Photochemistry of Nonconjugated Bichromophoric Systems. Cyclomerization of 7,7′-Polymethylenedioxycoumarins and Polymethylenedicarboxylic Acid (7-Coumarinyl) Diesters[1]

LUC H. LEENDERS,[2] ERIC SCHOUTEDEN,[3] AND FRANS C. DE SCHRYVER*[4]

Department of Chemistry, Universiteit Leuven, Celestijnenlaan 200 F, 3030 Heverlee, Belgium

Received August 17, 1972

Upon irradiation of dicoumarins with ultraviolet light, intramolecular cycloadducts with the syn configuration are formed. The structure of the isomers was proved unequivocally by nmr spectral study and dipole moment measurements. Upon irradiation of 7,7′-polymethylenedioxycoumarins with a chain length exceeding four units, the syn head-to-tail isomer is the most abundant regioisomer. On irradiation of the polymethylenedicarboxylic acid (7-coumarinyl) diesters, the syn head-to-head isomer is formed predominantly. In the former class neither the chain length nor the solvent polarity seem to exert an important influence on the ratio between the two regioisomers. In the latter this ratio is more affected by length of the link between the two chromophores. Upon increase of the concentration of the dioxycoumarins, the amount of intermolecular photoproducts increases. Upon sensitization, intermolecular reaction prevails. Steric factors such as methyl substitution on the photoreactive double bond were investigated. The photocycloadditions are reversible upon irradiation at λ ~ 300 nm.

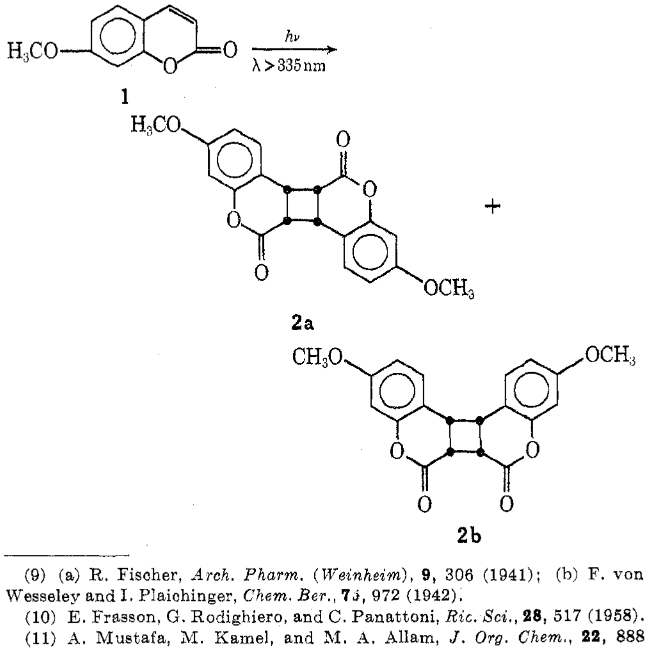
During recent years some examples of intramolecular photopolymerization between suitable chromophores, which are linked by a flexible chain, have been reported.[5] In all cases mentioned except the biscinnamates,[5h] the 1,7 dimer[5o,q] and the *N*,*N*′-alkylene bismaleimides,[5r] the intramolecular reaction is limited to systems in which the two functions are separated by three methylene units.

In view of the hypothesis put forward in the photocyclomerization of *N*,*N*′-alkylene bismaleimides[5r] and in view of the assumption that an excimer could be an intermediate in the coumarin dimerization,[6] the photochemistry of some symmetric and asymmetric dicoumarins[7] was studied. We wish here to report some synthetic aspects of this study.

Although the dimerization of coumarins is a long-known reaction,[8] only a limited number of photoreactions of substituted coumarins has been reported.[9-12] Therefore the photochemistry of the model compounds was looked into.

Results

Photochemistry of 7-Methoxycoumarin.—7-Methoxycoumarin was synthesized in analogy with the synthesis of 7,7′-methylenedioxycoumarin.[13] Although it has been reported[9] that the title compound did not photodimerize in solution, dimer **2a** was isolated in 75% yield upon irradiation of a 5 × 10^{-2} *M* solution in dichloromethane using light with λ > 335 nm.[14] Dimer **2b** is formed in 25% yield and its percentage is raised to 30 upon a tenfold increase in concentration of **1**. Dimer **2a** is identical with the one obtained predominantly upon direct irradiation of **1** in the solid state,[9]



---

[1] Abstracted in part from the Ph.D. thesis of L. H. Leenders. Presented in part at the 6th International Photochemistry Conference, Bordeaux, France, Sept 1971.

[2] Predoctoral Fellow, N. F. W. O. (aspirant, Belgisch National Fonds voor Wetenschappelijk Onderzoek).

[3] Predoctoral Fellow, I. W. O. N. L. (Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw).

[4] All inquiries should be addressed to this author.

(5) (a) F. D. Greene, *Bull. Soc. Chim. Fr.*, 1356 (1960); (b) N. D. Weinschencker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (c) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *ibid.*, **77**, 3852 (1953); (d) D. E. Applequist, M. A. Lintner, and R. Searle, *J. Org. Chem.*, **33**, 254 (1968); (e) J. H. Golden, *J. Chem. Soc.*, 3741 (1961); (f) R. Livingston and Kei Sin Wei, *J. Amer. Chem. Soc.*, **89**, 3098 (1967); (g) I. Roitt and W. Waters, *J. Chem. Soc.*, 2695 (1952); (h) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 703 (1970); (i) N. J. Leonard, K. Golanckiewicz, R. J. McCredie, S. M. Johnson, and I. C. Paul, *ibid.*, **91**, 5855 (1969); (j) K. T. Potts and E. Brugel, IUPAC International Symposium, Boston, Mass., 1971, Abstracts, p 94; (k) J. C. Doty, S. Y. Farid, D. Specht, and J. L. R. Williams, IUPAC International Symposium, Boston, Mass., 1971, Abstracts, p 156; (l) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971); (m) S. R. Kurowski and H. Morrison, *ibid.*, **94**, 507 (1972); (n) J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 144 (1971); (o) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971); (p) J. R. Scheffer, R. A. Wostradowski, and K. C. Dooley, *Chem. Commun.*, 1217 (1971); (q) J. R. Scheffer and B. A. Boire, *Tetrahedron Lett.*, 4741 (1970); (r) J. Put and F. C. De Schryver, *J. Amer. Chem. Soc.*, **95**, 737 (1973); (s) K. Golanckiewicz, *Bull. Acad. Polon. Sci.*, **19**, 383 (1971).

(6) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).

(7) L. H. Leenders and F. C. De Schryver, *Angew. Chem.*, **83**, 359 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 338 (1971).

(8) (a) G. Ciamician and P. Silber, *Chem. Ber.*, **35**, 4128 (1902); (b) G. Ciamician and P. Silber, *ibid.*, **47**, 640 (1914); (c) R. Anet, *Chem. Ind. (London)*, 897; (1960); *Can. J. Chem.*, **40**, 1249 (1962); (d) G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962); (e) G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Amer. Chem. Soc.*, **86**, 3103 (1964); (f) C. H. Krauch, S. Farid, and G. O. Schenk, *Chem. Ber.*, **99**, 625 (1966); (g) H. Morrison, H. Curtis, and T. McDowell, *J. Amer. Chem. Soc.*, **88**, 5415 (1966).

(9) (a) R. Fischer, *Arch. Pharm. (Weinheim)*, **9**, 306 (1941); (b) F. von Wesseley and I. Plaichinger, *Chem. Ber.*, **75**, 972 (1942).

(10) E. Frasson, G. Rodighiero, and C. Panattoni, *Ric. Sci.*, **28**, 517 (1958).

(11) A. Mustafa, M. Kamel, and M. A. Allam, *J. Org. Chem.*, **22**, 888 (1957).

(12) (a) H. Umemoto, T. Kitao, and K. Konishi, *Kogyo Kagaku Zasshi*, **73**, 1146 (1970); (b) H. Umemoto, T. Kitao, and K. Konishi, *ibid.*, **73**, 2200 (1970).

(13) M. G. Parekh and K. N. Trivedi, *J. Indian Chem. Soc.*, **46**, 1068 (1969).

(14) The light beneath 335 nm was cut off by using a solution of sodium bromide and lead acetate or lead nitrate, as was described by Rappoldt.[15]

(15) M. P. Rappoldt, Thesis, University of Leiden, 1958.

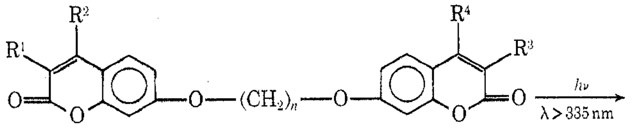
as is shown by the melting point and nmr-spectral analysis.

