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HEAD-TO-HEAD MIXED PHOTODIMERS BETWEEN MONOMESOSUBSTITUTED ANTHRACENES ; CONTROL OF PHOTOCYCLOADDITION SELECTIVITY BY CHARGE-TRANSFER AND DIPOLE-DIPOLE INTERACTIONS.

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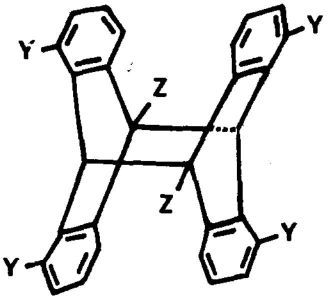
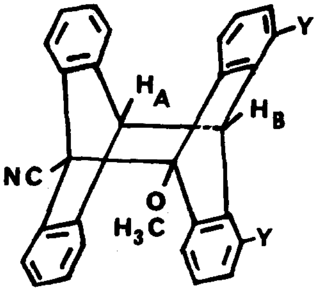
Summary : Although monomesosubstitued anthracenes are known to yield head-to-tail photodimers, the irradiation of 1:1 mixture of 9-methoxy (donor) and 9-cyano (acceptor) anthracenes leads, in great majority, to the head-to-head(regiospecific) mixed photodimer.

It is well established that a number of monomesosubstituted anthracenes give head-to-tail (h-t) photodimers 1 under u.v. light[1]. The fact that no head-to-head (h-h) photodimer has been isolated so far may be ascribed to steric and/or electrostatic repulsion between the substituents ; in contrast, dipole-dipole interaction should favor h-t orientation. We wish to report here on the control of selectivity through electrostatic, steric and charge-transfer interactions, in order to design the first h-h mixed photodimer.

It was thus required to cross a monomer substituted by an electron-donating group with a monomer substituted by an electron- withdrawing group ; good charge-transfer was indeed expected to help produce the mixed dimer with respect to the two possible "true" photodimers, but complete electron-transfer was to be avoided as the radical-ions formed would not undergo photodimerization[2] ; finally the substituents should not be too bulky because steric hindrance would prevent the generation of the h-h dimer[3].

All these requirements were fulfilled with a 1:1 mixture of 9-methoxy and 9-cyano anthracenes ; irradiated in ether, this mixture (at $\approx$ 30°C, total conc.$\approx 2\text{x}10^{-2}$M) gave smoothly the h-h mixed dimer 2a in majority (table 1) with no trace of the h-t mixed dimer. Evidence for the h-h structure of 2a rests essentially on the n,m.r. spectrum (Brücker WH 90, ref. TMS, solvent $CDCl_3$, 1000 scans ; δ_A : 4.60 ppm (1 H meso) δ_B : 4.52 ppm (1 H meso) J_{AB} = 10.5 Hz).





1 a Y = H Z = OCH

b Y = H Z = CN

c Y = Cl Z = OCH_3

2 a Y = H

b Y = Cl

This new mixed dimer is not thermally stable at room temperature and its rapid decomposition into the starting monomers can be monitored by n.m.r. in $CDCl_3$. Irradiation in a polar solvent such as acetonitrile, able to stabilise efficiently radical-ions, dramatically decreases the ratio of mixed/true dimers (table 1) ; this result is in agreement with other reports on exciplexes[2,4].

TABLE 1

Solvent	% Conversion	% Relative yield			Ratio mixed/true
		1a	1b	2a	
Ether	96	3	7	90	9/1
Acétonitrile	82	28	50	22	1/4

Irradiation of a 1 : 1 mixture of 9-methoxy and 9-cyano anthracenes through Pyrex with a high pressure mercury lamp (30 min. exposure).

In addition, the very efficient formation of 2a (table 2), in ether, at the expense of 1a and 1b might suggest the existence of a ground-state complex between 9-methoxy and 9-cyano anthracenes but no deviations from Beer's law was found by u.v. spectroscopy over a large concentration range (10^{-4} to 10^{-1} M in ether).

Table 2

Compound	Solvent (outgassed)	ϕ_D	ϕ°_D	Ref
A	benzene	0.07	0.34	6
	toluene	0.06	0.16	7
9-MeO-A	benzene	0.10	-	6
	toluene	0.06	0.16	7
9-CN-A	benzene	0.09	0.24	6
9-CNA+9-MeOA	benzene	0.29	0.70	

A = Anthracene. Quantum yields of photodimerization (ϕ_D) at 10^{-2} M, and extrapolated at infinite conc, (ϕ°_D) of several compounds for comparison (λ = 366 nm).

In view of the regiospecificity of the reaction, and by analogy with recent results in the phenanthrene series[5], we postulate the intermediacy of a h-h exciplex. However no exciplex fluorescence could be detected in our conditions*, probably because the dimerization is too fast[6]. In order to allow exciplex fluorescence to compete, we expected the rate of dimerization to be slowed down by increasing the substituent bulk[5]. But mixtures of 9-CNA with 9-isopropoxy or 9-trimethylsiloxy anthracenes in benzene did not exhibit exciplex fluorescence* ; instead, irradiation of these mixtures resulted in white precipitates containing the thermally unstable white dimers.

The failure to get a mixed photodimer between 9, 10-dimethoxyanthracene and 9, 10-dicyanoanthracene was not unexpected because of the high electron affinity[8] of the latter derivative, which may lead to the production of radical-ions. In contrast, irradiation of 9-methoxy-10 cyanoanthracene in ether readily gave an unstable photodimer which was isolated and assigned the h-t structure by analogy with the present results (MeO and CN must be h-h).

A slight modification of the conditions required to obtain a mixed h-h photodimer (for instance the donating power of one member of the mixture) was expected to modify the ratio of mixed/true dimers ; thus, 1, 8-dichloro-10 methoxyanthracene, irradiated with an equimolecular amount of 9-cyanoanthracene in ether (same experimental conditions as in table 1) gives, after 80 % conversion, **2b** : 62 % (n.m.r., ref TMS, solvent $CDCl_3$, δ_A : 4,58 ppm ; δ_B = 5,71 ppm ; J_{AB} = 11 Hz), **1b** : 31 % and **1c** 7 %. Indeed, the presence of the two chlorine atoms decreases the charge-transfer.

In conclusion, the factors conditioning stabilization and stereochemistry of the intermediates in the photodimerization of polynuclear aromatic hydrocarbons now seem to be qualitatively well understood.

* Hitachi Perkin-Elmer MPF 3-Photomultiplier R 446, uncorrected spectra.

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