, sh (11.1)	59.4 [~60.9]	0.29	Ie ~344 (21.1)	58.4 [~59.7]	0.59	Ii ~352 (19.7)	57.4 [59.2]	0.68
	Ib ~320, sh (12.2)	59.2	0.28	If 338 (20.3)	58.3	0.71	Ij 347 (21.2)	57.3	0.92
	Ic ~330, sh (10.5)	58.9	0.92	Ig 343 (19)	58.0	0.94	Ik 351 (19.5)	56.8 [~58.3]	0.96
	Id ~333, sh (9)	58.3	0.86	Ih 352 (18.6)	57.2	0.96	Il 364 (19.5)	56.0	0.90

[a] In benzene. [b] From the phosphorescence spectra in EPA at 77°K.

[c] In Kcal/mol; the values in brackets are from different rotamers (see text).

Table 2. Absorption data,[a] triplet energies,[b] and isc quantum yields[a] of unsubstituted and alkoxy-substituted carbonylbiscoumarins



	R_1	R_2	R_3	R_4	λ_{max} nm	$\epsilon(10^3)$	E_T[c]	ϕ_{isc}
2a	H	H	H	H	350	24	57.9	0.90
2b	H	MeO	H	MeO	375	41	57.1	0.65
2c	MeO	MeO	H	H	377	33	56.0	0.46
2d	MeO	MeO	H	MeO	383	43	56.3	0.65
2e	MeO	MeO	MeO	MeO	392	43	56.2	0.70

[a] In benzene. [b] From the phosphorescence spectra in EPA at 77°K.

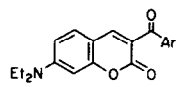
[c] Kcal/mol.

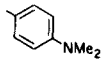
temperature. As shown in the example of **2h**, the absorption spectrum at this temperature shows some vibrational structure with a vibrational frequency ($\Delta\nu$) of *ca.* 1320 cm^{-1}. At this low temperature, there is also a strong enhancement in the intensity of the 0–0 transition, $\epsilon \sim 137{,}000$ (Fig. 2).[11]

Intersystem crossing

The isc yields were determined by the Hammond–Lamola[12] triplet-counting technique by measuring the quantum yields of stilbene isomerization sensitized by the ketocoumarins. To confirm the values obtained in this way, other energy acceptors were used. These included *trans*-methyl *p*-methoxycinnamate (at 0.05M), which gave 40% *cis* isomer at the photostationary state when high-energy sensitizers were used. We also used the dimerization of methyl 1,2-diphenylcyclopropene-3-carboxylate[13] as an energy acceptor to determine ϕ_{isc}. The dimerization (0.1M) efficiency[13] of this compound is 0.8. The values for ϕ_{isc} obtained by using these reactants were within a few percent of those obtained by using stilbene. One exception, however, was compound **1n**. For this sensitizer an isc yield of 0.22 ± 0.02 was measured by using the methoxycinnamate isomerization or the cyclopropene dimerization, but only *ca.* half this value was obtained when stilbene was used as energy

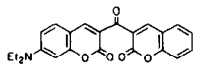
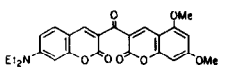
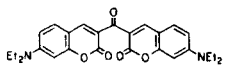
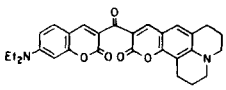
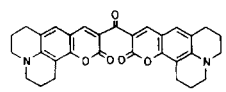
Table 3. Absorption data,[a] triplet energies,[b] and quantum yields of fluorescence and isc of dialkylamino-substituted 3-aroylcoumarins



	Ar	λ_{max}, nm (ϵ, 10^3)	E_T[c]	ϕ_{fl} (C_6H_6)	ϕ_{isc} (C_6H_6)
1m		415 (38)	50.8-52.3	0.35	0.45
1n		405 (40)	52.6-53.2	0.001	0.22
1o		416 (35)	51.5-52.5	0.10	0.83
1p		430 (38)	50.2-52.1	0.04	0.87

[a] In benzene. [b] From the Phosphorescence spectra in EPA at 77°K. [c] Kcal/mol.

Table 4. Absorption data,[a] triplet energies,[b] and isc quantum yields of dialkylamino-substituted carbonyl-biscoumarins

3,3' Carbonyl Biscoumarin	λmax nm	ϵ (10^3)	E_T[c]	ϕ_{fl} (C_6H_6)	ϕ_{isc} (C_6H_6)	ϕ_{isc} (Polymers)
2f 	446	62	49.8±0.2	~0.001	0.03	0.18
2g 	441	54	50.4	~0.001	0.3	0.75
2h 	449	92	50.8	~0.01	0.92	(0.92)
2i 	462	70	48.6	~0.001	0.42	0.6
2j 	468	83	48.5	~0.005	0.62	d

[a] In benzene. [b] From the phosphorescence. [c] Kcal/mol. [d] Insufficient solubility

acceptor. There is precedence in the literature for such a phenomenon, namely, in the fluorenone–stilbene reaction,[14] where a decay of a triplet exciplex intermediate is postulated as the source of inefficient energy transfer.

The derivatives of **1** and **2** having alkoxy or no substituents on the coumarin moieties exhibit virtually no fluorescence in benzene at room temperature or in EPA at 77K.

The dialkylamino derivatives, however, show various degrees of fluorescence. The isc efficiency of the dialkylamino derivatives of **1** is strongly dependent on the substituent Ar (*cf* Table 3). Compound **1m** has an isc efficiency of only 0.45 and relatively strong fluorescence ($\phi_{fl} = 0.35$). With Ar being thienyl (**1o**) or benzofuryl (**1p**), however, the isc efficiency reaches 0.85 ± 0.02 as the fluorescence quantum yield drops to 0.1 and 0.04, res-

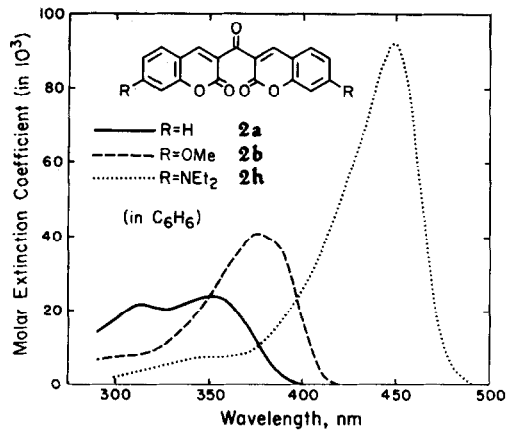


Fig. 1. Absorption spectra of **2a**, **2b** and **2h** in benzene.