The structure of **2a**[16] was established on the basis of nmr absorptions as compared with those of the cyclomers of the dioxycoumarins (*vide infra*) and on the basis of the dipole moment which has a value of 2.9 D in benzene, and is much lower than the value of 4.5 D for 7-methoxycoumarin itself.

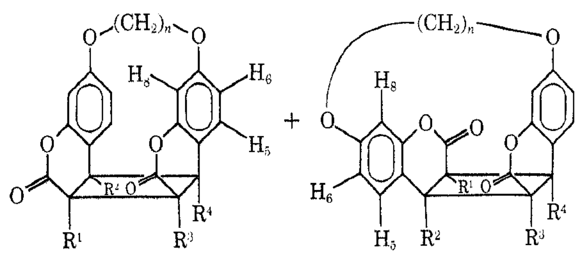
Photochemistry of 7,7′-Polymethylenedioxycoumarins.—The symmetric 7,7′-polymethylenedioxycoumarins **3** and **9** were synthesized in analogy with the synthesis of 7-methoxycoumarin. The asymmetric dioxycoumarin **6** was prepared by refluxing an acetone solution of 4-methyl-7-hydroxycoumarin and α-(7-oxycoumarinyl)-ω-bromoalkane in the presence of potassium carbonate.[17]

Bifunctional molecules can undergo an intra- or intermolecular reaction. On direct irradiation of the 7,7′-polymethylenedioxycoumarins using light with $\lambda > 335$ nm, the absorption characteristics of the -CH=CH- system in the ir and nmr spectra disappeared.

If the chain between the two coumarin chromophores is long enough, four different cis-fused isomers may theoretically be formed: the syn head-to-head, syn head-to-tail, anti head-to-head, and anti heat-to-tail configuration.

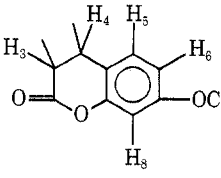


3, $R^1 = R^2 = R^3 = R^4 = H$
6, $R^1 = R^2 = R^3 = H; R^4 = CH_3$
9, $R^1 = R^3 = H; R^2 = R^4 = CH_3$



4, $R^1 = R^2 = R^3 = R^4 = H$ **5**
7, $R^1 = R^2 = R^3 = H; R^4 = CH_3$ **8**
$R^1 = R^3 = H; R^2 = R^4 = CH_3$ **10**
a,b,c,d,e,f,g,h,i,j, n = 2,3,4,5,6,7,8,9,10,11, respectively

Out of the photolysis mixtures of all the dioxycoumarins two cycloadducts have been isolated. The intramolecular nature of the reaction products was proved by mass spectroscopy. The structural proof of the cycloadducts was carried out on the two isomers of 7,7′-trimethylenedioxycoumarin (**3b**). The cyclomers formed must have a syn configuration in view of the shortness of the polymethylene linkage. However, two regioisomers are still possible: syn head-to-head **4b**[18] or syn head-to-tail **5b**.[18] The respective configuration of **4b** and **5b** was elucidated by a comparative nmr study of 3,4-dihydro-7-methoxycoumarin (**11**) and the two isomers. In deuterated chloroform, the phenyl protons of **11** appear as an ABX system: the absorption of H_5, calculated from a 100-MHz spectrum, is found at δ 7.10, H_6 at 6.67, and H_8 at 6.63, the first of these being coupled with the aliphatic protons H_4. Upon addition of EuFOD,[19] paramagnetic downfield shifts were observed: protons H_3 which are nearest to the complexing site are shifted the most; the shift of $H_3 \gg$ shift of $H_4 >$ shift of $H_8 >$ shift of $H_5 >$ shift of H_6. These 100-MHz spectra are represented in Figure 1a. In **5b**, protons H_5, H_6, and H_8 can be described as part of an AMX system. In comparison with the absorptions of the same protons in **11**, H_5 (absorption at δ 6.97) and H_6 (absorption at 6.60) are shifted slightly upfield, while H_8 is shifted over δ 0.62 to a stronger field with respect to the H_8 absorption in **11** (*cf.* Figures 1a and 1b). This effect on H_8 is caused by the diamagnetic anisotropy of a phenyl nucleus situated in front of this proton. This situation is possible only if the molecule has a syn head-to-tail configuration.



11

The 100-MHz nmr spectrum of **4b** (H_5, H_6, and H_8 absorb as a complex between δ 6.6 and 6.3) indicates that such a strong selective shift does not exist for the H_8 absorption. All the phenyl protons are shifted to a higher field in comparison with the same protons in **11**, as may be seen in Figure 1c, in agreement with a proposed syn head-to-head configuration.[20]

Strong supporting evidence for this interpretation was found upon examining the 100-MHz nmr spectra of **4b** and **5b** after adding EuFOD:[21] in **4b**, the phenyl proton which undergoes the strongest downfield shift is H_8 as was the case in **11**, the absorption of H_5 and H_6 being affected almost equally. Owing to the low solubility of **4b** in $CDCl_3$, it was impossible to determine the positions of the absorptions of the different protons accurately. Therefore we examined the spectra of **4f**. The absorptions are H_5 δ 6.62, H_6 6,45, and H_8 6.39; upon adding EuFOD,[22] the chemical shifts became H_5 6.95, H_6 6.72, and H_8 6.96. The 100-MHz nmr spectra of **4b** and **4f** prior to and after adding EuFOD are represented in Figure 1c.

On the contrary, in **5b**, H_5 undergoes the strongest downfield shift upon adding EuFOD (*cf.* Figure 1b), indicating that this proton is now nearest to the complexed C=O, which is only possible in a syn head-to-tail configuration.

---

[16] This dimer may be called 3,9-dimethoxy-6a*H*,6b*H*,12a*H*,12b*H*-cyclobuta[1,2-*c*:3,4-*c*′]-*syn*-biscoumarin.

[17] This synthesis was worked out simultaneously and reported by Fisons Pharmaceuticals Ltd., French Patent Specification 1,593,304.

[18] In general the *syn* head-to-head regioisomer can be called 3,10-alkylenedioxy-6a*H*,6b*H*,12b*H*,12c*H*-cyclobuta[1,2-*c*;4,3-*c*′]-*syn*-biscoumarin, while the *syn* head-to-tail isomer should be named 3,9-alkylenedioxy-6a*H*,6b*H*,12a*H*,12b*H*-cyclobuta[1,2-*c*;3,4-*c*′]-*syn*-biscoumarin.

[19] 2,2-Dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, europium(III) derivative.

[20] (a) The same phenomenon was observed in the syn photodimers of vitamin K_3: H. Werbin and E. T. Strom, *J. Amer. Chem. Soc.*, **90**, 7296 (1968). (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[21] Since the ratio between the concentrations of EuFOD and of the different compounds studied was not kept constant, we did not compare the change in chemical shifts of all these products with one another. The only comparable aspect is the relative change in chemical shift of the different protons within one compound.

[22] To 10 mg of **4f** in $CDCl_3$, 20 mg of EuFOD was added.

This interpretation was confirmed by the dipole moments of 6.7 D for **4b** and 2.0 D for **5b**[23] in dioxane. The more polar isomer can only be the one with the head-to-head configuration. These measurements agreed with the different solubilities of the two photoproducts in solvents with different polarities.

The configuration of the cyclomers of the other 7,7′-polymethylenedioxycoumarins was determined by comparison of their nmr spectra with these of **4b** and **5b**.

The nmr spectrum of the 7-methoxycoumarin photodimer **2a** resembles the spectrum of **5b**. In $CDCl_3$, the absorption of H_8 is located at δ 6.18, which in comparison with the H_8 absorption in **11** is moved to a higher field. In view of the strong spectral similarity with an isomer with the syn head-to-tail configuration together with the lower value of the dipole moment, we conclude that **2a** has a syn head-to-tail configuration.

From the nmr spectrum of a photolysis mixture of **1** in $CDCl_3$ the syn head-to-head structure of **2b** is put forward. Indeed the cyclobutane protons absorb at δ 4.15. This is at a slightly higher field than the cyclobutane of a syn head-to-tail dimer and is in agreement with the observed trend for cyclobutane proton absorption in syn head-to-head cyclomers (see Table V). The anti head-to-head dimer **13** of 7-acetoxycoumarin absorbs at higher field (δ 3.91) in $CDCl_3$ (*vide infra*). Also the absorption pattern in the phenyl region corresponds to that of a syn head-to-head cyclomer.

The percentages of the head-to-head and head-to-tail cyclomers of the nonsubstituted (**3**), monosubstituted (**6**), and disubstituted (**9**) 7,7′-polymethylenedioxycoumarins with varying numbers of methylene units are assembled in Table I.

