

Photochemistry of Nonconjugated Bichromophoric Systems.¹ Mechanism of the Intramolecular Photocycloaddition of Biscoumarins in Solution

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Abstract: Upon irradiation of 7,7'-polymethylenedioxy coumarins **1**, an intramolecular cycloaddition occurs. Both the head-to-head and the head-to-tail isomers were formed. The quantum yield of the cyclomerization varies with the chain length and has a maximum value for $n = 5$. Uv absorption studies of **1** indicated a slight difference between their spectra and that of 7-methoxycoumarin; the differential spectrum shows the presence of new bands in the longer wavelength region. Nonlinear Stern-Volmer plots in the reaction quenching of **1** indicated the involvement of more than one excited state in the product formation. Comparison of fluorescence quenching and reaction quenching showed the longer living species to be the singlet excited state of the isolated, coumarin chromophore. Other excited states, with a shorter lifetime, still react even by extensive quenching of the singlet state and thus are, at least partly, formed upon direct excitation. It is suggested that those excited states are formed directly from favorable ground-state conformations. The importance of interchromophoric interactions in the ground state on the photocyclomerization of nonconjugated bichromophoric systems and on the dimerization of their respective monofunctional model compounds is discussed.

Nonconjugated bichromophoric compounds are very interesting systems for the study of the photo-physical and photochemical properties of the respective chromophores. They afford a gain of insight in the behavior of excited states of these chromophores, in particular of those states which might be too short lived to manifest themselves in the monochromophoric model.⁴ Intramolecular processes, such as delocalization of the excitation energy,⁴⁻⁶ excitation transfer,^{4,7} and cyclomerization,^{1,4,8} as well as intermolecular polyaddition,^{4,9} have been reported.

On the basis of previous results,^{1c} we have proposed that the possibility for the occurrence of an intramolecular excited-state process is governed by the probability

to reach a favorable conformation within the lifetime of the state involved and by the stability of this conformation. In the special case of the cyclomerization of bichromophoric systems, where the link is attached to an atom that is involved in bond formation, the process is limited to systems where four saturated bonds separate the chromophores, as has been reported previously.^{1e,f,10}

We now wish to report some additional factors which might be of importance in excited-state behavior of the bichromophoric system and which are relevant also in the photochemistry of the monofunctional model. In the present study, these factors are exemplified by the 7,7'-polymethylenedioxy coumarins **1**, and the monofunctional analog.

The photochemical behavior of coumarin^{11a-g} and its derivatives^{1d,12a-f} has been a point of interest since the first report by Ciamician. On the basis of extensive mechanistic studies, it was proposed^{11e-h} that the syn dimers were derived from the singlet manifold, while the anti dimers were obtained *via* the triplet excited state.

Although less data are available for the substituted coumarins, a recent study by Ulrich^{12g} indicated that 6-methoxycoumarin reacted from the triplet excited state only, to form the anti head-to-head dimer.

(1) For previous papers in this series, see (a) F. C. De Schryver and J. Put, *Angew. Chem., Int. Ed. Engl.*, **8**, 213 (1969); (b) L. Leenders and F. C. De Schryver, *ibid.*, **10**, 338 (1971); (c) J. Put and F. C. De Schryver, *J. Amer. Chem. Soc.*, **95**, 137 (1973); (d) L. Leenders, E. Schouteden, and F. C. De Schryver, *J. Org. Chem.*, **38**, 957 (1973); (e) M. Van Meerbeck, S. Toppet, and F. C. De Schryver, *Tetrahedron Lett.*, **22**, 2247 (1972); (f) F. C. De Schryver, M. De Brackeleire, S. Toppet, and M. Van Schoor, *ibid.*, **15**, 1253 (1973).

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(4) For a review of intramolecular processes in bichromophoric systems up to 1971, see F. C. De Schryver and J. Put, *Ind. Chim. Belge*, **37**, 1107 (1972).

(5) For a review of the intramolecular excimer and exciplex formations, see W. Klöpffer, "Organic Molecular Photophysics," J. D. Birks, Ed., Wiley, New York, N. Y., in press. The authors thank W. Klöpffer for a preprint of this review.

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(9) For a recent review of the photopolyadditions, see F. C. De Schryver, *Pure Appl. Chem.*, **34**, 213 (1973).

(10) F. C. De Schryver, M. Van Meerbeck, and S. Toppet, submitted for publication.

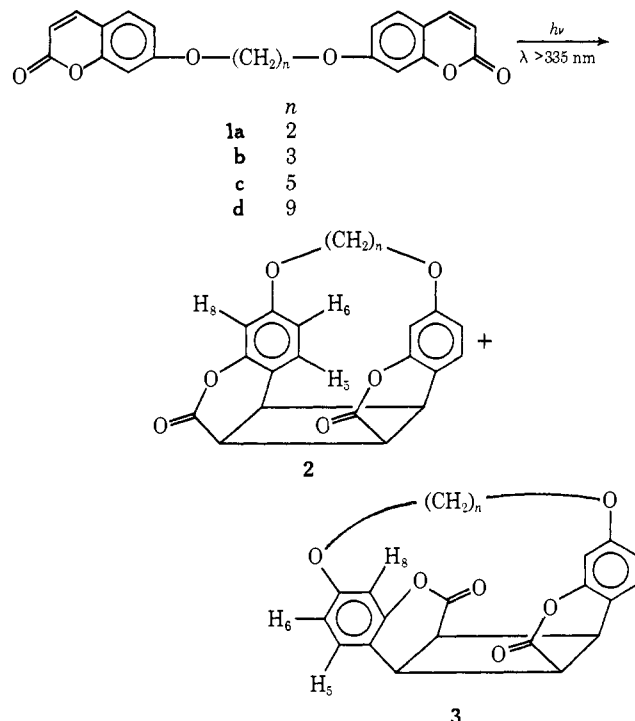
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Results