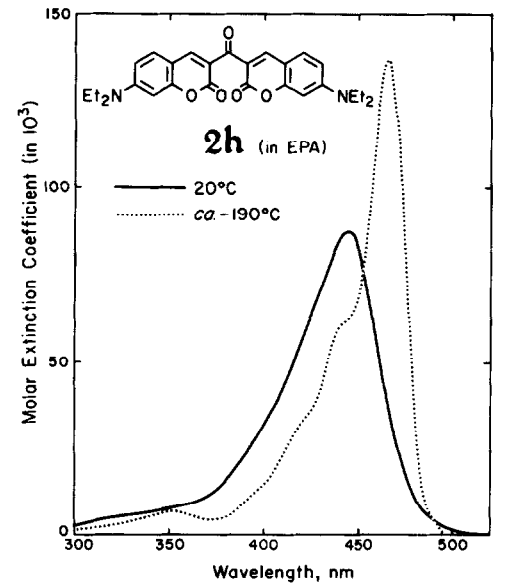


Fig. 2. Absorption spectra of **2h** in EPA at 20°C and *ca.* −190°C.

pectively. The efficiency of these compounds to sensitize the crosslinking of light-sensitive polymers can be used as a measure for ϕ_{isc} in such rigid matrices. From these measurements, the isc efficiencies of **1m**, **1o** and **1p** are estimated to be very similar to the values obtained in benzene.

In contrast to these three compounds, with $\phi_{isc} + \phi_f \geq 0.8$, the dimethylaminophenyl derivative (**1n**) shows very low isc efficiency (0.22) and virtually no fluorescence in benzene; i.e. a nonradiative process dominates the fate of the singlet-excited state of this compound. This process, however, seems to be readily suppressed in the polymeric matrices, as the efficiency of crosslinking of several polymers indicates that in these media ϕ_{isc} is *ca.* 0.85, i.e. about four times that in benzene. It is possible that such an energy-wasting, radiationless process requires the attainment of certain rotamers, a process which could easily be slowed down in a rigid matrix. If we assume that the reaction constant for isc is not dependent on the medium rigidity, then we can estimate from the quantum yields of isc that the reaction constant for the radiationless decay in the polymeric matrix is *ca.* 20 times slower than that in the fluid medium.

Similar behavior is observed in the series of dialkylamino-substituted carbonylbiscoumarins (**2f–2j**). With the substitution pattern of the latter changing from 7-diethylamino (**2h**) to 5,7-dimethoxy (**2g**) to no substituents (**2f**), ϕ_{isc} in benzene drops from 0.92 to 0.3 to 0.03 (Table 4). Again, the radiationless decay from the singlet excited state seems to be partially suppressed in polymeric matrices. This is inferred from the increase in ϕ_{isc} of **2g** and **2f** in these rigid media to 0.75 and 0.18, respectively. Again, on the assumption that the reaction constants for isc are not dependent on the medium rigidity, one can estimate from these quantum yields that in both cases the rates of radiationless decay in the polymer matrix are 7–8 times slower than those in benzene. The isc efficiency of these two compounds seems to be even higher in EPA at 77K, as their phosphorescence intensities are similar to that of **2h**.

Triplet energies

The triplet energies of these ketocoumarins were determined from the 0–0 transition of the phosphorescence spectra at 77K in EPA. Some measurements in methyltetrahydrofuran and in methylcyclohexane–toluene gave similar results. Some of these ketocoumarins show phosphorescence spectra that suggest the presence of "frozen-in" rotamers. This phenomenon is more obvious with the thiophene derivatives (**1a, e, i**), especially in the spectrum of **1i** (Fig. 3), which shows two similarly structured vibrational bands separated by 630 cm^{-1}. Extensive purification did not alter the ratio of the components (a) and (b) in the phosphorescence spectrum of this compound. Excitation at the long-wavelength edge of the absorption spectrum leads to a decrease in the proportion of the high-energy component (a). These data are best rationalized in terms of two frozen-in rotamers with only a slight difference in their absorption spectra. The proportion of the higher-energy rotamer seems to be lower in less polar glasses. The ratio a/b is *ca.* 30% lower in 2-methyltetrahydrofuran than in EPA and is considerably diminished in methylcyclohexane–toluene. The corresponding high-energy components in **1a** and **1e** are less pronounced. There is also

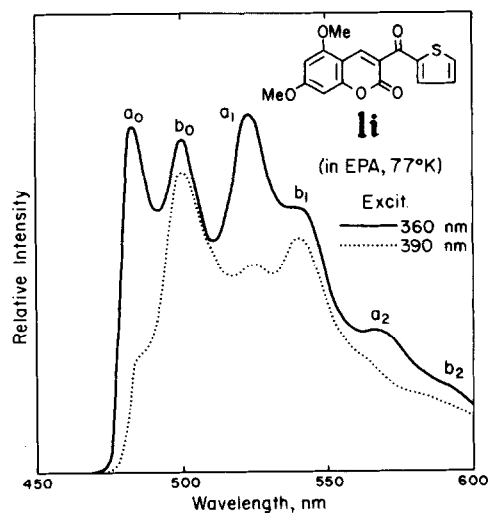


Fig. 3. Phosphoresence spectra of **1i** in EPA at 77K.

indication that compound **1k** behaves similarly, although the higher-energy component in this case appears only as a weak shoulder. The vibrational structure of most of the derivatives in Table 1 is not as well resolved as that of the carbonylbiscoumarins (**2**). A typical example is that of **1g** (Fig. 4).

The phosphorescence spectra of the unsubstituted and alkoxy-substituted carbonylbiscoumarins show very sharp and well-resolved vibrational structure (*cf.* Fig. 5). The sharpness of these bands and the presence of only one component in the phosphorescence spectra of these compounds can be attributed to higher molecular symmetries compared to those of the derivatives of **1**.