TABLE I

PHOTOISOMERIZATION OF 7,7′-POLYMETHYLENEDIOXYCOUMARINS[a]

Starting compd	n	Head-to-head,[b,d] %	Head-to-tail,[b,d] %
3a	2	85	15
3b	3	41	59
3c	4	42	58
3d	5	40	60
3e	6	30	70
3f	7	40	60
3g	8	28	72
3h	9	33	67
3i	10	32	68
3j	11	33	67
6c	4	30	70
9d	5	3[c]	97

[a] All the dioxycoumarins were irradiated in dichloromethane at a concentration of 10^{-2} M, except **3a**, which was irradiated at a concentration of 2×10^{-3} M in the same solvent. [b] In the concentration range studied, 3% (irradiation of **3b**) up to 15% (irradiation of **3j**), intermolecular reaction occurred. [c] 3% head-to-head isomer was isolated by column chromatography. This isomer was not detected in the nmr spectrum of the photolysis mixture. [d] The ratio remains constant up to high conversions.

The non- and monosubstituted dioxycoumarins photoisomerized to both the head-to-tail and the head-to-head structures, while the dimethyl-substituted dioxycoumarin formed predominantly the head-to-tail isomer.

Upon photolysis in different solvents, no correlation was found between the dielectric constant of the solvent and the ratio between the two isomers. The irradiation of 7,7′-pentamethylenedioxycoumarin in benzene (ϵ 2), as well as in acetonitrile (ϵ 38), yielded the head-to-head (**4d**) and the head-to-tail (**5d**) isomers in the ratio of 3:7, while in dichloromethane (ϵ 8) a 2:3 ratio was found.

Upon irradiation of more concentrated solutions a larger amount of oligomeric material was formed; using a concentration of 5×10^{-2} and 10^{-1} M, 30 and 35% of oligomers were formed, respectively.

Upon benzophenone-sensitized irradiation of the higher 7,7′-polymethylenedioxycoumarins intermolecular adducts with an anti configuration were formed: 7,7′-deca- and 7,7′-undecamethylenedioxycoumarins yielded polymers with an intrinsic viscosity in chloroform at 25° of 0.25 and 0.38, respectively.[24] The anti configuration of this polymer was proved by the 100-MHz nmr spectrum of the polymer from **3j**. In $CDCl_3$, H_5 absorbed at δ 7.04, H_8 and H_6 as the AB part of an ABX system between 6.6 and 6.8. These absorptions correspond to these of the respective phenyl protons of **11**, excluding any interaction between adjacent phenyl nuclei.[20] At δ 3.83 and 3.75 two peaks were observed which could be attributed to cyclobutane protons absorbing considerably higher than any of the syn cyclobutane protons. This shielding effect is caused by the diamagnetic anisotropy effect of a C=O group in front of the cyclobutane proton if the molecule has an anti configuration, and such shieldings have been observed.[26]

Photochemistry of 7-Acetoxycoumarin.—7-Acetoxycoumarin (**12**) was prepared as reported in the literature[27] by the condensation reaction of acetylchloride and 7-hydroxycoumarin.

7-Acetoxycoumarin did not dimerize upon direct irradiation at 335 nm in dichloromethane, even if the concentration was increased to a value of 1 M.[28]

Upon benzophenone-sensitized irradiation, 7-acetoxycoumarin dimerized to form **13**, which has an anti head-to-head structure[29] as proved by the 60-MHz nmr spectrum in DMSO-d_6 and by the dipole moment. Nmr analysis showed the same results as in the case of the polymer derived from **3j**: the cyclobutane protons, absorbing as a singlet at δ 3.91, are shielded in comparison with the same protons in, *e.g.*, **4b** (4.35) and **5b** (4.08). The same explanation can be invoked. Also, the phenyl proton pattern in the nmr spectrum did not resemble that of a syn head-to-tail photocyclomer. The head-to-head arrangement of the two

---

[23] The dipole moments were determined by measuring the dielectric constants, the densities, and the refractive indices of isomer solutions, and using the formula of P. Huyskens and F. Cracco, *Bull. Soc. Chim. Belg.*, **69**, 422 (1960).

[24] The polymerization of these bifunctional molecules is another example of the recently defined new concept "photopolymerization."[25] Further results concerning the photopolymerization of dicoumarins will be published elsewhere.

[25] (a) F. C. De Schryver, W. J. Feast, and G. Smets, *J. Polym. Sci., Part A-1*, **8**, 1939 (1970); (b) F. C. De Schryver, N. Boens, and G. Smets, *ibid.*, **10**, 1687 (1972).

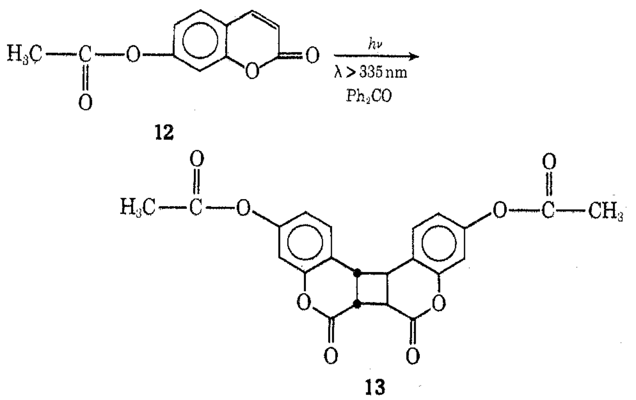
[26] (a) H. Werbin and E. T. Strom, *J. Amer. Chem. Soc.*, **90**, 7296 (1968); (b) O. L. Chapman and H. G. Smith, *ibid.*, **83**, 3914 (1961).

[27] H. Hlasiwetz, *Chem. Ber.*, **4**, 550 (1871).

[28] The only detectable change in the reaction mixture was an intense violet coloration, the cause of which is under study. It should be mentioned that the same coloration took place upon irradiation of 7-methoxycoumarin, 7,7,-polymethylenedioxycoumarins, as well as of coumarin itself in dichloromethane and in acetonitrile.

[29] Dimer **13** can be named 3,10-diacetoxy-6aH,6bH,12bH,12cH-cyclobuta[1,2-c:4,3-c']-*anti*-biscoumarin.

coumarin units was proved by determining the dipole moments of **12** and **13** in benzene. Values of 4.8 and 7.1 D, respectively, were found. Only a head-to-head position can cause this relative increase in polarity.



Photochemistry of Polymethylenedicarboxylic Acid (7-Coumarinyl) Diesters.—This class of dicoumarins (**14**) was synthetized in analogy with 7-acetoxycoumarin by the condensation of a dicarboxylic acid chloride and 7-hydroxycoumarin in benzene.

In contrast to 7-acetoxycoumarin, the analog bifunctional systems react upon direct irradiation in solution. Two cyclobutane ring containing regioisomers were formed in very divergent yields, as can be seen in Table II.

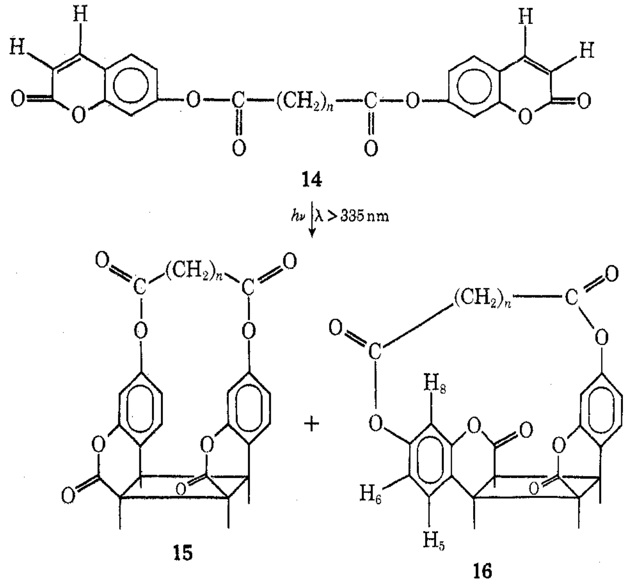
TABLE II

PHOTOISOMERIZATION OF POLYMETHYLENEDICARBOXYLIC ACID (7-COUMARINYL) DIESTERS[a]

Starting compd	n	Head-to-head **15**, %	Head-to-tail **16**, %
14c	4	90	10
14d	5	80	20
14e	6	87	13
14f	7	100	

[a] The dicoumarins **14d,e,f** were irradiated in dichloromethane at a concentration of 10^{-2} *M*. **14c** was irradiated in DMSO at a concentration of 5×10^{-3} *M*.