A. Cyclomerization of 7,7'-Polymethylenedioxy-coumarins 1. The biscoumarins **1a-d** undergo intramolecular and intermolecular cycloaddition upon irradiation.^{1b,d} If the chain between the two coumarin chromophores is long enough, four different cis-fused regioisomers are theoretically possible, syn head-to-head, syn head-to-tail, anti head-to-head, and anti head-to-tail. On irradiation of dioxycoumarins **1**, two intramolecular cycloadducts **2** and **3** are isolated (Scheme I).

Scheme I



The intramolecular character of the reaction was proved by mass spectroscopy and molecular weight determination, and the structure of the two regioisomers was characterized by nmr spectroscopy. The relative yields of each of the regioisomers of those dioxycoumarins, relevant for the further discussion, are assembled in Table I. Sensitization with benzophenone of the higher polymethylenedioxy-coumarins leads to intermolecular adducts with an anti configuration.^{13,14}

The isomer ratio depends on the excitation wavelength. The amount of head-to-tail cyclomer increases with higher wavelengths as is shown in Table II.

B. Quantum Yield of the Cyclomerization. The quantum yields of the intramolecular cycloaddition were determined by irradiating degassed samples of the dioxycoumarins in dichloromethane at a concentration of 5×10^{-4} M with monochromatic light of 334 ± 7

(13) The polymerization of these bifunctional molecules is another example of the recently defined new concept: "photopolymerization" (see ref 9). Results concerning this process will be published elsewhere.

(14) Since on sensitization selective irradiation of the sensitizer is impossible, and since the quantum yields of cyclomerization are higher in the analogs with a shorter chain (*vide infra*), competition between inter- and intramolecular cycloaddition occurs. The course of the reaction is still further complicated by the fact that benzophenone sensitizes the cycloreversion of **3** and **2** to **1**, probably with different efficiencies, as could be shown in independent experiments (H. Loos, unpublished results).

Table I. Cyclomerization of Biscoumarin. Relative Yield of the Different Isomers and Quantum Yield of the Reaction

Compd	<i>n</i>	% head-to-head ^a	% head-to-tail ^a	$\Phi_c \times 10^2$ ^{b,c}
1a	2	85	15	0.24
1b	3	41	59	1.25
1c	5	40	60	1.42
1d	9	33	67	0.44

^a Irradiation with light $\lambda > 335$ nm; determined by nmr spectroscopy. ^b Initial concentration of the biscoumarins was 5×10^{-4} M. ^c Accuracy $\pm 3\%$; less than 10% conversion.

Table II. Dependence of the Ratios of **2c** and **3c** as a Function of λ Excitation

λ , ^a nm	313	334	360
2c , %	43.5	40	37.5
3c , %	56.5	60	62.5

^a ± 7 nm.

nm.¹⁵ The light intensity was measured by actinometry with hexamethylenedimaleimide.^{1c} The disappearance of the biscoumarins was followed by uv analysis at 324 nm. The course of the reaction was linear as long as light absorption was complete. Quantum yields for the different chain lengths are tabulated in Table I. Their respective values in the diether series **1** indicate a maximum for $n = 5$, contrary to the observations made in the 1,1'-polymethylenebisthymines^{8c} and the *N,N'*-polymethylenedimaleimides,^{1c} where the quantum yields decrease with lengthening of the chain (from three to six methylene units). There is small influence of the excitation wavelength on the quantum yield of the cyclomerization of **1**, in the region 310 to 350 nm. The quantum yield of reaction of 7,7'-pentamethylenedioxy-coumarin varied between 1.3×10^{-2} at 312 nm and 1.6×10^{-2} at 350 nm.

C. Uv Absorption Studies. The uv absorption spectra of the bis ethers **1a** and **1c** show a broad band in the long-wavelength region, with a maximum at 324 nm with a molar extinction coefficient of the order of 30,000 and a shoulder around 290 nm (Figure 1). The wavelength of the maximum matches that of 7-methoxycoumarin (**4**). The molar extinction coefficient at the maximum is approximately the double of that of 7-methoxycoumarin (**4**), but appreciable deviations are observed at the long-wavelength side of the absorption band. Differential uv spectra of **1a** and **1c**, obtained either by calculation or experimentally using an equal chromophoric concentration of **4** as reference, indicate the presence of a new absorption band in the bichromophoric systems. This is indicative of ground-state interactions which are more pronounced in **1c** than **1a** (Figure 2).