The dialkylamino-substituted derivatives of **1** showed phosphorescence spectra which varied with the excitation wavelength (Table 3). However, contrary to the case of **1i**, which seems to phosphoresce from just two distinct conformers (Fig. 3), the dialkylamino derivatives apparently can be frozen into several rotamers (EPA, 77K) which give rise to a gradually varying phosphorescence spectrum. Of these derivatives, **1p** showed the widest range in phosphorescence and excitation spectra. Changing the excitation wavelength from 465 to 420 nm by 5 nm increments gave phosphorescence spectra with a gradual variation in onsets and maxima of both the 0–0 and 0–1 transitions. Three of these spectra are reproduced in Fig. 6. Since irradiation at the longest wavelength excites predominantly one rotamer, this gives the sharpest spectrum. At shorter wavelength, however, where the absorption spectra of several rotamers overlap, broader phosphorescence spectra are obtained (Fig. 6). The 0–0 transitions in these phosphorescence spectra vary over a range of *ca.* 2 kcal/mol. A similar difference in energy is observed in the excitation spectra monitored at different wavelengths of emission (Fig. 7). The excitation spectra monitored at the short-wavelength edge of emission should reflect primarily the absorption spectrum of the highest-energy rotamer (the dashed curve in Fig. 7). The excitation spectra monitored at longer wavelengths of phosphorescence reflect, however, a complex sum of several overlapping absorption spectra of different rotamers.

The carbonylbis(dialkylaminocoumarin) derivatives (**2f–j**) show relatively sharp, well-resolved vibrational structure in their phosphorescence spectra with 0–0 transitions ranging from 48.5 to 50.8 kcal/mol (Table 4).

The singlet–triplet gap of the ketocoumarins was measured for those compounds, which show some fluorescence, from the difference between the 0–0 transitions of the fluorescence and phosphorescence bands in EPA at 77K. This gap is *ca.* 9 kcal/mol for **2h** and 10 kcal/mol for **1p**.

Sensitization of light-sensitive polymers

The potential of these ketocoumarins as sensitizers for photocrosslinkable polymers such as poly(vinyl cin-

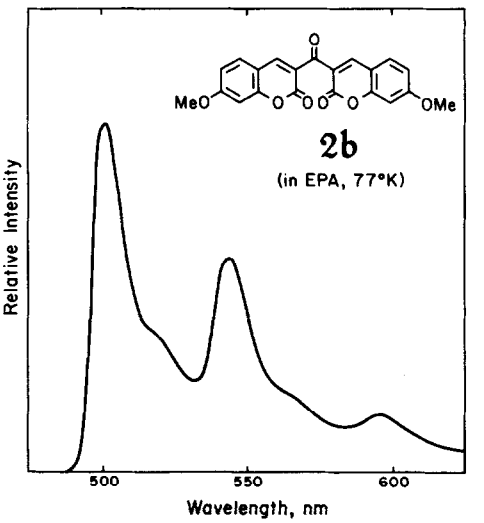


Fig. 5. Phosphorescence spectrum of **2b** in EPA at 77K (λ_{excit} = 310–390 nm).

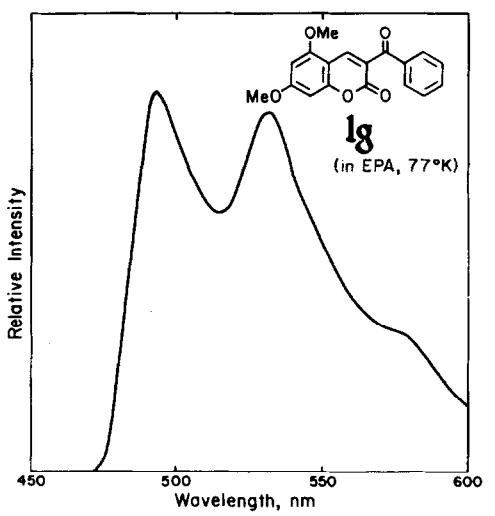


Fig. 4. Phosphorescence spectrum of **1g** in EPA at 77K (λ_{excit} = 330–380 nm).

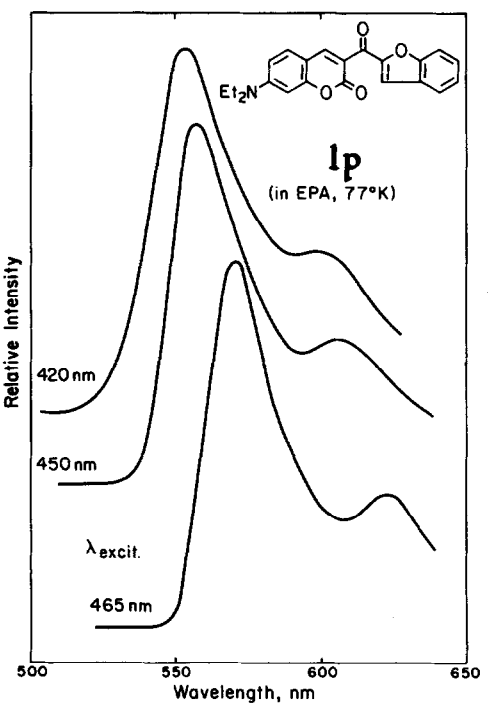


Fig. 6. Phosphorescence spectra of **1p** in EPA at 77K at different wavelengths of excitation.

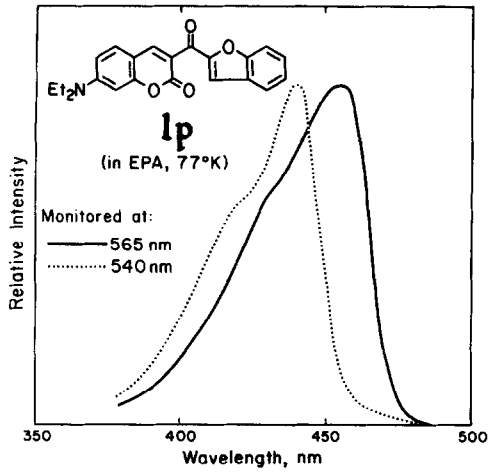
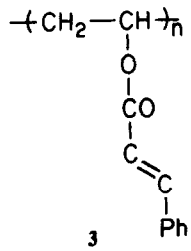


Fig. 7. Excitation spectra for the phosphorescence of **1p** in EPA at 77K.

namate)[15] (**3**), the diphenylcyclopropene polymer[16] (**4**), or the phenylene diacrylate polyester[2b] (**5**) can be demonstrated with a few derivatives which cover a wide range in spectral response.