The structure of the photoisomer **15**[30] and **16** was established on the basis of nmr analysis. Since in **15d** and in **16d** the pentamethylene chain is too short to allow the formation of an anti isomer, these photoisomers should have the syn configuration. This was substantiated by the fact that, in the nmr spectra, the cyclobutane protons absorb at a lower field (**15d**, δ 4.24; **16d**, δ 4.20; both in DMSO-d_6) than the ones in the 7-acetoxycoumarin anti photodimer **13** (δ 3.91 in DMSO-d_6) where they are shielded by the C=O group of the opposite lactone function. The absence of a selectively shielded phenyl proton H_8 suggests a head-to-head structure for isomer **15d**. A further proof for the syn head-to-head structure follows from the comparison of the cyclobutane proton absorptions of $CDCl_3$ solutions of **4f** and **15d** in 100-MHz nmr spectra after addition of EuFOD.[21] The pattern of the AA′XX′ cyclobutane system of the syn head-to-head molecule **4f**, complexed with EuFOD, is rather complicated, as may be seen in Figure 1c. The coupling constants are $J_{AA'}$ (or $J_{XX'}$) = 10, $J_{XX'}$ (or $J_{AA'}$) = 8.3, $J_{AX} + J_{AX'}$ = 10.3 cps. The cyclobutane AA′XX′ system of **15d** with EuFOD has exactly the same pattern. The minor photoisomer **16d** has a syn head-to-tail structure, since protons H_8 are shielded in comparison with the same protons in **11**. This conclusion was substantiated by the nmr spectrum in $CDCl_3$ containing EuFOD. In the syn head-to-tail molecule **5b**, the protons AA′ and XX′ of the AA′XX′ cyclobutane system absorb as two virtual triplets (Figure 1b); this is explained by the almost equal values of J_{AX} and $J_{AX'}$ (protons A and A′ are shifted the most since they are nearest to the complexed C=O; $J_{AX} + J_{AX'}$ = 15 cps. Upon addition of EuFOD to **16d**, the absorptions of protons AA′ and XX′ appear also as two virtual triplets with $J_{AX} + J_{AX'}$ = 16.2 cps.



14,15,16c,d,e,f, n = 4, 5, 6, 7, respectively

Photoreversibility.—All the cyclomers can be cleaved upon irradiation with shorter wavelength light. Upon irradiation of a dichloromethane solution of **4b** and **5b** (5×10^{-5} *M*) with $\lambda \geq 300$ nm, the uv spectra of the photolyzed solutions showed the absorption characteristics of the dioxycoumarin. Upon irradiation of **5b** on a preparative scale, the nmr spectrum of the crude photolysis mixture showed the presence of 35% **3b**, 45% **4b**, and 20% **5b**.

Further work on the mechanism of the photocyclomerization and on the reverse reaction will be reported in the near future.

Conclusions

In the photolysis of the 7,7′-polymethylene dioxycoumarins containing more than two methylene units, neither the chain length between the two coumarin functions nor the solvent polarity seem to exert an important influence on the product distribution. The intramolecular syn reaction is predominant, even when the two chromophores are separated by 13 atoms (n = 11). In the case of the diesters, the syn head-to-head to syn head-to-tail ratio seems to be more strongly affected by the chain length and the former isomer is now the most abundant one.

Upon irradiation of the 7,7′-pentamethylenedi(4-methyl)oxycoumarin **9** steric factors play a role in the

---

[30] In general the *syn* head-to-head regioisomer may be called 3,10-alkylenedicarboxy-6a*H*,6b*H*,12b*H*,12c*H*-cyclobuta[1,2-*c*; 4,3-*c*′]-*syn*-biscoumarin, while the *syn* head-to-tail isomer should be named 3,9-alkylenedicarboxy-6a*H*,6b*H*,12a*H*,12b*H*-cyclobuta[1,2-*c*; 3,4-*c*′]-*syn*-biscoumarin.

determination of the reaction products. Almost no syn head-to-head isomer is formed.

Even upon irradiation of 10^{-1} *M* solutions the intramolecular reaction remains the most important one. Upon sensitized irradiations of the dioxycoumarins with 10 and 11 methylene units in the chain intermolecular adducts, having an anti configuration, are formed. All the photocyclomerizations are reversible.

Experimental Section

Materials.—7-Hydroxycoumarin (umbelliferon) (Fluka, pract.) was used as received. Dichloromethane (Fluka, puriss.), benzene (Merck, pro analysis), and acetonitrile (Baker Analytical Reagent) were treated with Merck 4 Å molecular sieve before use. Acetic acid (Merck, pro analysis) was used as supplied. Dimethyl sulfoxide (Carlo Erba, RP grade) was dried over sodium and distilled; it was stored over a molecular sieve. Benzophenone (Schuchardt) was distilled and recrystallized from cyclohexane. The α,ω-dibromoalkanes used were purchased from Fluka (1,8-, 1,11-dibromoalkanes), from Schuchardt (1,4-, 1,5-, 1,6-, 1,7-, 1,9-, 1,10-dibromoalkanes), from UCB (1,3-dibromopropane), and from Aldrich (1,2-dibromoethane). Methyl iodide was purchased from Merck. The 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione europium(III) derivative was from Aldrich (Resolve-Al EuFOD).

Spectra and Physical Data.—Infrared spectra were measured in KBr pellets with a Perkin-Elmer 257 grating infrared spectrophotometer. Ultraviolet spectra were measured with a Cary Model 17 recording spectrometer. Melting points are from a Leitz Wetzlar melting point measurement microscope and are not corrected. Nmr spectral data were obtained from a Varian A-60 and a Varian XL-100 apparatus. Mass spectral data were measured with a AEI-MS902S. Molecular weights were determined with a Mechrolab 301A vapor pressure osmometer.

Irradiation Equipment.—A Rayonet photochemical reactor, type RPR 208, from the Southern New England Ultraviolet Co., was used in all the experiments. This reactor was fitted with a set of either RUL 3500-Å lamps. For the photocleavage, either RUL 3000-Å lamps were used.

Inside the reaction chamber the temperature varied between 35 and 40°. Most of the photoreactions have been carried out in double-chamber Pyrex vessels. The outer chamber contained a solution of 479 g of sodium bromide and 3 g of lead acetate of 3 g of lead nitrate[15] in 1 l. of water. A 0.5-cm layer of the solution has optical densities of 0.075, 0.44, and 1.0 at 350, 340, and 335 nm, respectively. The path length of the filter solution was 10 mm and that of the reaction solution was 24 mm.

Irradiation Procedure.—After loading, the tubes were flushed with a stream of nitrogen or argon, which was dried over $CaCl_2$. In some cases, the tubes have been degassed by three freeze–thaw cycles, sealed off, and irradiated.

Synthesis of the Model Compounds 7-Methoxycoumarin (1) and 7-Acetoxycoumarin (12).—7-Methoxycoumarin was prepared by refluxing for 8 hr 7-hydroxycoumarins (0.06 mol) with methyl iodide (0.148 mol) in dry acetone in the presence of anhydrous potassium carbonate (0.12 mol). Acetone was distilled off and the residual mixture was transferred into an excess of water. The precipitate was filtered off and washed with distilled water. The crude product was dried and sublimed at 100° under reduced pressure. Finally, the compound was recrystallized from a methanol–water mixture, mp 119–120° (lit.[31] mp 114°; lit.[9] mp 117–118°).

7-Acetoxycoumarin was prepared as described[27] and recrystallized from ethanol, mp 142–144° (lit.[31] mp 140°), yield 85%.

Synthesis of the 7,7′-Polymethylenedioxycoumarins 3, 6, and 9.—All the 7,7′-polymethylenedioxycoumarins 3 were synthesized following the same general procedure as used in the synthesis of the 7-methoxycoumarin. The precipitate contained the dioxycoumarin and a small amount of the α-(7-oxycoumarinyl),-ω-bromoalkane. It was taken up in chloroform or in acetone, treated with carbon black, and precipitated in diethyl ether or in diethyl ether–petroleum ether (bp 40–60°) (up to n = 6, no petroleum ether was used; from n = 7 on, petroleum ether must be present in the precipitating medium since the dioxycoumarins with a longer polymethylene chain are slightly soluble in diethyl ether). The precipitate was filtered off and this procedure was repeated twice, without the carbon black treatment, in order to remove the monofunctional bromo compound. The purity of the product was checked by tlc (silica gel, chloroform or chloroform–5% acetone as developing solvent). Before use, the dioxycoumarins were purified further by column chromatography on Florisil 60–100 mesh (Merck) eluting with chloroform. About 25 g of Florisil was used in a column with a diameter of 18 mm. After the solvent was evaporated off on a rotary evaporator, the residue was taken up and recrystallized several times in an appropriate solvent. The physical data concerning the polymethylenedioxycoumarins are collected in Table III.

The 7,7′-polymethylenedi(4-methyl)oxycoumarin (9) was prepared following the same procedure as in the synthesis of the nonsubstituted dioxycoumarins. The physical data of the 7,7′-pentamethylenedi(4-methyl)oxycoumarin are reported in Table III.