D. Emission Characteristics. The fluorescence spectra of **1a**, **1c**, and **4** appear in dichloromethane as a broad structureless band with a maximum at 379 ± 1 nm (Figure 3). The shape of the fluorescence spectra of **1a** and **1c** are identical with that of the model compound **4**. A deviation in the wavelength region of 250–290 nm is observed in the excitation spectrum in comparison with the absorption spectrum. The quantum yields of the fluorescence of compounds **1a** and **1c** increase with lengthening of the chain (Table III).

(15) Under these reaction conditions no intermolecular reaction occurs.

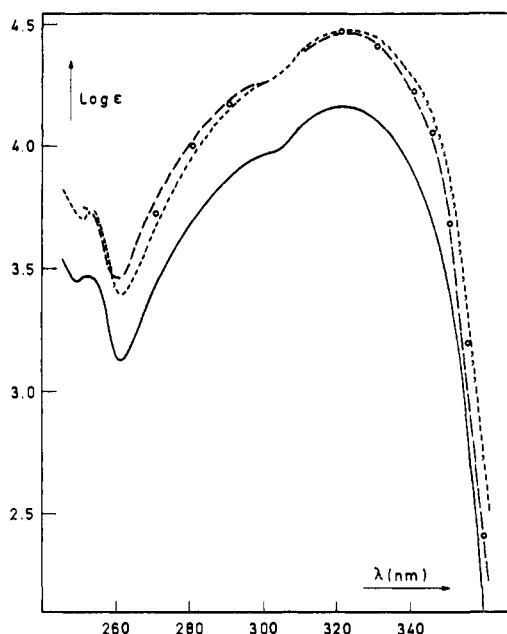


Figure 1. Ultraviolet absorption spectra in dichloromethane at 20° of **1a** (—), **1c** (---), **4** (····), and 2×4 (O).

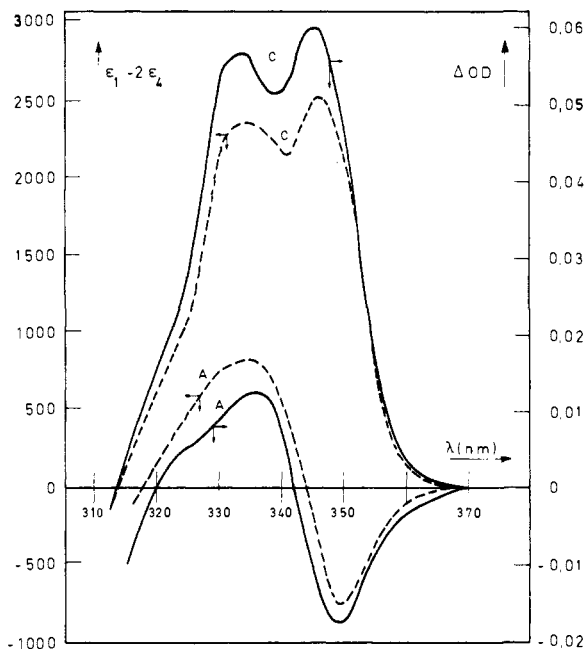


Figure 2. Calculated differential absorption spectra of **1a** (A, ---) and **1c** (C, ---) and experimentally differential absorption spectra of **1a** (A, ····) and **1c** (C, ····) in dichloromethane at 20°.

The phosphorescence spectra of compounds **1** and **4** in EPA at 77°K are identical, and the shape of the phosphorescence spectra is similar to that of coumarin.^{16b} The spectra show maxima at 472, 486, and 506 nm (Figure 3). The triplet energy, calculated from the maximum at 472 nm, was found to be 60.5 kcal/mol.

E. Quenching of the Cyclomerization. To obtain more information about the excited states involved in the intramolecular cycloaddition, quenching experiments were carried out with biacetyl. Samples were irradiated with monochromatic light of 334 ± 7 nm

(16) (a) J. B. Gallivan, *Mol. Photochem.*, **2**, 191 (1970); (b) P.-S. Song and W. H. Gordon, *J. Phys. Chem.*, **74**, 4234 (1970).

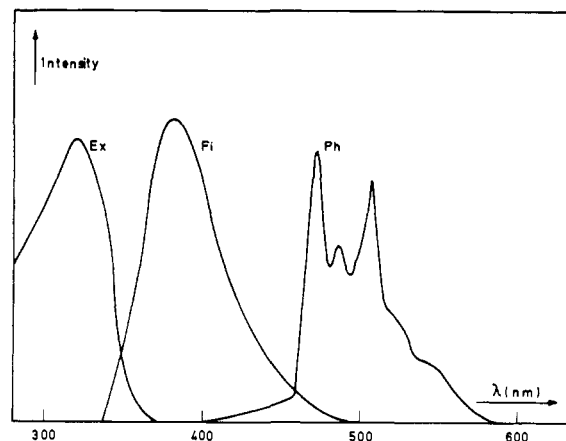


Figure 3. Excitation and emission spectra of **1a**: Ex, excitation spectrum in dichloromethane at 20°; F1 fluorescence spectrum in dichloromethane at 20°, λ_{excit} 324 nm; Ph, phosphorescence spectrum in EPA at 77°K, λ_{excit} 340 nm.