If it is desirable to have a colorless polymeric film, a compound such as **1g** can be used. This compound would be most effective with the 366-nm line of the mercury lamp. A compound such as **2e** (or preferably the more soluble tetraethoxy analogue **2e'**) is most effective with the 405-nm and to some extent with the 436-nm mercury line. Comparison of this compound and the widely used sensitizer BN[2b,c,17] revealed that at 405 nm, where both compounds have equal absorbance, BN has only 65–70% of the efficiency of **2e'**. This difference is almost certainly due to the higher isc efficiency of the latter compound.



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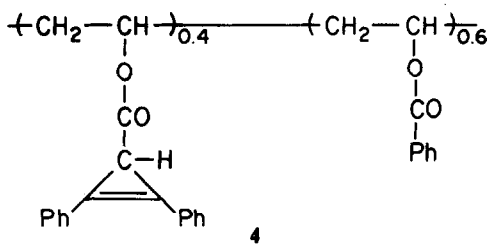

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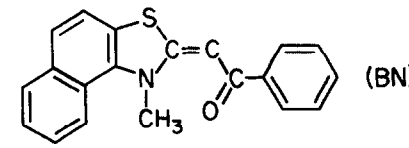
Finally, the carbonylbiscoumarin **2h**, with an extended absorption in the visible range, very efficiently induces the crosslinking of polymers such as **3–5** when irradiated with broad spectral lamps (e.g. xenon arcs) and in particular with lasers emitting in the visible region (e.g. HeCd laser, 441.6 nm; argon-ion laser, 488 nm). We are not aware of any compound which can sensitize the crosslinking of such polymers in the 480–500 nm range with an efficiency anywhere close to that obtained with **2h**. The small singlet–triplet gap, high isc efficiency, and high extinction coefficient are undoubtedly the reason for this efficient sensitization.



(BN)

In conclusion, the ketocoumarins described in this work are excellent triplet sensitizers ranging in energy between 48 and 60 kcal/mol. The carbonylbiscoumarin derivatives **2** are particularly attractive for kinetic studies of energy transfer both in solution and in polymeric matrices because of their well-defined triplet energies. Except for a few derivatives with low isc efficiency, such as **2f**, most of these ketocoumarins are efficient sensitizers for photocrosslinkable polymers.

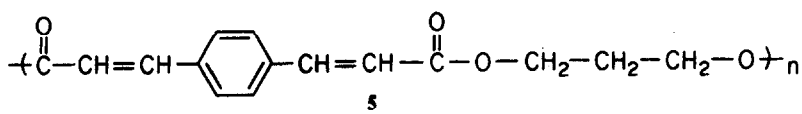
In cases where there might be doubt about interference from electron transfer or complex formation in competition with energy transfer, compounds such as **1j** and **1h**, which have almost the same triplet energy but different redox potentials, could be used to distinguish between the different possibilities. Compounds **1j** and **1h** have oxidation potentials (vs SCE, in CH_3CN) of 1.68 and 1.94 V, respectively; their reduction potentials (vs SCE, in CH_3CN) are -1.40 and -1.16 V, respectively.

Although the unsubstituted coumarin molecule shows extremely low isc[18] and virtually no fluorescence, some coumarin derivatives are among the best known optical brighteners[19] as well as laser dyes,[20] i.e. highly fluorescing compounds. We have now shown that by proper substitution, primarily by an aroyl group in the 3-position, coumarin derivatives can have very high isc yields and can be used as efficient triplet sensitizers.

EXPERIMENTAL

M.ps were taken on a Mel-Temp m.p. apparatus and are not corrected. The H^1 NMR spectra were recorded on a Varian EM-390 instrument with tetramethylsilane as an internal standard. Mass spectra were determined using an LKB type 9000 mass spectrometer. The absorption and phosphoresence spectra were recorded on Cary 15 and Spex Fluorolog instruments, respectively. Elemental analyses were performed in our Microanalytical Laboratory.

The following compounds are commercially available and were used without further purification: salicylaldehyde, 2-hydroxy-*p*-anisaldehyde, ethyl benzoylacetate (Kodak Laboratory Chemicals); 4,6-dimethoxysalicylaldehyde, dimethyl 1,3-acetonedicarboxylate (Aldrich Chemical Company); *p*-diethylaminosalicyl-



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aldehyde (Lachat Chemicals, Inc); ethyl 2-thenoylacetate (Chemical Procurement Laboratories, Inc).

p-N,N-*Dimethylaminosalicylaldehyde.* Dimethylformamide (45 ml) was stirred in an ice bath as $POCl_3$ (30.6 g) was added dropwise. The mixture was allowed to stand at room temp for 30 min. *m*-Dimethylaminophenol (24 g) dissolved in the minimum amount of DMF was added dropwise with stirring. After the addition, the mixture was heated on a steam bath for 30 min, cooled, poured into water and stirred for several hr before the product was collected. The material was used without further purification: m.p. 72–75°.

9-*Formyl*-8-*hydroxy*-2,3,6,7-*tetrahydro*-1H,5H-*benzo[ij]quinolizine.* $POCl_3$ (10.7 g) was added dropwise to 20 mL DMF with stirring; the temp was kept at 20–25° with an ice bath. The mixture was stirred at room temp for 15 min. 8-Hydroxyjulolidine (12 g) dissolved in the minimum amount of DMF was added dropwise with stirring; the temp was kept at 20–25° with an ice bath. After the addition, the mixture was stirred at room temp for 30 min, then heated on a steam bath for 30 min. The mixture was cooled, poured into water, and stirred for several hr. The product was collected, washed with water, dried, and recrystallized from 700 mL hexane: yield 10.9 g, m.p. 70–72°.