The asymmetric monomethyl-substituted dioxycoumarin 6 was synthesized by refluxing α-(7-oxycoumarinyl)-ω-bromoalkane (0.03 mol) and 7-hydroxy-4-methylcoumarin (0.03 mol) in dry acetone in the presence of 0.06 mol of dry potassium carbonate followed by the same purification procedures as for the symmetric compounds. The bromo-containing compound was obtained as a secondary product in the synthesis of the dioxycoumarins. The data concerning 1-(7-oxycoumarinyl)-4-(4-methyl-7-oxycoumarinyl) butane 6c are given in Table III.

Synthesis of Polymethylenedicarboxylic acid (7-Coumarinyl) Diesters.—To a suspension of 0.06 mol of 7-hydroxycoumarin in 300 ml of dry benzene, 0.06 mol of dried and distilled pyridine was added. While the reaction mixture was warming up gently to about 40–50°, 100 ml of a benzene solution of 0.03 mol of diacid chloride was added dropwise. The reaction mixture was then warmed up until reflux. After an appropriate refluxing time, the benzene was evaporated off and the residue was transferred into a small quantity of acetone, and then into an excess of water. The precipitate was filtered off and washed several times with slightly alkaline water until fluorescence of the filtrate is no longer observed. After drying, the crude products were recrystallized several times in the appropriate solvents. Physical data concerning the diesters are given in Table IV.

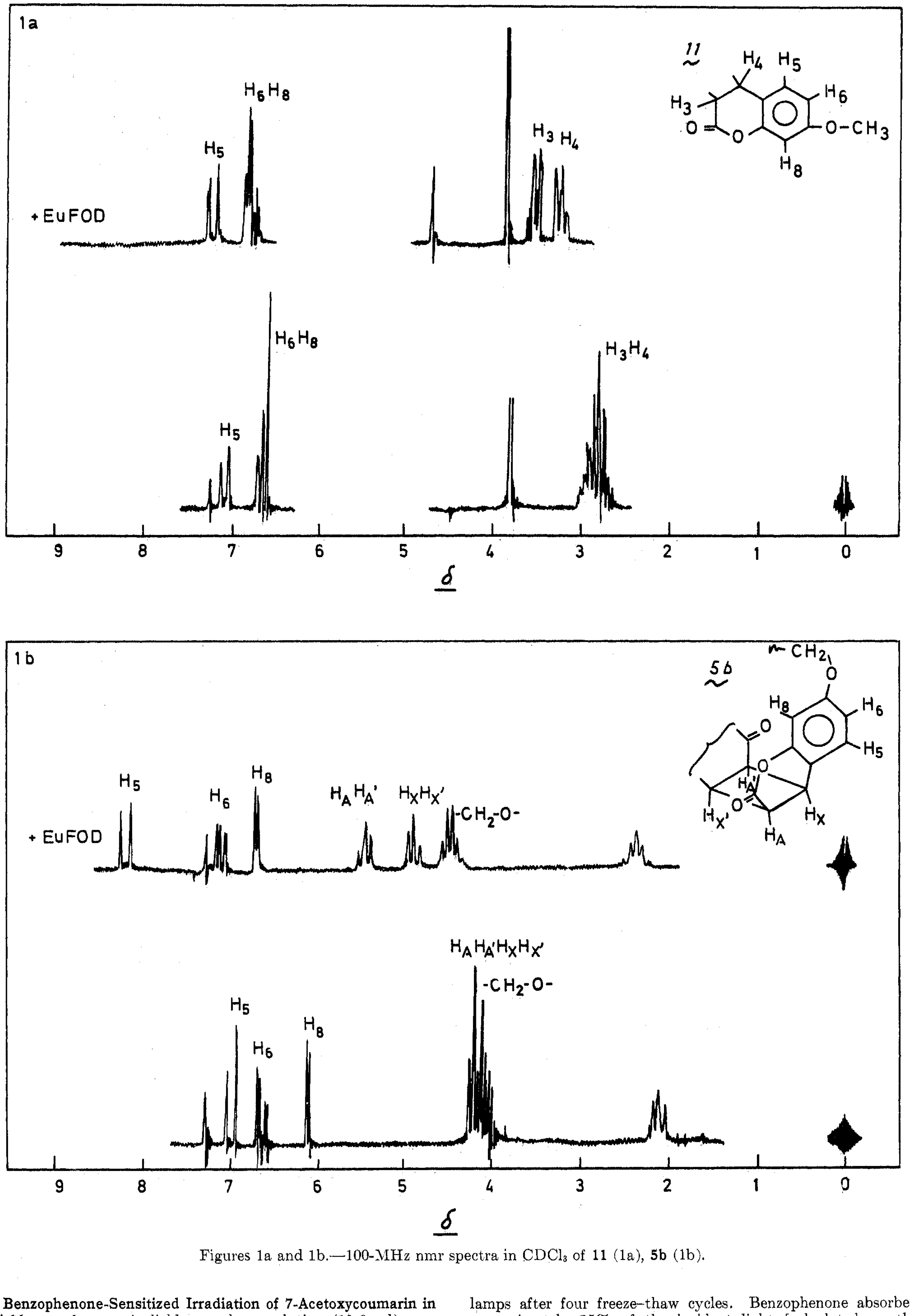
Synthesis of 3,4-Dihydro-7-methoxycoumarin (11).—11 was prepared by hydrogenation of 7-methoxycoumarin in benzene in the presence of palladium on charcoal. 7-Methoxycoumarin (2.85 g) was dissolved in 40 ml of benzene, containing 0.8 g of Pd/C catalyst. The apparatus was flushed with hydrogen prior to bubbling hydrogen through the suspension at about 50° for 4.5 hr. After the catalyst was filtered off, the solvent was evaporated. A colorless oil which solidified upon cooling was left. It was recrystallized from cyclohexane–carbon tetrachloride, yield 100%, mp 38.5–39.5°.

Direct Irradiation of 7-Methoxycoumarin in Dichloromethane.—A solution of 0.440 g of 7-methoxycoumarin in 50 ml of dichloromethane (5×10^{-2} *M*) was irradiated after flushing with dry argon for 1 hr, using RUL 3500-Å lamps in a Rayonet reactor and a sodium bromide–lead acetate[15] solution in the filter compartment of the reaction vessel. After a few hours, an intense violet coloration was observed which changed readily upon further irradiation to yellowish-brown. The solvent was evaporated off on a rotary evaporator under diminished pressure. The evaporation residue was dried extensively. The nmr spectrum of this crude photolysis mixture indicated that the reaction proceeded to an extend of 40%, the only detectable reaction product being one of the possible isomeric forms of the dimer of 7-methoxycoumarin. The mixture was purified by passage through a column with Florisil (60–100 mesh, Merck), using chloroform as eluent. The solvent of the slightly yellow eluents was evaporated off and the residue was taken up in ethanol. The photodimer precipitated while the starting material remained in solution. The physical data concerning this dimer are given in Table V.

Direct Irradiation of 7-Acetoxycoumarin in Dichloromethane.—Neither upon irradiation for 72 hr of a degassed solution of 0.156 g of 7-acetoxycoumarin in 7.5 ml of dichloromethane (1.02×10^{-1} *M*), nor upon irradiation for 184 hr of 9.1 ml of a solution containing 2.04 g of 12 (1.1 *M*), could dimer formation be observed. The only detectable change during the photolysis was the intense purple coloration of the solution.

---

(31) F. Tiemann and C. L. Reimer, *Chem. Ber.*, **12**, 993 (1879).



Figures 1a and 1b.—100-MHz nmr spectra in $CDCl_3$ of **11** (1a), **5b** (1b).

