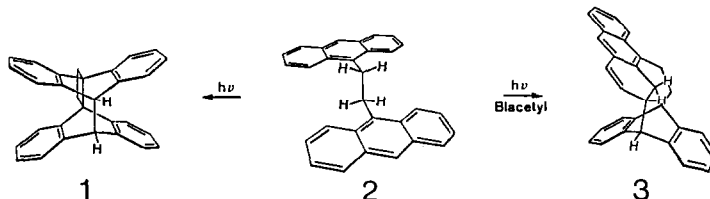


PHOTOCHEMISTRY OF THE ANTHRACENE CHROMOPHORE:
TRIPLET-SENSITIZED ISOMERIZATIONS OF DIANTHRYLETHANES

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Abstract: The photochemical isomerization of 1,2-di(9-anthryl)ethane can be sensitized by biacetyl to proceed by intramolecular Diels-Alder reaction. The molecular geometry of dianthrylethanes affects their triplet state reactivity.

The photochemical isomerization of dianthrylethane 2 by [4+4] cycloaddition to give 1 has been studied extensively, and the reaction has been established to involve the excited singlet state.¹ Intersystem crossing to the excited triplet state may be partly responsible for the radiationless decay of photoexcited 2, but its contribution to the [4+4] cycloaddition has been found to be negligible.^{1a} Previous attempts to bring about the photoisomerization of dianthrylethane by acetophenone sensitization have not been successful.²



We have now found that the photochemical isomerization of dianthrylethanes can be sensitized by biacetyl, and that the products of triplet-sensitized reactions, significantly, may differ characteristically from those of the singlet state reactions. Thus, selective photoexcitation of biacetyl (2.4 g) in a solution of dianthrylethane (0.1 g) in benzene (140 mL; immersion well apparatus; 125 W high-pressure mercury lamp; $\lambda_{exc} > 420$ nm through 0.5 cm of filter solution consisting of 380 mg of potassium chromate in 200 mL of water; 15 °C; argon atmosphere; irradiation time 5 h) does not produce the previously known [4+4] cycloadduct 1 but results in an intramolecular Diels-Alder reaction to give 3 with a quantum yield of 0.1 (cf. Table 1).³ The biacetyl-sensitized isomerization of 2 proceeds cleanly, as is evident from the exhibition of an isosbestic point in the set of reaction spectra (see Fig. 1a). The formation of 3 is remarkable insofar as the isomerization of linked anthracenes by intra-

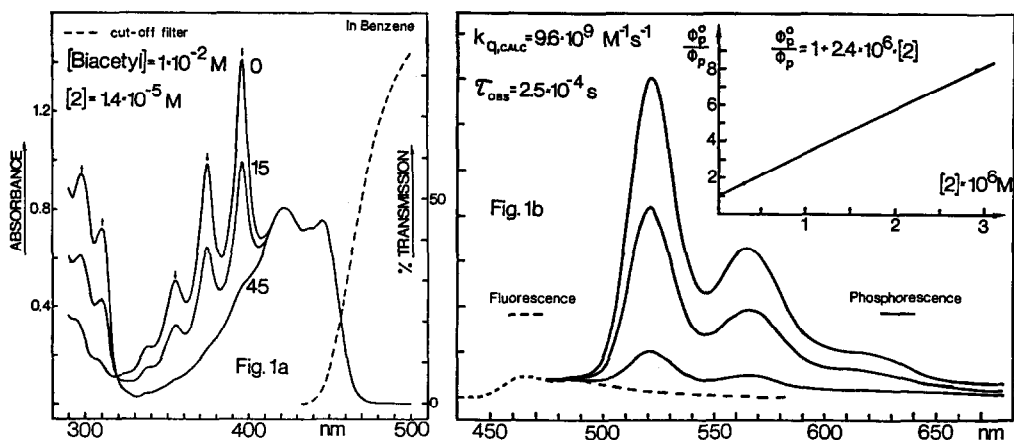
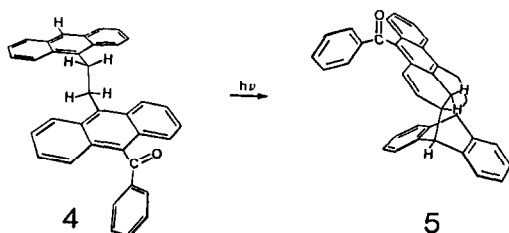


Fig. 1. a: Reaction spectra of biacetyl-sensitized isomerization of 2 after 15 and 45 sec. b: Biacetyl phosphorescence quenching by 2. Insert: Stern-Volmer plot of quenching data. The calculated quenching constant is based on the quenching constant found for anthracene (cf. Bäckström, H.L.J.; Sandros, K. *Acta Chem. Scand.* 1958, 12, 823).

molecular Diels-Alder reaction has rarely been observed previously,⁴⁻⁷ and sensitized isomerizations of dianthrylethanes appear to be unprecedented.