Ethyl (p-*dimethylaminobenzoyl*)*acetate.* A suspension of 16.8 g of 57% NaH mineral oil dispersion in 100 mL of dry 1,2-dimethoxyethane was stirred, heated under reflux on a steam bath, and kept under N_2. *p*-Dimethylaminoacetophenone (16.3 g) was added as a solid. Diethyl carbonate (29.5 g) was added dropwise. After ~5 mL of diethyl carbonate had been added, an exothermic reaction began. Heating and addition of diethyl carbonate were stopped until the reaction subsided, then continued as before. After the addition, the mixture was stirred and heated at reflux for 1 hr, then stirred at room temp for 2 hr. EtOH (25 mL) was added dropwise to decompose the excess NaH. The mixture was poured into 1000 mL water containing 38 mL 37.7% HCl and stirred for 10 min. The product was collected, washed with water, dried and recrystallized from a mixture of 950 ligroin and alcohol: m.p. 90–93° (Lit.[21] 64°).

Ethyl p-*anisoylacetate.* A suspension of 58 g of 57% NaH mineral oil dispersion in 200 mL dry 1,2-dimethoxyethane was placed in a 2000-mL, 3-neck, round-bottom flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser. The flask was flushed with N_2, and the reaction was carried out under N_2. A soln of 100 g of methyl anisate in 100 mL dry 1,2-dimethoxyethane was added all at once. The soln was stirred and heated to reflux on a steam bath. The heat was removed, and a soln of 106 g of EtOAc in 100 mL dry 1,2-dimethoxyethane was added dropwise. After the addition, the mixture was stirred and heated at reflux for 4 hr. After the mixture was cooled to room temp, the excess NaH was decomposed by the cautious addition of EtOH. The soln was poured into 2500 mL water containing 140 mL of 37.7% HCl and stirred for 1 hr. The oily product was pipetted from the bottom of the flask and dissolved in ether. The ethereal soln was dried with $MgSO_4$ and evaporated. The product was used without further purification.

Ethyl p-*cyanobenzoylacetate.* A suspension of 12 g of 50% NaH mineral oil dispersion in 40 mL dry 1,2-dimethoxyethane was placed in a 500-mL, 3-neck flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser. The flask was flushed with N_2, and the reaction was carried out under N_2. A soln of 25 g of methyl *p*-cyanobenzoate in 40 mL dry 1,2-dimethoxyethane was added all at once. The soln was stirred and heated to reflux on a steam bath. The heat was removed, and a soln of 15.7 g EtOAc in 20 mL 1,2-dimethoxyethane was added dropwise. After the addition, the mixture was stirred and heated at reflux for 3 hr. After the mixture was cooled to room temp, the excess NaH was decomposed by the cautious addition of EtOH. The soln was poured into 1200 mL water containing 25 mL 37.7% HCl and stirred for 1 hr before the product was collected. The product was washed with water, dried, washed twice with 950 ligroin, and used without further purification: yield 22 g; m.p. 61–64°.

Ethyl coumariloylacetate. A suspension of 14.5 g 50% NaH mineral oil dispersion in 45 mL dry 1,2-dimethoxyethane was placed in a 500-mL, 3-neck flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser. The flask was flushed with N_2, and the reaction was carried out under N_2. A soln of 25 g methyl coumarilate in 40 mL dry 1,2-dimethoxyethane was added all at once. The soln was stirred and heated under reflux on a steam bath. The heat was removed, and a soln of 17.2 g EtOAc in 25 mL 1,2-dimethoxyethane was added dropwise. After the addition, the mixture was stirred and heated under reflux for 3 hr. After the mixture was cooled to room temp, the excess NaH was decomposed by the cautious addition of EtOH. The soln was poured into 1200 mL water containing 30 mL 37.7% HCl and stirred for 1 hr. The oily product was pipetted from the bottom of the flask and dissolved in ether. The ethereal soln was washed with water, dried with $MgSO_4$, and evaporated. The material was used without further purification.

Preparation of the ketocoumarins

Procedure A. The salicylaldehyde (0.01 mol) and the β-ketoester (0.01 mol) were dissolved in 20 mL warm alcohol. Piperidine (20–40 drops) was added, and the mixture was heated at reflux on a steam bath for 10 min to 2 hr. The mixture was chilled, and the product was collected, washed with a little alcohol, and recrystallized.

Procedure B. The salicylaldehyde (0.02 mol) and dimethyl 1,3-acetonedicarboxylate (0.01 mol) were dissolved in ~20 mL warm alcohol, acetonitrile, or a mixture of the two solvents. Piperidine (20–40 drops) was added, and the mixture was heated at reflux on a steam bath for 10 min to 2 hr. The mixture was chilled, and the product was washed with a little alcohol and recrystallized.

Procedure C. The salicylaldehyde (0.01 mol) and dimethyl 1,3-acetonedicarboxylate (0.01 mol) were dissolved in 10–20 mL warm alcohol. Piperidine (10 drops) was added, and the mixture was heated at reflux on a steam bath for 10 min to 2 hr. The mixture was chilled, and the monocondensation product was collected, washed with a little alcohol, and recrystallized from a mixture of alcohol and acetonitrile.

The monocondensation product (0.01 mol) and a second salicylaldehyde (0.01 mol) were dissolved in 25 mL warm alcohol, acetonitrile, or a mixture of the two solvents. Piperidine (1–2 mL) was added, and the mixture was heated at reflux on a steam bath for 10 min to 2 hr. The mixture was chilled, and the asymmetrical biscoumarin was collected, washed with a little alcohol, and recrystallized.

3-*Thenoylcoumarin* (**1a**) (Procedure A), m.p. 148–150° from alcohol. NMR ($CDCl_3$) δ 7.10 (d, d, H-4', part of ABX system, $J_{4',5'} = 4.8$ Hz, $J_{3',4'} = 4.1$ Hz, $J_{3',5'} = 0.8$ Hz), 7.50–7.75 (m, H-6, 7, 8, 3', 5'), 8.03 (s, H-4). (Found: C, 65.7; H, 3.3; S, 12.6. $C_{14}H_8O_3S$ Requires: C, 65.6; H, 3.1; S, 12.5%).