Benzophenone-Sensitized Irradiation of 7-Acetoxycoumarin in Dichloromethane.—A dichloromethane solution (19.6 ml) containing 0.621 g of 12 (1.55×10^{-1} *M*) and 0.112 g of benzophenone (3.1×10^{-2} *M*) was irradiated for 63 hr with RUL 3500-Å lamps after four freeze–thaw cycles. Benzophenone absorbed approximately 25% of the incident light [calculated on the basis of the concentrations and molar extinction coefficients at 350 nm of benzophenone (110 l. mol^{-1} cm^{-1}) and 7-acetoxy-

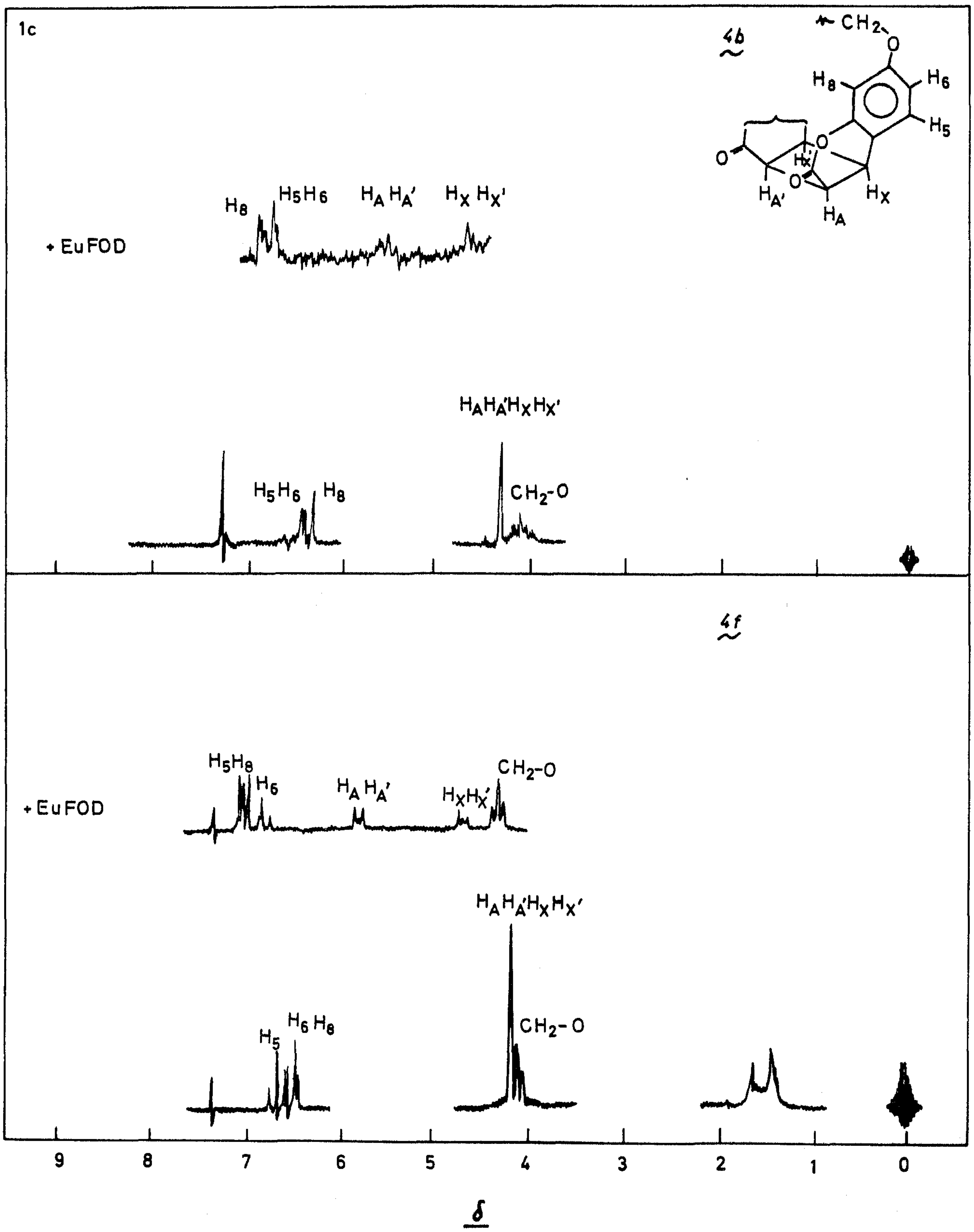


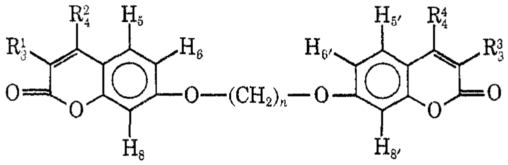
Figure 1c.—100-MHz nmr spectra in $CDCl_3$ of **4b** and **4f** (1c) prior and after addition of EuFOD.

coumarin (90 l. mol^{-1} cm^{-1}) in dichloromethane]. After reaction, the solvent was evaporated off and the residual mixture was triturated twice with ether. The ether solution contained only benzophenone, as was checked by tlc. The precipitate was dried extensively. The nmr spectrum in DMSO of this crude product showed only one signal in the cyclobutane region at δ 3.91. Apart from a weak spot due to residual starting compound, a tlc (silica gel) developed by chloroform–acetone (95:5) showed only one other spot at a higher R_f value. The crude product was taken up and recrystallized from carbon tetrachloride–chloroform (2:1). The physical data are given in Table VI.

Direct Irradiation of 7,7′-Polymethylenedioxycoumarins.—In general the two isomers in the case of shorter polymethylene chains ($n \leq 8$) were separated by taking up the evaporation residue of a photolyzed solution in dry benzene, out of which the

Table III

Physical Data of 7,7′-Polymethylenedioxycoumarins

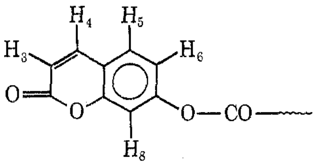


Compd	n	Reflux time, hr	Yield, %[a]	Recrystn solvent	Mp, °C[c]	Infrared spectrum, ν, cm⁻¹,[d] C=O[e,f]	Ultraviolet spectrum[g] λ_{max}, nm	Ultraviolet spectrum[g] ε, M^{-1} cm⁻¹	Nmr spectrum, δ, TMS[h,i] H_8	Nmr spectrum, δ, TMS[h,i] H_6H_8[j]	Nmr spectrum, δ, TMS[h,i] R_3	Nmr spectrum, δ, TMS[h,i] R_4	Mass spectrum, M·⁺, m/e
3a	2	21	33	HOAc	237–238	1730	323	30,540	7.60	7.05–6.85	6.24	7.95	350
3b[b]	3	12.5	67	PhH	184–185.5	1720	324	30,960	7.55	7.0–6.75	6.22	7.88	364
3c	4	12.5	54	$CHCl_3/CCl_4$	182–183.5	1715	324	31,680	7.54	7.0–6.7	6.17	7.83	378
									7.38[k]	7.0–6.7	6.24	7.65	
3d	5	13	72	EtOH/PhH	138–138.5	1718	324	31,640	7.55	7.0–6.7	6.21	7.90	392
3e	6	18	77	PhH	163–164	1717	324	32,060	7.52	7.0–6.7	6.20	7.86	406
3f	7	14.5	64	PhH	132.5–134	1727	324	31,860	7.56	7.0–6.7	6.23	7.92	420
3g	8	13.5	67.5	PhH	148.5–149.5	1722	324	31,840	7.55	7.0–6.7	6.22	7.90	434
3h	9	13.5	63	CCl_4/CH_3CN	99–101	1727	324	32,000	7.33[k]	6.95–6.65	6.18	7.60	448
3i	10	13.5	46	PhH	135–136	1724	324	31,420	7.53	7.0–6.7	6.20	7.87	462
3j	11	17	68	PhH/hexane	117–117.5	1718	324	31,480	7.35[k]	6.95–6.65	6.21	7.60	476
6c	4	15[n]	75	$PhCH_3$	171–172.5	1715	322	31,600	7.48	6.95–6.65	R_3^1 6.11[l]	R_4^2 7.75	392
									H_5, 7.42		R_3^3 6.01	R_4^4 2.33	
9d	5	34	84	CH_3CN	177–178	1742	322	31,400	7.59	7.0–6.6	6.09[m]	2.36	420

[a] Yield calculated on the basis of converted 7-hydroxycoumarin. [b] Found C, H, and O values were within 0.3% of calculated (actual results were supplied to Editor). [c] Uncorrected. [d] In KBr. [e] The C=O absorption appears as a complex structure which is centered at the given position. [f] The δ CH(cis) vibrations of **3a–j** absorb as a doublet between 1390 and 1415 cm⁻¹. [g] In CH_2Cl_2. [h] In DMSO-d_6. [i] R = H. [j] H_6 and H_8 are described as the AB part of an ABX system. [k] In $CDCl_3$. [l] $R_3^1 = R_4^2 = R_3^3 = H$; $R_4^4 = CH_3$. [m] $R_3^1 = R_3^3 = H$; $R_4^2 = R_4^4 = CH_3$. [n] Refers to the reaction between 1-(7-oxycoumarinyl)-4-bromobutane and 4-methyl-7-hydroxycoumarin. Yield based on converted 4-methyl-7-hydroxycoumarin.