Table III. Quantum Yield of Fluorescence and Singlet Lifetimes

Compd	$\Phi_F \times 10^3$ ^{a,b}	$k_q \tau^c$	$\tau \times 10^9$ sec	k_{1a}^e
1a	9.5 ± 0.5	84 ± 26	5.5 ± 1.7	334 ± 156
1c	13.5 ± 0.5	42 ± 45	2.8 ± 0.3	145 ± 79
4	20 ± 1^d			

^a Taken in degassed solution in CH_2Cl_2 at a concentration of 3.2×10^{-6} M; $T = 20^\circ$; excitation wavelength 324 nm. ^b Quantum yields were obtained with quinine sulfate as reference ($\Phi_F = 0.5$) in 1 N H_2SO_4 . ^c $k_q = 1.51 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$; see ref 17. ^d Concentration is 1.3×10^{-6} M. ^e Initial slope of the reaction quenching.

to avoid direct absorption by the quencher under the experimental conditions ($\epsilon^{324 \text{ nm}} (\text{CH}_2\text{Cl}_2) = 1.7 \text{ M}^{-1} \text{ cm}^{-1}$ for biacetyl). The conversion of dioxy-coumarins was measured by uv analysis at 324 nm after dilution. The obtained Stern-Volmer plots for compounds **1a** and **1c** are represented in Figure 4. All the dioxy-coumarins studied have nonlinear Stern-Volmer plots, indicating that more than one excited state is involved in the reaction. A remarkable difference exists between the plot obtained for the cyclomerization quenching of **1a** and that of **1c**. The plot of **1a** indicates that one excited state is responsible for approximately 85% of the reaction, and the other part of the reaction cannot be quenched. In the case of **1c**, a second quenchable excited state seems to be involved, and even at high quencher concentrations the cyclomerization is quenched only for a much smaller amount than for **1a**.

F. Fluorescence Quenching. Reaction quenching of the cyclomerization of compounds **1a** and **1c** shows that more than one excited state is involved. To determine this nature, fluorescence quenching was carried out with biacetyl and compared with reaction quenching. Linear Stern-Volmer plots were obtained for the two compounds as can be seen in Figure 5. Their respective slopes showed the same trend and are in the same order of magnitude as those of the first part of the reaction curves. The lifetimes of the emitting species, calculated assuming diffusion-controlled quenching and a value of $1.51 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for k_q ,¹⁷ are assembled in Table III.

(17) A value for k_q was calculated assuming diffusion-controlled quenching from the equation: $k_q = 8RT/3000\eta$.

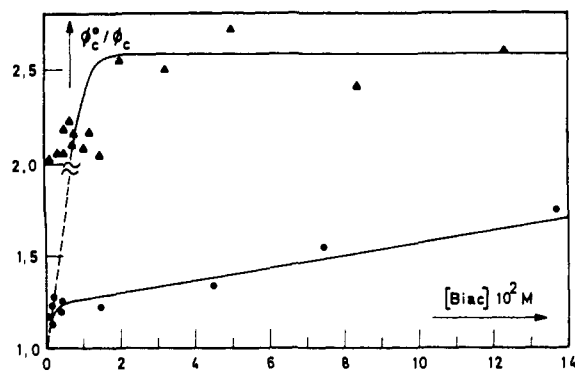


Figure 4. Quenching of the cyclomerization of **1a** (\blacktriangle) and **1c** (\bullet) in dichloromethane at 20°.

G. Preparative Quenching. As there is more than one excited state involved in the reaction which could result in different isomer ratios, it seemed of interest to determine the isomer ratios at different quencher concentrations. As can be seen in Table IV, the relative

Table IV. Ratio^a of **2c** and **3c** as a Function of Quencher^b Concentration^c

[Q], 10 ² M	2c , %	3c , %
0	40	60
0.6	39	61
1	39	61
2	40	60
6	41	59
8	45.5	54.5
8	46	54

^a λ_{excit} 334 nm, ratio determined by 100-MHz nmr. ^b Biacetyl. ^c In degassed CH_2Cl_2 , initial concentration 10^{-2} M, at 10% conversion.

amount of head-to-head isomer increases for biacetyl concentration corresponding to those which constitute the second part of the quenching curve. Quenching curves for respectively head-to-head **2c** and head-to-tail **3c** cyclomer formation of **1c** are represented in Figure 6.

Discussion

Contrary to coumarin,¹⁶ methoxycoumarin **4** and the dioxycoumarins **1** do emit at room temperature in CH_2Cl_2 . That emission occurs from S^1 could be ascertained by the excitation spectrum, the maximum of which coincides with that of the absorption and also by the small Stokes shift. The second transition is, however, much less intensive in the excitation spectrum, indicating that radiationless deactivation from this state could compete with internal conversion to S^1 . Lowering the temperature does diminish the importance of this process and enhances the fluorescence of **1b**.¹⁸

The unusual observation¹⁹ that **1a** has the longest singlet lifetime, although its quantum yield of fluorescence is lowest, could reflect, in view of the preceding discussion, a diminished probability to reach on excita-

(18) The authors thank Professor Förster and Dr. Hoffmann for these measurements.

(19) Analogous results were obtained in the study of a series of dianthracene compounds derived from anthrol-1 and -dicarboxylic acid: F. C. De Schryver and R. Arien, unpublished results.