As the phosphorescence of biacetyl is quenched by dianthrylethane 2 in a nearly diffusion controlled process (cf. Fig. 1b), the sensitized photochemical isomerization by Diels-Alder reaction most likely is explicable in terms of triplet energy transfer. Moreover, photochemical isomerizations of dianthrylethanes by intramolecular [4+2] cycloaddition appear to be characteristic of the excited triplet state. For example, benzoyl-dianthrylethane 4, whose low fluorescence quantum yield suggests enhanced intersystem crossing to the triplet state due to benzoyl substitution, isomerizes in benzene solution exclusively by intramolecular Diels-Alder reaction to give 5 both upon direct excitation, and by biacetyl sensitization. Likewise, biacetyl sensitized isomerization of dianthrylethane⁸ 6 in benzene gives mainly (97%) the two conceivable Diels-Alder products 7 and 8 (ratio 75:22). Only 3% of the isomerization proceeds by [4+4] cycloaddition to give 9. Direct excitation of dianthrylethane in degassed benzene ($\lambda_{exc} > 400$ nm) gives 7, 8, and the [4+4] cycloolmer 9 in a ratio of 6:2:2. Irradiation of 6 in air-saturated solution so as to quench excited triplet state species does not give any of isomers 7 and 8, but yields 9 (ϕ 0.036) as only cycloaddition product.



Note: Depending on the rate of heating, the photoproducts undergo cycloreversion around 200-220 °C.

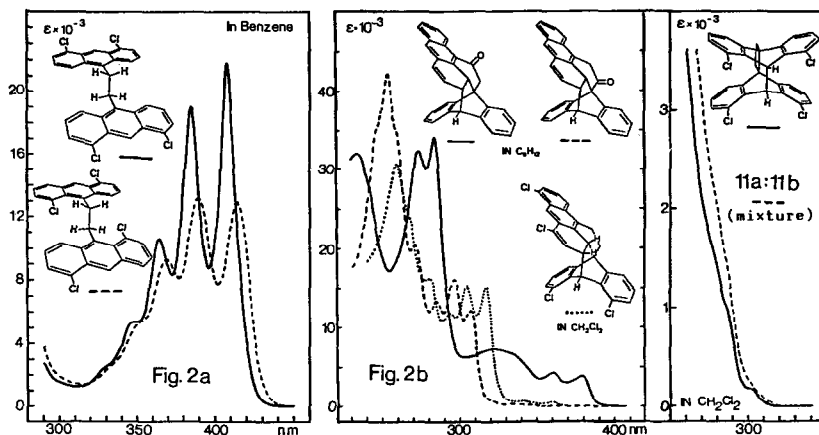


Fig. 2. Electron spectra of 10, 13, and cyclomers 7, 8, 11, 12, and 14.

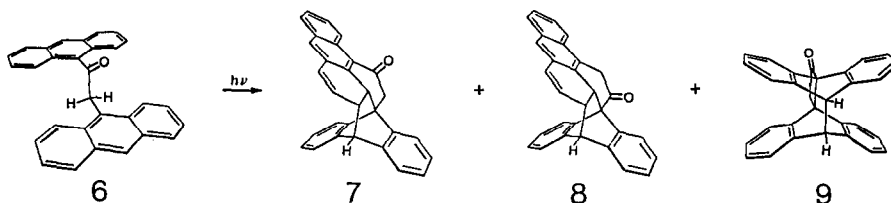
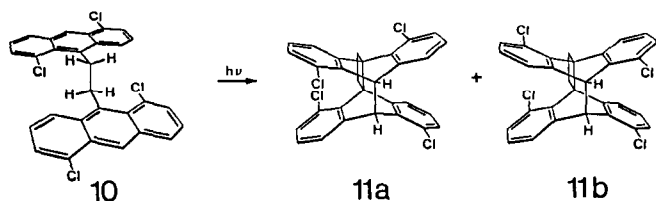


Table 1. Deactivation of Electronically Excited Dianthrylethanes in Benzene by Fluorescence (Φ_F) and Cycloaddition (Φ_R)