Table IV

Physical Data of Polymethylenedicarboxylic Acid (7-Coumarinyl) Diesters



Compd[a]	n	Reflux time, hr	Yield, %[b]	Recrystn solvent	Mp °C[c]	Ultraviolet spectrum[d] λ_{max}, nm	Ultraviolet spectrum[d] ϵ_{max}, M^{-1} cm⁻¹	Nmr spectrum, δ, TMS[e] H_8	Nmr spectrum, δ, TMS[e] H_6H_8[f]	Nmr spectrum, δ, TMS[e] H_3	Nmr spectrum, δ, TMS[e] H_4	Nmr spectrum, δ, TMS[e] J_{34}	Mass spectrum, M·⁺ m/e
14c	4	8	86	CH_3CN/DMSO	222–223	277	20,700						
						283	20,760	7.70	7.24–7.0	6.38	7.97	9.5	434
						313	17,200						
14d	5	6	80	EtOH/$CHCl_3$	138–139	277	20,000						
						283	20,000	7.75	7.3–7.0	6.45	8.04	9.5	448
						313	17,000						
14e	6	5	82	CH_3CN	176–178	277	20,870						
						283	20,830	7.74	7.3–7.0	6.44	8.03	9.5	462
						313	17,500						
14f	7	6	80	CH_3CN/CCl_4	123–124	277	21,250						
						283	21,330	7.72	7.3–7.0	6.42	8.01	9.5	476
						313	18,100						

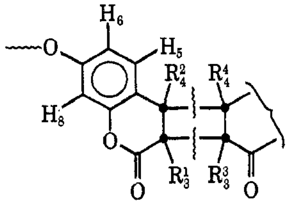
[a] In the infrared spectra, the phenyl ester carbonyl vibrations absorb at 1768 ± 2 cm⁻¹, the α,β-unsaturated lactone δ-lactone carbonyl at 1745 ± 1 and 1710 cm⁻¹, and the δ =CH (cis) vibrations absorb as a doublet between 1380 and 1405 cm⁻¹. [b] Yield based on converted 7-hydroxycoumarin. [c] Uncorrected. [d] In CH_2Cl_2. [e] In DMSO-d_6. [f] H_6 and H_8 are described as the AB part of an ABX system.

head-to-head isomer precipitates upon cooling. The irradiation products of the dioxycoumarins with a longer polymethylene chain were best separated by column chromatography.

As a typical example of the former class, a solution of 0.500 g of 7,7′-tetramethylenedioxycoumarin in 132 ml of dichloromethane (10^{-2} M) was degassed three times, sealed off *in vacuo*, and irradiated for 39 hr through a 1-cm filter solution.[15] After a few hours of irradiation, a violet color was observed which disappeared upon prolonged illumination. After irradiation the solvent was evaporated and the ir spectrum showed that the reaction was complete. A nmr spectrum of this crude mixture allowed the calculation of the percentages of the two isomers, based on the absorptions of the phenyl protons: 42% head-to-head and 57% head-to-tail isomer. Upon fractionated crystallization out of dry benzene, 0.173 g (34.6%) head-to-head isomer was separated. The filtrate was evaporated to dryness. A nmr spectrum of this residue showed the presence of an additional amount of about 7% of the head-to-head isomer. This mixture (0.291 g) in chloroform was brought on a column of 24-mm diameter filled with Florisil (60–100 mesh) to a height of about 10 cm.

TABLE V

PHYSICAL DATA OF THE PHOTOISOMERS OF THE DIOXYCOUMARINS



Compd	n	Recrystn solvent	Mp, °C^a	Infrared spectrum, ν, cm^{-1},^{c} C=O	Nmr spectrum, δ, TMS^d				Mass spectrum, M·$^+$, m/e
					H$_5$	H$_6$	H$_8$	R^f	
2		EtOH	205.5–207	1750	6.98	6.69	6.30	4.21	352
					7.04^e	6.64	6.18	4.20	
4a	2	CCl$_4$/CH$_2$Cl$_2$	216–218	1764		6.5–6.2		4.28	350
4b	3	PhH	241–242^b	1760		6.8–6.3		4.35	364
5b	3	PhCH$_3$	271–273^b	1752	6.87	6.60	6.18	4.08	364
					6.97^e	6.60	6.01	4.03	
4c	4	PhH	252–254^b	1765		6.8–6.3		4.30	378
5c	4	PhCH$_3$	279–282^b	1750	6.88	6.59	6.13	4.08	378
4d	5	PhH	236.5–238.5^b	1760		6.8–6.3		4.25	392
5d	5	PhCH$_3$	291.5–294^b	1748	6.88	6.62	6.15	4.09	392
4e	6	PhH	218	1765		6.8–6.3		4.18	406
5e	6	PhCH$_3$	b	1746	6.84	6.62	6.09	4.09	406
4f	7	PhCH$_3$/hexane	212–214	1768		6.7–6.3		4.13	420
						6.8–6.3		4.12	
5f	7	PhCH$_3$	286–287.5^b	1754	6.84^e	6.55	6.02	4.09	420
4g	8	CCl$_4$/CHCl$_3$	216–220	1764		6.9–6.2		4.13	434
5g	8	PhCH$_3$/hexane	246–249^b	1752	7.00^e	6.60	6.06	4.13	434
4h	9	CCl$_4$/CH$_3$CN	184.5–186	1767		6.7–6.2^e		4.06	448^l
5h	9	CCl$_4$	234.5–236^b	1753	6.98^e	6.59	6.06	4.12	448^l
5i^k	10	PhCH$_3$		1750	7.00^e	6.62	6.11	4.17	462
5j^k	11	Et$_2$O/hexane		1752	7.01^e	6.62	6.11	4.16	476
7c	4	PhH	233–236	1760	6.73	6.40	6.27	g	392
8c	4	PhCH$_3$	215.5–217.5^b	1757	7.09^e	6.69	6.02	h	392
					H$_5$, 7.02	H$_6$, 6.66	H$_7$, 6.00		
10d	5	CCl$_4$/hexane	212–215	1757	6.88	6.57	6.04	i	420
					7.07^e	6.63	6.05	j	

[a] Uncorrected; some of these compounds decompose to the open form upon heating. [b] These compounds sublime. [c] In KBr. [d] In DMSO-d_6. [e] In CDCl$_3$. [f] The absorption is centered at the position cited. [g] Absorptions of R_3^1 = H at δ 4.31, R_4^2 = H at 3.76, R_3^3 = H at 3.92, and R_4^4 = CH$_3$ at 1.76. [h] Absorptions of R_3^1 (or R_3^3) = H at δ 3.72, R_4^2 = H between 3.8 and 4.5 with –OCH$_2$–, R_3^3 (or R_3^1) = H at 3.69, and R_4^4 = CH$_3$ at 1.66. [i] Absorption of R_3^1 = R_3^3 = H at δ 3.50, R_4^2 = R_4^4 = CH$_3$ at 1.52. [j] Absorption of R_3^1 = R_3^3 = H at δ 3.37, R_4^2 = R_4^4 = CH$_3$ at 1.63. [k] **4i**, **5i**, **4j**, and **5j** were not isolated in pure form. [l] Tonometry (Mechrolab) in CHCl$_3$ indicated for **4h** a molecular weight of 460 and for **5h** 464.

Elution with 1 l. of chloroform yielded, after the evaporation of the solvent, 0.180 g of crude head-to-tail isomer. The column was freed of organic material by eluting with glacial acetic acid; the fraction contained a small amount of head-to-head isomer and some oligomeric species. The acid was evaporated and the residual product was extensively washed with water. The isomers were purified by recrystallization from the appropriate solvents. The photoisomers of the dioxycoumarins with a longer polymethylene chain could not be separated easily by fractionated crystallization and were isolated by column chromatography. As a typical example for this class, a degassed solution of 0.492 g of **3h** in 110 ml of dichloromethane (10^{-2} M) was irradiated for 115.5 hr. The head-to-tail isomer was isolated by elution of the crude photolysis mixture on a column of 24 mm diameter filled with Florisil (60–100 mesh) together with 11% of starting material (0.230 g after recrystallization from carbon tetrachloride). Subsequently acetic acid was used as eluent; the solvent was evaporated off and the residual mixture was washed extensively with water. The brown-colored residue (0.130 g) contained the head-to-head isomer and some oligomeric species, as was shown by a vapor pressure osmometric measurement of the molecular weight 627 (molecular weight of the starting material is 448). The oligomers were only slightly soluble in acetone. The acetone-soluble part was transferred into water. Upon evaporation of the acetone on a rotary evaporator, a pale yellow precipitate was formed, being the head-to-head regioisomer (0.095 g). A white crystalline precipitate was separated upon recrystallization from carbon tetrachloride–acetonitrile (15:1). Knowing the nmr absorptions of all the products present in the crude photolysis mixture, its composition was calculated to be 52% of **5h**, 26% of **4h**, 11% of **3h**, and 11% of oligomeric species.

The irradiation of the monomethyl-substituted dioxycoumarin **6c**, the analysis, and the separation of the photolysis mixture proceeded in the same way as in the latter class.