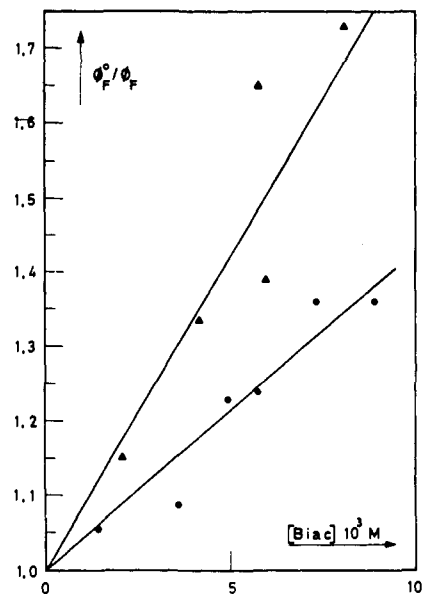


Figure 5. Quenching of the fluorescence of **1a** (\blacktriangle) and **1c** (\bullet) in dichloromethane at 20°.

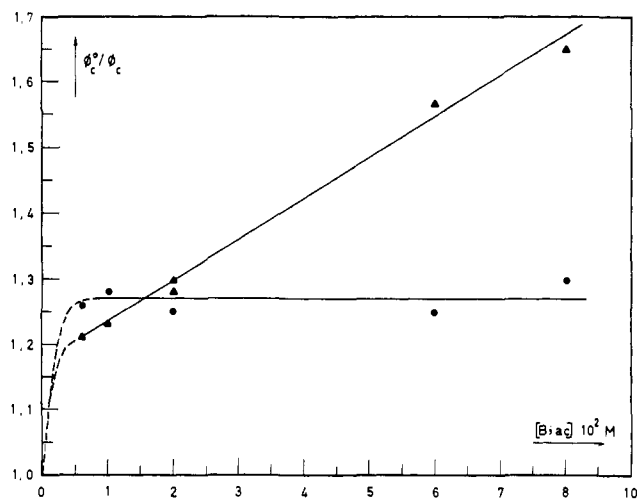


Figure 6. Quenching of the formation of **2c** (\bullet) and **3c** (\blacktriangle) in dichloromethane at 20°.

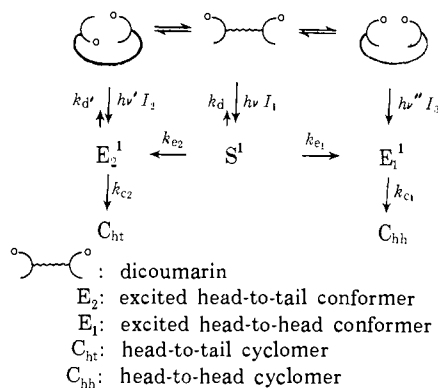
tion the S^1 level.²⁰ An alternative explanation would be a variation of the rate constant for radiative decay from the singlet excited state. On quenching of the cyclomerization, nonlinear Stern-Volmer plots are obtained, indicating that reaction occurs from more than one excited state. The first part of the quenching curve is, by comparison with fluorescence quenching, found to reflect singlet reactivity. Since the slope of the second part of the quenching curve is smaller, this is indicative of the intermediacy of one or more states with a shorter lifetime than the singlet, and which are formed upon direct excitation.

These states cannot be but directly excited, favorable conformations or ground-state complexes. Evidence for the existence of ground-state interaction is found in the ultraviolet absorption spectra of **1c** in comparison with **4**. Specific excitation of **1c** in the spectral region,

(20) P. J. Wagner, "Creation and Detection of Excited States," Vol. I, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 173.

where these interactions are manifest, results in an increase of the head-to-tail regioisomer **3c**. This suggests that the observed deviations in the ultraviolet spectra are due to conformations in which the two chromophores are in a head-to-tail spatial arrangement in the ground state. The existence of head-to-head interaction in the ground state must be considered on the basis of the trend of the regioisomer ratio in the preparative reaction quenching studies. These data can be explained on the basis of Scheme II. If it is assumed that in this

Scheme II



scheme the excited state S^1 and E_2 can be quenched, while E_1 has too short a lifetime to be susceptible to quenching, the observed Stern–Volmer curves can be explained. In **1c**, two excited states, S^1 and E_2 , are quenched, giving a nonlinear curve. In **1a**, however, favorable head-to-tail conformers do not exist in the ground state, and the Stern–Volmer plot reaching an horizontal asymptote can be attributed to a case where three excited states, S^1 , E_1 , and E_2 , react. E_2 is formed only from S^1 which can be quenched, while E_1 is not quenchable. Clearly, a horizontal asymptote for the plot also must exist in the quenching of **1c**, but this is not reached yet at the quencher concentration used. The involvement of excited head-to-head conformers in **1c** must be considered on the basis of the change in the isomer ratio on adding different concentrations of quencher. Upon addition of increasing amounts of quencher, E_2 is progressively quenched, resulting in an increase of the amount of head-to-head isomer, arising from E_1 , which is not quenchable at those quencher concentrations.

On the basis of the proposed schemes, the total quantum yield of product disappearance, which under the experimental conditions equals the quantum yield of cyclomerization, is the sum of the quantum yields of product formation from three excited states. The maximum value for the quantum yield of cyclomerization for **1c**, which is quite different from other systems reported up to now^{1a–c, 4, 8} where reactivity decreases with lengthening of the chain, can be explained as follows. The contribution to the reaction from the singlet excited state is maximal for this compound as is reflected in its shorter singlet lifetime. This increase in singlet reactivity is, however, not sufficient to explain the sixfold increase in quantum yield of cyclomerization. Hence, the contribution of reaction derived from chromophores interacting in the ground state must be also maximal for **1c**.