Compound:	2	4	6	10	13
Φ_F :	0.20	0.002	<0.0001	0.013	0.07
Addition:	4+4	4+2	4+2 (80%); 4+4 (20%)	4+4	4+4
Φ_R :	0.26	0.005	0.11(*)	0.39	0.16
Sensitized:	4+2	4+2	4+2 (97%); 4+4 (3%)	4+4	4+2
Φ_R :	0.1	0.007	(*)	0.43	0.02

(*) Concentration-dependent quantum yield

Interestingly, the ground state molecular geometry of dianthrylethanes appears to govern the course of their triplet state reaction. This feature is borne out in the excited state properties of chloro-dianthrylethanes whose molecular geometry is affected by their substitution pattern. For example, the ground state geometry of 1,1',5,5'-tetrachlorodianthrylethane (10) is characterized by partially overlapping aromatic moieties, as is evident from its broadened UV-absorption spectrum (see Fig. 2a). Upon direct photoexcitation, and by biacetyl sensitization,⁹ 10 undergoes [4+4] cycloaddition with fairly high quantum yield (cf. Table 1) to give 11. By contrast, the molecular geo-



Product Ratio 11a : 11b

direct exc: 68 : 32

sensitized: 86 : 14

metry of the isomeric 4,4',5,5'-tetrachlorodianthrylethane (13)¹⁰ most likely resembles that of the parent dianthrylethane 2, and should be characterized by anti-conformation, as we conclude from their similar absorption spectra. The excited state properties of 13 indeed parallel those of 2. Direct photoexcitation of 13 in benzene gives the [4+4] cycloaddition product 12 (ϕ 0.16), but biacetyl sensitization of 13 leads to exclusive formation of the intramolecular Diels-Alder adduct 14 (ϕ 0.02). ¹H-NMR spectral data of the cycloaddition products are summarized in Table 2. The Diels-Alder adducts also are easily distinguishable from their isomeric [4+4] cycloadducts by their characteristic 1,2-dihydroanthracene UV spectra (see Fig. 2b; cf. ref. 5, 6, and 7a).

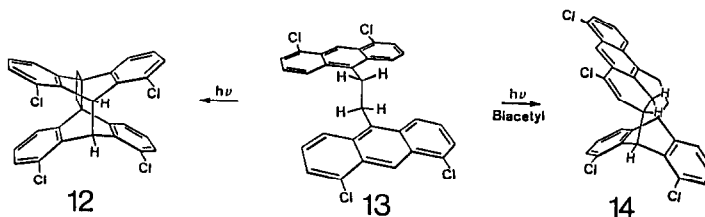


Table 2. 270 MHz ¹H-NMR Spectral Data of Isomeric Cycloadducts 11, 12, and 14 in Deuterated Chloroform (δ , ppm downfield from TMS)

11a:	7.17-6.70, m, 12 H;	5.06, s, 2 H;	3.76, m, 2 H;	3.45, m, 2 H
11b:	7.10-6.75, m, 12 H;	5.15, s, 2 H;	4.19, m, 2 H;	2.94, m, 2 H
12:	7.03-6.84, m, 12 H;	5.98, s, 2 H;	2.99, s, 4 H	
14:	8.18, s, 1 H;	7.92-6.69, m, 9 H;	6.31, d, J=4.4 Hz, 1 H;	5.45, d, J=1.7 Hz, 1 H;
			3.84, m, 1 H;	3.42, m, 1 H;
			3.38, d, J=11.5 Hz, 1 H;	3.27, ddd, 11.5, 4.4, 1.7 Hz, 1 H;
			3.09, m, 2 H	

In conclusion, triplet-sensitized isomerizations of dianthrylethanes proceed by [4+2] cycloaddition, unless their low-energy ground conformation is such as to be characterized by partially overlapping π -systems. The quantum yields of triplet-sensitized geometrically favored [4+4] cycloadditions are remarkably high, and they exceed those of the corresponding excited singlet state reactions.¹¹

References and Notes

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- (3) Cf. Becker, H.-D.; Andersson, K. *Tetrahedron Symposium*, **1985**, in press.
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- (8) The synthesis and photochemistry of 6 will be published in detail.
- (9) Oxygen quenching experiments suggest the formation of 11 by direct excitation of 10 to involve mainly (>90%) the excited singlet state.
- (10) Compound 13, mp 343-344 °C, was prepared by thermolysis of the corresponding lepidopterene (Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549. see also ref. 6).
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