3-(4-*Methoxybenzoyl*)*coumarin* (**1b**) (Procedure A), m.p. 174–175° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 3.86 (s, $-OCH_3$), 6.90 and 7.82 (AA'BB' system, H-3', H-2', respectively), 7.17–7.70 (m, H-5, 6, 7, 8), 7.95 (s, H-4). (Found: C, 72.7; H, 4.5. $C_{17}H_{12}O_4$ Requires: C, 72.8; H, 4.3%).

3-*Benzoylcoumarin* (**1c**) (Procedure A), m.p. 137–139° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 7.16–7.69 (m, H-5, 6, 7, 8, 3', 4'), 7.81 (m, H-2'), 7.99 (br, s, H-4). MS: *m/e* (%Rel. int): 250 (M^+, 80), 249 (9), 222 (24), 221 (48), 194 (8), 173 (20), 145 (8), 105 (100). (Found: C, 76.7; H, 3.9. $C_{16}H_{10}O_3$ Requires: C, 76.8; H, 4.0%).

3-(4-*Cyanobenzoyl*)*coumarin* (**1d**) (Procedure A), m.p. 240–242° from alcohol/acetonitrile then toluene. MS: *m/e* (%Rel. int.): 275 (M^+, 100), 274 (9), 247 (40), 246 (92), 219 (14), 173 (48), 145 (36), 130 (75), 102 (86). (Found: C, 74.2; H, 3.3; N, 4.9. $C_{17}H_9NO_3$ Requires: C, 74.2; H, 3.3; N, 5.1%).

3-*Thenoyl*-7-*methoxycoumarin* (**1e**) (Procedure A), m.p. 205–206° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 3.91 (s, $-OCH_3$), 6.82 (br, d, H-8), 6.87 (m, H-6), 7.09 (part of ABX system, q, H-4', $J_{4',5'} = 5.1$ Hz, $J_{3',4'} = 3.9$ Hz), 7.34–7.74 (m, H-5, 3', 5'), 8.03 (s, H-4) (Found: C, 62.7; H, 3.3; S, 11.0. $C_{15}H_{10}O_4S$ Requires: C, 62.9; H, 3.5; S, 11.2%).

7-*Methoxy*-3-(4-*methoxybenzoyl*)*coumarin* (**1f**) (Procedure A), m.p. 227–229° from alcohol/acetonitrile. MS: *m/e* (%Rel. int.): 310 (M^+, 79), 295 (10), 282 (11), 281 (9), 279 (14), 278 (6), 267 (7), 251 (13), 239 (5), 203 (13), 155 (8), 135 (100), 107 (12). (Found: C, 69.6; H, 4.7. $C_{18}H_{14}O_5$ Requires: C, 69.7; H, 4.5%).

3-*Benzoyl-7-methoxycoumarin* (**1g**) (Procedure A), m.p. 152–153° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 3.89 (s, $-OCH_3$), 6.82 (br, d, H-8), 6.85 (m, H-6), 7.28–7.64 (m, H-5, 3', 4'), 8.01 (s, H-4). (Found: C, 73.0; H, 4.2. $C_{17}H_{12}O_4$ Requires: C, 72.9; H, 4.3%).

3-(4-*Cyanobenzoyl*)-7-*methoxycoumarin* (**1h**) (Procedure A), m.p. 227° from alcohol/acetonitrile. MS: *m/e* (%Rel. int.): 305 (M^+, 100), 277 (28), 276 (49), 262 (7), 246 (15), 234 (8), 203 (69), 175 (17), 130 (34), 119 (21), 102 (48). (Found: C, 70.8; H, 3.9; N, 4.5. $C_{18}H_{11}NO_4$ Requires: C, 70.8; H, 3.6; N, 4.6%).

5,7-*Dimethoxy*-3-*thenoylcoumarin* (**1i**) (Procedure A), m.p. 195–196° from alcohol/acetonitrile. NMR ($CDCl_3$/DMSO-d_6 3:1) δ 3.90 and 3.92 ($2CH_3O$–), 6.38 (d, H-6, $J_{6,8}$ = 2.1 Hz), 6.48 (br, d, H-8), 7.17, 7.70, and 7.81 (ABX system, H-4', H-3', H-5', respectively, $J_{3',4'}$ = 3.9, $J_{4',5'}$ = 4.9, $J_{3',5'}$ = 1.1$_5$ Hz), 8.36 (H-4, weak coupling between H-4 and H-8 broadens their signals). (Found: C, 60.5; H, 3.7; S, 9.9. $C_{16}H_{12}O_5S$ Requires: C, 60.8; H, 3.8; S, 10.1%).

5,7-*Dimethoxy*-3-(4-*methoxybenzoyl*)*coumarin* (**1j**) (Procedure A), m.p. 186–187° from alcohol/acetonitrile. NMR ($CDCl_3$) δ (3.86 (s, $-OCH_3$), 3.88 (br, s, 2 overlapping $-OCH_3$), 6.28 (d, H-6, $J_{6,8}$ = 2.1 Hz), 6.43 (br, d, H-8) 6.91 and 7.83 (AA'BB' system, H-3', H-2', respectively), 8.34 (d, H-4, $J_{4,8}$ = 0.6 Hz). (Found: C, 66.9; H, 4.9. $C_{19}H_{16}O_6$ Requires: C, 67.1; H, 4.7%).

3-*Benzoyl*-5,7-*dimethoxycoumarin* (**1k**) (Procedure A), m.p. 178–179° from acetonitrile. NMR ($CDCl_3$) δ 3.88 (s, 2-OCH_3), 6.27 (d, H-6), 6.41 (br, d, H-8), 7.27–7.68 (m, H-3', 4'), 7.79 (m, H-2'), 8.36 (d, $J_{4,8}$ = 0.6 Hz).

3-(4-*Cyanobenzoyl*)-5,7-*dimethoxycoumarin* (**1l**) (Procedure A), m.p. 271° from acetonitrile/pyridine. MS: *m/e* (%Rel. int.): 335 (M^+, 100), 334 (6), 320 (4), 310 (10), 307 (22), 306 (22), 304 (6), 292 (11), 264 (7), 234 (10), 233 (69), 205 (7), 177 (6), 167.5 (5), 135 (14), 130 (30), 102 (35). (Found: C, 67.9; H, 4.1; N, 4.1. $C_{19}H_{13}NO_5$ Requires: C, 68.1; H, 3.9; N, 4.2%).