The differences in lifetime and susceptibility for quenching of E_1 and E_2 can be understood, in view of recently proposed theory²¹ concerning the course of photochemical reaction. E_2 is an energy minimum of the excited-state hypersurface resulting from an avoided crossing between excited and ground state, while E_1 is a funnel on the excited-state hypersurface through which very fast crossing to the ground state occurs. Other deactivations of E_1 can consequently be neglected, while those of E_2 will be very small. The favorable ground-state conformers, although they are present only for a very small percentage, contribute to a great extent to the reaction because of the high efficiency with which they collapse to cyclomer once they are excited. The importance of favorable ground-state conformations²² and of interaction²³ has been observed in the photochemistry of other systems.²³ The quantum yield of the cyclomerization can be expressed on the basis of the proposed scheme as

$$\Phi_{co} = \alpha + k_{e1}\tau_s + k_{e2}\tau_{E_2}(\beta + k_{e2}\tau_s) \quad (1)$$

where α is the fraction of the total absorbed light intensity absorbed by the head-to-head conformers and equals

$$\alpha = \frac{I_3}{I_1 + I_2 + I_3} \cong \frac{I_3}{I_1} \quad (2)$$

β is the fraction of the total absorbed light intensity absorbed by the head-to-tail conformers and equals

$$\beta = \frac{I_2}{I_1 + I_2 + I_3} \cong \frac{I_2}{I_1} \quad (3)$$

In the presence of a quencher, the expression for the Stern–Volmer equation then becomes

$$\frac{\Phi_{co}}{\Phi_{coq}} = \frac{\Phi_{co}(1 + k_q\tau_s[q])(1 + k_q\tau_{E_2}[q])}{\alpha(1 + k_q\tau_s[q])(1 + k_q\tau_{E_2}[q]) + k_{e1}\tau_s(1 + k_q\tau_{E_2}[q]) + [\beta k_{e2}\tau_{E_2}(1 + k_q\tau_s[q]) + k_{e2}k_{e1}\tau_{E_2}\tau_s]} \quad (4)$$

This equation describes a curve which has a horizontal asymptote (slope = 0) with an intercept equal to Φ_{co}/α , which allows us to determine a value of α in the case of **1a**.

Furthermore, the ratio of the quantum yields of formation of the two cyclomers can be determined from the isomer ratio and equals

$$\frac{[C_1]}{[C_2]} = \frac{\Phi_{c1o}}{\Phi_{c2o}} = \frac{\alpha + k_{e1}\tau_s}{k_{e2}\tau_{E_2}(\beta + k_{e2}\tau_s)} \quad (5)$$

Knowing their sum and their ratio, we can calculate Φ_{c1o} and Φ_{c2o} . This provides a value for k_{e1} if α and τ_s are known. Values for τ_s can be obtained from fluorescence quenching. In the same way, it is possible to calculate the quantum yields of formation of each isomer at each quencher concentration, Φ_{c1q} and Φ_{c2q} , from the isomer ratio at each quencher concentration and from

(21) J. Michl, *Mol. Photochem.*, **4**, 243 (1972).

(22) F. D. Lewis and R. W. Johnson, *J. Amer. Chem. Soc.*, **94**, 8914 (1972), and references cited therein.

(23) (a) Y. L. Bahmel, D. G. McGregor, T. L. Prenner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 637 (1972); (b) R. Kleopfer and H. Morrison, *ibid.*, **94**, 255 (1972).

the total quantum yield of product formation at that quencher concentration. In this way, Stern–Volmer plots for each of the isomers (Figure 6) can be calculated separately from the overall plot. The expressions for the two equations are as follows

$$\frac{\Phi_{c1o}}{\Phi_{c1q}} = \frac{\Phi_{c1o}(1 + k_q\tau_s[q])}{\alpha(1 + k_q\tau_s[q]) + k_{e1}\tau_s} \quad (6)$$

$$\frac{\Phi_{c2o}}{\Phi_{c2q}} = \frac{\Phi_{c2o}(1 + k_q\tau_{E2}[q])(1 + k_q\tau_s[q])}{k_{c2}\beta\tau_{E2}(1 + k_q\tau_s[q]) + k_{c2}k_{e2}\tau_s\tau_{E2}} \quad (7)$$

The curve according to eq 6 has an initial slope (s_i) equal to

$$s_i = k_{e1}k_q\tau_s^2/\Phi_{c1o} \quad (8)$$

and a horizontal asymptote with an intercept equal to

$$b = \Phi_{c1o}/\alpha \quad (9)$$

while eq 7 describes a curve with an oblique asymptote with an intercept equal to

$$b' = \frac{\Phi_{c2o}(\beta - k_{e2}\tau_{E2})}{k_{c2}\beta^2\tau_{E2}} \quad (10)$$

and a slope equal to

$$a' = k_q\Phi_{c2o}/k_{c2}\beta \quad (11)$$

If one assumes that

$$k_{e2}\tau_{E2} \ll \beta \quad (12)$$

eq 10 is simplified to

$$b' = \Phi_{c2o}/k_{c2}\beta\tau_{E2} \quad (13)$$

and

$$a'/b' = k_q\tau_{E2} \quad (14)$$

According to the above equations, values for some kinetic constants of pentamethylenedioxy coumarin from the preparative quenching experiments of **1c** were calculated and are assembled in Table V. In view of the limited accuracy of the method used, the obtained values give only an idea of the order of magnitude of the rate constants involved. Furthermore, the assumption made in eq 12 is substantiated; τ_{E2} is in the order of 10^{-10} sec, while $k_{e2}\tau_{E2}$ will be in the order of 10^{-5} , since k_{e2} will be in the same magnitude as k_{e1} . This is substantially smaller than β which should be at least in the same order of magnitude as α .