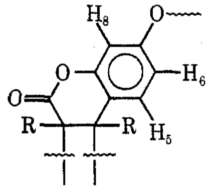
After irradiation of 7,7′-pentamethylenedi(4-methyl)oxycoumarin (**9d**), a nmr spectrum of the photolysis mixture showed that the syn head-to-tail isomer was formed predominantly (95%); 3% syn head-to-head isomer was isolated by column chromatography on Florisil with acetic acid as eluent.

The polymethylenedioxycoumarins **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, and **3j** were irradiated as 300, 132, 16.6, 100, 100, 150, 110, 100, and 100 ml, respectively, of 10^{-2} M solutions in tubes with a 24-mm diameter through a 1-cm filter solution layer. The irradiation times were 72, 39, 15.5, 29.75, 52.75, 91, 115.5, 160, and 142 hr, respectively. **3a** was irradiated as a 2×10^{-3} M solution for 216 hr. Irradiation of more concentrated solutions of **3a** resulted in the formation of insoluble polymeric material. **6c** and **9d** were irradiated as 86 and 100 ml of 10^{-2} M solutions for 44 and 65 hr, respectively. The physical data concerning the photoisomers of **3**, **6**, and **9** are given in Table V.

Benzophenone-Sensitized Irradiation of 7,7′-Polymethylenedioxycoumarins.—A mixture of 5×10^{-2} M 7,7′-decamethylenedioxycoumarin and 2.98 M benzophenone (50% of the light absorbed by the sensitizer) in dichloromethane was degassed and irradiated through a 1-cm filter solution[14] for 65 hr. The solvent was evaporated on a rotary evaporator and the residue

TABLE VI

PHYSICAL DATA OF THE PHOTOISOMERS OF THE POLYMETHYLENEDICARBOXYLIC ACID (7-COUMARINYL) DIESTERS



Compd	n	Recrystn solvent	Mp, °C[a]	Infrared spectrum, ν, cm^{-1} [b]	Nmr spectrum, δ, TMS[c] $H_5H_6H_8$[d]	Nmr spectrum, δ, TMS[c] R[e,f]	Mass spectrum, M·+, m/e
13		$CCl_4/CHCl_3$	228–231	1762	7.1–6.85	3.91	408
15c	4	$PhCH_3/CH_3CN$	215–217.5	1767	7.1–6.6	4.31	434
15d	5	PhH/CH_3CN	229–233	1762	6.8–6.3	4.24	448
					6.8–6.5[g]	4.27	
16d	5	$CCl_4/CHCl_3$	237–241	1759	H_5H_6 6.96,[f] H_8 6.06[f]	4.20	448
				1750	H_5 7.10, H_8 6.28[g] H_6 6.94	4.20	
15e	6	$PhCH_3$	229.5–232	1767	7.0–6.5	4.25	462
15f	7	$PhCH_3$	216.5–218	1787 1756	6.9–6.5	4.22	476

[a] Uncorrected. [b] In KBr. [c] In DMSO-d_6. [d] Protons H_5, H_6, and H_8 are the constituents of an ABC system. [e] R = H. [f] The absorption is centered at the position cited. [g] In $CDCl_3$.

was triturated three times with 20 ml of diethyl ether. The residual solid was dissolved in dichloromethane and precipitated in n-hexane. This procedure was repeated three times. The precipitate was dried under vacuum at room temperature, yield 80%.

Direct Irradiation of the Polymethylenedicarboxylic Acid (7-Coumarinyl) Diester.—All the solutions were irradiated through a 1-cm filter solution layer.[14] Tetramethylenedicarboxylic acid (7-coumarinyl) diester (**14c**) was irradiated in dried and distilled dimethyl sulfoxide, owing to the low solubility in dichloromethane. A solution of 0.327 g in 150 ml of DMSO (5×10^{-3} M) was flushed with dry argon and irradiated for 187 hr. After irradiation, the solution was slightly yellow. The dimethyl sulfoxide was distilled off under reduced pressure. The residual mixture was precipitated into water. The precipitate was filtered, washed with water, and dried.

An nmr spectrum of this mixture, 0.251 g, indicated the presence of 7% starting material. This mixture (0.194 g) was recrystallized from toluene–acetonitrile (4:1); 0.128 g of the head-to-head isomer precipitated upon cooling. The second isomer has not yet been separated. Pentamethylenedicarboxylic acid (7-coumarinyl) diester (**14d**) was irradiated for 119 hr as a 10^{-2} M solution (0.672 g in 150 ml of dichloromethane) which was flushed with dry argon for 1 hr. The ratio of syn head-to-head to syn head-to-tail isomer was calculated from the integration of the cyclobutane proton region in the nmr spectrum. The two isomers were separated by crystallizations from benzene–acetonitrile (50:1) out of which **15d** precipitated as white needles upon cooling (0.490 g). The filtrate was evaporated off and brought on a Florisil column, which was eluted with chloroform. The first fractions contained predominantly the head-to-tail isomer **16d**, which was further purified by recrystallization from carbon tetrachloride–chloroform (30:1) (0.104 g after recrystallization).

14e and **14f** were irradiated as 10^{-2} M degassed solutions in dichloromethane for 69 and 88 hr, respectively. The composition of the reaction mixture was determined by nmr spectroscopy. The head-to-head isomers **15e** and **15f** were separated from the starting compound by recrystallizations from 50:1 toluene–acetonitrile and from benzene, respectively, and further purified by repeated crystallizations from toluene. The physical data of the photoisomers of **14** are given in Table VI.

Photocleavage of the Cycloadducts.—The reversibility of the photocycloaddition was checked by uv spectroscopy. A 5×10^{-5} M solution (10 ml) of **4b** or **5b** was irradiated in a Pyrex tube which was fitted with a uv cell. The solution was flushed with dry argon for 0.5 hr and irradiated with RUL 3000-Å lamps; 0.109 g of **5b** was irradiated in 100 ml of dichloromethane (3×10^{-3} M) for 139.5 hr with the same lamps. The solvent was evaporated off and the composition of the reaction mixture was calculated from the nmr spectrum.

Registry No.—**1**, 531-59-9; **2a**, 37786-10-0; **2b**, 37818-63-6; **3a**, 37786-11-1; **3b**, 34333-09-0; **3c**, 34333-10-3; **3d**, 34333-11-4; **3e**, 37818-64-7; **3f**, 37786-15-5; **3g**, 37786-16-6; **3h**, 37818-65-8; **3i**, 37818-66-9; **3j**, 37786-17-7; **4a**, 37786-18-8; **4b**, 37786-19-9; **4c**, 37782-96-0; **4d**, 37782-97-1; **4e**, 37782-98-2; **4f**, 37782-99-3; **4g**, 37783-00-9; **4h**, 37783-01-0; **5b**, 37783-02-1; **5c**, 37783-03-2; **5d**, 37783-04-3; **5e**, 37783-05-4; **5f**, 37818-67-0; **5g**, 37783-06-5; **5h**, 37783-07-6; **5i**, 37783-08-7; **5j**, 37783-09-8; **6c**, 37783-13-4; **7c**, 37783-10-1; **8c**, 37783-11-2; **9d**, 23863-89-0; **10d**, 37783-12-3; **11**, 20921-02-2; **12**, 10387-49-2; **13**, 37783-17-8; **14c**, 37783-18-9; **14d**, 37783-19-0; **14e**, 37783-20-3; **14f**, 37783-21-4; **15c**, 37783-22-5; **15d**, 37783-23-6; **15e**, 37783-24-7; **15f**, 37783-25-8; **16d**, 37783-26-9; 7-hydroxycoumarin, 93-35-6; 1,8-dibromooctane, 4549-32-0; 1,11-dibromoundecane, 16696-65-4; 1,4-dibromobutane, 110-52-1; 1,5-dibromopentane, 111-24-0; 1,6-dibromohexane, 629-03-8; 1,7-dibromoheptane, 4549-31-9; 1,9-dibromononane, 4549-33-1; 1,10-dibromodecane, 4101-68-2; α-(7-oxycoumarinyl)-ω-bromobutane, 37783-33-8; 7-hydroxy-4-methylcoumarin, 90-33-5; 1,4-butanedicarboxylic acid dichloride, 111-50-2; 1,5-pentanedicarboxylic acid dichloride, 142-79-0; 1,6-hexanedicarboxylic acid dichloride, 10027-07-3; 1,7-heplanedicarboxylic acid dichloride, 123-98-8.

Acknowledgment.—The authors are indebted to the Belgisch Nationaal Fonds voor Wetenschappelijk Onderzoek for financial support and for a fellowship to one of us (L. L.). They thank the Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw for a fellowship (E. S.). They thank Dr. S. Toppet for discussion of the nmr data and Mr. M. Stroobants for valuable technical assistance.