3-*Benzoyl*-7-*diethylaminocoumarin* (**1m**) (Procedure A), m.p. 150–151° from alcohol. NMR ($CDCl_3$) δ 1.23 (t, $-CH_3$), 3.45 (q, $-CH_2$–), 6.4 (br, d, H-8), 6.58 (q, H-6), 7.24–7.60 (m, H-5, 3', 4'), 7.76 (m, H-2'), 8.01 (s, H-4). (Found: C, 74.8; H, 6.1; N, 4.1. $C_{20}H_{19}NO_3$ Requires: C, 74.7; H, 6.0; N, 4.4%).

7 - *Diethylamino* - 3 - (4 - *dimethylaminobenzoyl*)*coumarin* (**1n**) (Procedure A), m.p. 194–195° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 1.23 (t, ($\underline{CH_3}$–CH_2)$_2$N–, J = 7.1 Hz), 3.07 (s, $(CH_3)_2$N–), 3.46 (q, (CH_3–$\underline{CH_2}$)$_2$N–), 6.51, 6.58, and 7.30 (ABX system, H-8, H-6, H-5, respectively, $J_{5,6}$ = 8.8 Hz, $J_{6,8}$ = 2.4 Hz), 6.63 and 7.79 (AA'BB' system, H-3', H-2', respectively), 7.91 (H-4, broadened by weak coupling with H-8). MS: *m/e* (%Rel. int.): 364 (M^+, 100), 350 (22), 349 (81), 321 (8), 320 (11), 174.5 (19), 160.5 (7), 160 (13), 148 (59). (Found: C, 72.5; H, 6.7; N, 7.9. $C_{22}H_{24}N_2O_3$ Requires: C, 72.5; H, 6.6; N, 7.7%).

7-*Diethylamino*-3-*thenoylcoumarin* (**1o**) (Procedure A), m.p. 140–141° from alcohol. NMR ($CDCl_3$) δ 1.23 (t, $-CH_3$), 3.45 (q, $-CH_2$–), 6.46 (br, d, H-8), 6.59 (q, H-6), 7.06, 7.61 and 7.70 (ABX system, H-4', 5', and 3', respectively, $J_{3',4'}$ = 3.9 Hz, $J_{4',5'}$ = 4.8 Hz, $J_{3',5'}$ = 0.9 Hz), 7.30 (d, H-5), 8.01 (s, H-4). (Found: C, 66.1; H, 5.2; N, 4.6; S, 10.1. $C_{18}H_{17}NO_3S$ Requires: C, 66.0; H, 5.2; N, 4.3; S, 9.8%).

3-(2-*Benzofuroyl*)-7-*diethylaminocoumarin* (**1p**) (Procedure A), m.p. 125–127° from alcohol. NMR ($CDCl_3$) δ 1.22 (t, ($\underline{CH_3}$–CH_2)$_2$N–, J = 7.2 Hz), 3.45 (q, (CH_3–$\underline{CH_2}$)$_2$N–), 6.48, 6.61, and 7.36 (ABX system, H-8, H-6, H-5, respectively, $J_{5,6}$ = 9.0, $J_{6,8}$ = 2.4 Hz), 7.65 (d, H-3', $J_{3',7'}$ = 0.8 Hz), 7.17–7.77 (multiplets, H-4'–H-7'), 8.22 (H-4). A weak coupling between H-4 and H-8, broadening their signals, is detected by decoupling. (Found: C, 73.4; H, 5.0; N, 3.8. $C_{22}H_{19}NO_4$ Requires: C, 73.1; H, 5.3; N, 3.9%).

3,3'-*Carbonylbiscoumarin* (**2a**) (Procedure B), m.p. 251–252° from acetonitrile. NMR ($CDCl_3$) δ 7.15–7.75 (m, 8H), 8.25 (d, J = 0.53 Hz). (Found: C, 71.5; H, 3.3. $C_{19}H_{10}O_5$ Requires: C, 71.7; H, 3.2%).

3,3'-*Carbonylbis*(7-*methoxycoumarin*) (**2b**) (Procedure B), m.p. 270–272° from acetonitrile. MS: *m/e* (%Rel. int.): 378 (M^+, 94), 363 (9), 351 (13), 350 (54), 335 (5), 322 (9), 307 (14), 204 (13), 203 (100), 175 (15), 161 (14). (Found: C, 66.8; H, 3.5. $C_{21}H_{14}O_7$ Requires: C, 66.7; H, 3.7%).

5,7-*Dimethoxy*-3,3'-*carbonylbiscoumarin* (**2c**) (Procedure C), m.p. 248° and 263–264° (different crystalline forms) from acetonitrile/pyridine. MS: *m/e* (%Rel. int.) : 378 (M^+, 100), 363 (3), 351 (9), 350 (41), 335 (6), 322 (11), 234 (13), 233 (85), 218 (8), 205 (8), 189 (8), 172 (25). (Found: C, 66.7; H, 3.8. $C_{21}H_{14}O_7$ Requires: C, 66.7; H, 3.8%).

5,7,7'-*Trimethoxy*-3,3'-*carbonylbiscoumarin* (**2d**) (Procedure C), m.p. 258–262° from acetonitrile. MS: *m/e* (%Rel. int.): 408 (M^+, 100), 393 (5), 381 (12), 380 (50), 365 (5), 352 (7), 337 (10), 234 (9), 233 (60), 218 (6), 205 (8), 204 (10), 203 (42), 176 (20), 119 (16). (Found: C, 64.5; H, 3.9. $C_{22}H_{16}O_8$ Requires: C, 64.7; H, 3.9%).