For **1a**, where no head-to-tail interaction exists in the ground state, (1) and (4) are reduced to (15) and (16).

$$\Phi_{co} = \alpha + k_{e1}\tau_s + k_{c2}\tau_{E2}k_{e2}\tau_s \quad (15)$$

$$\frac{\Phi_{co}}{\Phi_{cq}} = \frac{\Phi_{co}(1 + k_q\tau_s[q])(1 + k_q\tau_{E2}[q])}{\alpha(1 + k_q\tau_s[q])(1 + k_q\tau_{E2}[q]) + k_{e1}\tau_s(1 + k_q\tau_{E2}[q]) + k_{c2}k_{e2}\tau_{E2}\tau_s} \quad (16)$$

Equation 16 describes a curve with the same horizontal asymptote as eq 4 (slope = 0, intercept = Φ_{co}/α). For **1a**, one can calculate α and k_{c1} from Φ_{c1o} , as the horizontal asymptote of eq 16 and τ_s are known. The values are assembled in Table V.

The values of k_{e1} are small, when compared with other values found for intramolecular excimer formations⁴

Table V. Some Kinetic Data Obtained in the Analysis of the Photocyclomerization of **1a** and **1c**

	1a	1c
τ_s^a	5.5×10^{-9}	2.8×10^{-9}
a'		5
b'		1.3
τ_{E2}^b		2.5×10^{-10}
Φ_{c1o}	2.04×10^{-3}	0.47×10^{-2}
α	0.31×10^{-3}	0.45×10^{-2}
k_{e1}	3.1×10^5	2×10^5

^a From fluorescence quenching. ^b $k_q = 1.51 \times 10^{10} M^{-1} sec^{-1}$,¹⁷

and reactions^{1c} which are in the order of $10^9 sec^{-1}$. This probably reflects the longer length of the link and the greater volume of the reacting chromophores in the 7,7'-polymethylenedioxy coumarins. Further analysis of this and of analogous systems are under study to verify this hypothesis.

The present results clearly indicate the importance of ground-state interaction in this system. Furthermore it is tempting to suggest that the distribution of the regioisomer in the dimerization of **4**^{1d} can be in part due to excitation of interacting "dimers."

Experimental Section

The solvent used in all the experiments was dichloromethane (Fluka pa). 7,7'-Polymethylenedioxy coumarins **1a-d** and 7-methoxycoumarin (**4**) were synthesized and purified using the methods described earlier,^{1d} and the preparative irradiations were performed as reported.^{1d}

Uv Spectra. Uv spectra were recorded on a Cary 17 instrument, in a cell compartment thermostated at 20°. The differential uv spectra were taken; using as a reference a solution of 7-methoxycoumarin with the same chromophore concentration as the sample containing the bichromophore.

Fluorescence Measurements. Fluorescence spectra and excitation spectra were recorded on a Fica absolute differential fluorimeter. Optical densities of the samples were around 0.1. The fluorescence quantum yields were determined relative to quinine sulfate, in 1 N H₂SO₄, assuming a value of 0.50 for the fluorescence quantum yield of the latter.

The optical densities of the samples and that of the quinine sulfate reference were monitored to be the same at the excitation wavelength (324 nm). The areas under the obtained fluorescence curves were measured planimetrically and taken as a measure of the quantum yield. The samples of dioxycoumarins were degassed by four freeze-thaw cycles.

Fluorescence quenching was carried out by measuring the fluorescence of samples containing different concentrations of biacetyl. Biacetyl absorbed no excitation light at the concentrations used. The samples were degassed and thermostated at 20°. The obtained areas were measured and compared with those without biacetyl and/or with quinine sulfate as references to obtain Φ^0/Φ values.

Phosphorescence Spectra. Phosphorescence spectra were recorded on an Aminco-Bowman apparatus at 77°K. The excitation wavelength was 340 nm.

Quantum Yields of the Cyclomerization. The quantum yields of the cyclomerization were determined by irradiation of 4 ml of a $5 \times 10^{-4} M$ solution of the dioxycoumarin in dichloromethane with monochromatic light of 334 ± 7 nm. A high-intensity Bausch and Lomb monochromator equipped with a super-high-pressure mercury lamp was used as a light source. The cell was put in a fixed position on the optical back in a thermostated block at 20°. A magnetic stirring device was mounted under the block. It was checked that the course of the reaction was linear as long as light absorption was complete. The samples were degassed by four freeze-thaw cycles.