3,3'-*Carbonylbis*(5,7-*dimethoxycoumarin*) (**2e**) (Procedure B), m.p. 292–296° from acetonitrile/pyridine. NMR ($CDCl_3$) δ 3.88 and 3.92 ($2CH_3O$–), 6.27 (d, H-6, $J_{6,8}$ = 2.1 Hz), 6.42 (br, d, H-8), 8.58 (d, H-4, $J_{4,8}$ = 0.6 Hz). MS: *m/e* (%Rel. int.) 438 (M^+, 100), 423 (3), 411 (12), 410 (47), 395 (4), 382 (5), 367 (5), 234 (12), 233 (79), 219 (6), 218 (8), 205 (11), 191 (21). (Found: C, 63.0; H, 4.0. $C_{23}H_{18}O_9$ Requires: C, 63.0; H, 4.1%).

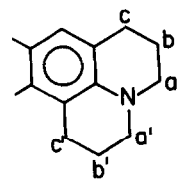
3,3'-*Carbonylbis*(5,7-*diethoxycoumarin*) (**2e'**) (Procedure B), m.p. 236–237° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 1.44 and 1.49 (overlapping triplets, $2\underline{CH_2}CH_2$–O–, J = 7 Hz), 4.09 and 4.13 (overlapping quartets, $2CH_3$–$\underline{CH_2}$–O–), 6.27 (d, H-6, $J_{6,8}$ = 2.1 Hz), 6.40 (br, d, H-8), 8.62 (d, H-4, $J_{4,8}$ = 0.6 Hz). (Found: C, 65.5; H, 5.4. $C_{27}H_{26}O_9$ Requires: C, 65.6; H, 5.3%).

7-*Diethylamino*-3,3'-*carbonylbiscoumarin* (**2f**) (Procedure C), m.p. 280–282° from acetonitrile. MS: *m/e* (%Rel. int.): 389 (M^+, 58), 375 (27), 374 (100), 360 (11), 244 (6), 200 (10), 173 (35). (Found: C, 70.7; H, 4.8; N, 3.6. $C_{23}H_{19}NO_5$ Requires: C, 70.9; H, 4.9; N, 3.6%).

7-*Diethylamino*-5',7'-*dimethoxy*-3,3'-*carbonylbiscoumarin* (**2g**) (Procedure C), m.p. 253° from acetonitrile/pyridine. NMR ($CDCl_3$) δ 1.24 (t, ($\underline{CH_3}$–CH_2)$_2$N–, J = 7.1 Hz), 3.45 (q, (CH_3–$\underline{CH_2}$)$_2$N–), 3.87 and 3.91 ($2CH_3O$–), 6.27 (d, H-6', $J_{6',8'}$ = 2.1 Hz), 6.43 (br, d, H-8'), 6.48 (br, d, H-8, $J_{6,8}$ = 2.4 Hz), 6.60 (dd, H-6, $J_{5,6}$ = 8.8 Hz), 7.37 (d, H-5), 8.22 (H-4), 8.48 (H-4'). The last two signals are broadened by weak long-range coupling with H-8 and H-8', respectively. **2g** ($CDCl_3CF_3COOH$ 3:1) δ 1.24 (($\underline{CH_3}$–CH_2)$_2$N–), 3.77 ((CH_3–$\underline{CH_2}$)$_2$N–), 3.97 and 4.00 ($2CH_3O$–), 6.43 (H-6'), 6.53 (H-8'), 7.59 (H-6), 7.62 (H-8), 7.95 (H-5), 8.32 (H-4'), 9.08 (H-4). MS: *m/e* (%Rel. int.): 449 (M^+, 77), 434 (100), 420 (6), 419 (7), 406 (7), 233 (30), 200 (13). (Found: C, 66.5; H, 5.4; N, 3.1. $C_{25}H_{23}NO_7$ Requires: C, 66.8; H, 5.2; N, 3.1%).

3,3'-*Carbonylbis*(7-*diethylaminocoumarin*) (**2h**) (Procedure B), m.p. 214–217° from alcohol/acetonitrile. NMR ($CDCl_3$) δ 1.22 (t, ($\underline{CH_3}$–CH_2)$_2$N–, J = 7 Hz), 3.43 (q, (CH_3–$\underline{CH_2}$)$_2$N–), 6.45, 6.56, and 7.34 (ABX system, H-8, H-6, H-5, respectively, $J_{5,6}$ = 8.8, $J_{6,8}$ = 2.4 Hz), 8.12 [H-4, broadened (half bandwidth = 1.6 Hz) by a weak coupling with H-8]. MS: *m/e* (%Rel. int.): 460 (M^+, 99), 446 (72), 445 (100), 401 (15), 281 (13), 244 (21), 215 (32), 207 (20), 200 (21). (Found: C, 70.7; H, 6.2; N, 6.1. $C_{27}H_{28}N_2O_5$ Requires: C, 70.4; H, 6.1; N, 6.1%).

9 - (7 - *Diethylamino* - 3 - *coumarinoyl*) - 1,2,4,5 - *tetrahydro* - 3H,6H,10H[1]*benzopyrano*[9,9a,1-gh]*quinolazine* - 10 - *one* (**2i**) (Procedure C), m.p. 250–253° from acetonitrile/pyridine. NMR ($CDCl_3$) δ 1.21 (t, $-CH_3$), 1.8–2.1 (m, b, b'), 2.7–3.0 (m, c, c'), 3.31 (m, a, a'), 3.43 (q, N–$\underline{CH_2}$–CH_3, J = 7.0 Hz), 6.44 (d, H-8), 6.55 (q, H-6), 6.91 (s, H-5'), 7.31 (d, H-5), 8.04 and 8.06 (s, H-4,4'). (Found: C, 72.0; H, 5.9; N, 6.0. $C_{29}H_{28}N_2O_5$ Requires: C, 71.9; H, 5.8; N, 5.8%).



9,9' - *Carbonylbis*(1,2,4,5 - *tetrahydro* - 3H,6H,10H[1]*benzopyrano*[9,9a,1 - gh]*quinolazine* - 10 - *one*) (**2j**) (Procedure B), m.p. 332° from acetonitrile/pyridine. NMR ($CDCl_3$) δ 1.75–2.15 (m, b, b'), 2.60–3.05 (m, c, c'), 3.30 (m, a, a'), 6.89 (s, H-5), 7.99 (s, H-8). (Found: C, 73.0; H, 5.7; N, 5.7. $C_{31}H_{28}N_2O_5$ Requires: C, 73.2; H, 5.5; N, 5.5%).

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