Light intensity was measured by actinometry with *N,N'*-hexamethylenedimaleimide.^{1c}

The conversion was measured after dilution (1:10) by measuring the optical density at 324 nm. Care was taken that conversion did not exceed 10%. To determine the influence of the excitation wavelength on the quantum yield, the intensity of the monochroma-

tor was determined with *N,N'*-hexamethylenedimaleimide at 360, 334, and 313 nm.

Quenching of the Cyclomerization. Quenching of the cyclomerization with biacetyl was carried out with monochromatic light of 334 ± 7 nm. Solutions of 5×10^{-4} M dioxycoumarins in dichloromethane, containing concentrations of biacetyl varying from 0.5×10^{-3} to 1×10^{-1} M, were degassed, thermostated at 20°, and irradiated to obtain $\pm 10\%$ conversion. Biacetyl does not absorb light under these conditions. The solutions were stirred vigorously by means of a magnetic stirrer. The conversion was determined after dilution by measuring the optical density at 324 nm. The difference in optical density before and after irradiation was compared with the difference in a reference sample without biacetyl, giving directly a value of Φ^0/Φ .

Preparative Quenching Experiments. A 10^{-2} M solution of **1c** in dichloromethane is degassed in the presence of variable biacetyl concentrations and irradiated with a Bausch and Lomb monochromator at 334 ± 7 nm with up to $12 \pm 3\%$ conversion. The solvent and biacetyl were evaporated under reduced pressure, and the residue was dissolved in DMSO-*d*₆. Nmr spectra of the reaction mixture were obtained by accumulation (25 scans) on a XL 100 nmr, and the ratios of the isomer were determined by the ratio of the area of part of the nmr absorptions of the protons H₅, H₆, and H₈ in the head-to-head cyclomer over the area of the absorption of proton H₈ in the head-to-tail cyclomer. The validity of this

determination was confirmed by comparison with mixtures prepared from pure cyclomers and starting materials.

Production Distribution. The relative ratios of cyclomer as a function of the excitation wavelength were determined by an analogous method as described in the preparative reaction quenching.

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Supplementary Material Available. A detailed kinetic analysis and data for obtaining Figure 6 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6994.

A Carbon-13 Nuclear Magnetic Resonance Study of the Visual Chromophores and Model Compounds

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Abstract: The ¹³C nmr spectra of *all-trans*-, *9-cis*-, *11-cis*-, and *13-cis*-retinals, β-ionone, and *cis*- and *trans*-crotonaldehydes have been obtained in acetone-*d*₆ solution. The ¹³C nmr spectra are also reported for β-ionone and *all-trans*-, *11-cis*-, and *13-cis*-retinals in cyclohexane-*d*₁₂ solution. Striking differences in chemical shifts were found among the protonated carbons of the polyene chain portion of the different retinal isomers. Many of these differences are attributed to the steric polarization effect. In comparing the chemical shifts of the olefinic carbons of each *cis* isomer relative to the corresponding carbons of *all-trans*-retinal, the *11-cis* isomer was found not to follow the pattern set by *9-cis*- and *13-cis*-retinals. Spin-lattice relaxation times *T*₁ are reported for β-ionone, *all-trans*- and *13-cis*-retinal, and *cis*- and *trans*-crotonaldehydes. The *T*₁ values imply that (a) the methyl groups of the retinal polyene chain rotate rapidly compared with the overall tumbling of the molecule, and (b) the rotational diffusion of *13-cis*-retinal and presumably *all-trans*-retinal is considerably anisotropic, with *D*_{||} = 4.6*D*_⊥ for *13-cis*-retinal.

The conjugated polyene aldehydes *11-cis*- and *all-trans*-retinal play a crucial role in vision. In the only photochemical reaction in the vision process *11-cis*-retinal is isomerized to the *trans* isomer, while attached through an imine linkage to the protein opsin. This initiates a sequence of reactions resulting ultimately in the sensation of vision.¹ The polyene aldehyde *9-cis*-retinal is also able to combine with opsin,² and *13-cis*-retinal has been implicated as the chromophore of the membrane protein bacteriorhodopsin.³

As part of a program to establish retinal as a nmr probe of the active site of rhodopsin, we have obtained the ¹³C nmr spectra of *all-trans*-, *9-cis*-, *11-cis*-, and *13-cis*-retinals free in solution. In addition, β-ionone and *cis*- and *trans*-crotonaldehyde have been studied as

model compounds. In particular the protonated carbons of the polyene chain portion of each of the retinal isomers have been independently and unequivocally assigned, without reference to model compounds, additive parameters, or substituent effects. We discuss the observed results in terms of substituent and conformational effects previously observed in systems other than conjugated polyenes. We also present and discuss longitudinal relaxation time measurements for *all-trans*-retinal, *13-cis*-retinal, and the model compounds.

Experimental Section

β-Ionone, *all-trans*-retinal, *9-cis*-retinal, *13-cis*-retinal, and *trans*-crotonaldehyde were purchased from Eastman. *11-cis*-Retinal was generously supplied by P. K. Brown. Acetone-*d*₆ and cyclohexane-*d*₁₂ were purchased from Stohler Isotope Chemical Co. Most samples were prepared in the concentration range 0.35–0.75 M. Samples were filtered through sintered glass, degassed with at least five freeze-pump-thaw cycles, and sealed under vacuum. Samples so prepared, protected from light, and stored at –15° were stable for

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