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THE FORMATION OF PHOTODIMERS FROM DIMETHYL NAPHTHALENE-1,8-DICARBOXYLATE AND METHYL NAPHTHALENE-2-CARBOXYLATE

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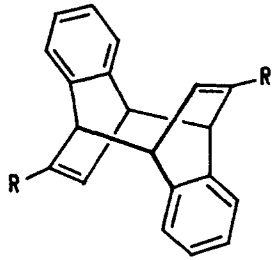
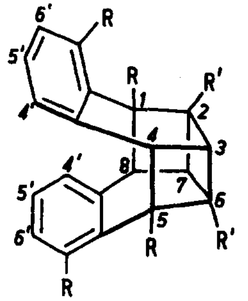
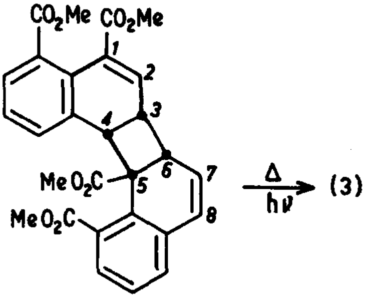
Like other light-induced processes the photodimerisation of aromatic compounds depends on the formation of 1:1-complexes between excited and unexcited molecules of the monomer, and it is generally accepted that the structure of a photodimer reflects the preferred orientation of the components in the excimer.[1] Interest in the geometry of excimers and exciplexes derived from substituted naphthalenes has prompted us to examine the structures of photodimers of naphthalene derivatives. It is already known that several 2-alkoxynaphthalenes form photodimers[2,3,4] and for the 2-methoxynaphthalene dimer the structure (1) has been confirmed by X-ray structure analysis.[5] The analogous structure (2), or the corresponding <u>cis</u> 1,4-1',4'-bridged structure, have recently been proposed for the photodimer of 2-cyanonaphthalene.[6] We now report that dimethyl naphthalene-1,8-dicarboxylate (3) and methyl naphthalene-2-carboxylate (4) form photodimers for which we propose on spectral and chemical grounds the structures (5) and (6), respectively.



(1): R = OMe
(2): R = CN



(5): R= COOMe; R'= H
(6): R=H; R'= COOMe
(8): R=H; R'= CN



(7)

A solution of (3)(6.8g) in benzene-cyclohexane (2:1; 180ml) was degassed at its boiling point and irradiated in a pyrex reactor[7] with a Philips HPK lamp (125W) for four days. The mixture was separated on silica gel using 40-45% chloroform in benzene. The photodimer (5)(0.63g) separated from benzene-ethanol in colourless rods, m.p. 167-169°.[8] The dimeric nature of this compound is established by its mass spectrum in which the molecular ion peak occurs at m/e 488 (2% relative abundance). Fragmentation to (3) predominates to give a peak at m/e 244(94%); this ion then loses MeO. to give the base peak at m/e 213. The ultraviolet spectrum [λ_{max}^{EtOH} at 286 nm(ε 4,500; virtually no absorption above 325 nm] is consistent with the presence of a 2,3-dialkylbenzoate chromophore. This is confirmed by the p.m.r. spectrum:[9] m, 2.8-3.8 (4H); s, 3.67 (6H; two equivalent MeO); s, 3.78 (6H; two equivalent MeO); d*, 5.18 (2H: J 8 Hz); t, 7.02 (2H; J 8 Hz; J 8 Hz; H-5'); dd*, 7.30(2H; J 2 Hz; J 8 Hz; H-4'); dd, 7.43 (2H; J 8 Hz; H-6'). Examination of the changes that occurred in the spectrum of the non-aromatic protons on the addition of tris(dipivalomethanato) europium [$Eu(dpm)_3$] gave the following chemical shifts, which are extrapolated to zero concentration of Eu $(dpm)_3$ [numbering based on (5)]: H-2 and H-6 at 3.03 (48%), H-3 and H-7, 3.40(12%), H-4 and H-8, 5.18(100%), two ester groups at 3.67(69%), and two ester groups at 3.78 (61%) with the relative induced shift of each proton (or MeO group) in brackets.[10] The major coupling constants[10] in the presence of $Eu(dpm)_3$ are as follows: $J_{2,3} = J_{6,7} = J_{2,7} = J_{3,6} = 7$ Hz; $J_{3,4} = J_{7,8} = 8$ Hz. Inspection of molecular models shows that these parameters are entirely consistent with the structure (5) for the photodimer of (3) and in conjunction with the evidence presented below they rule out other structures which can be produced by the formation of two or four new bonds between two molecules of (3).

Strong support for the structure (5) comes from the observation that the photodimer of (3) is converted on heating to a mixture of the monomer (3) and another dimer for which we propose the cyclobutane structure (7) on the basis of its spectral properties. When (5) was heated in tetrachloroethylene at 124° for four hours the relative concentrations of (3), (5), and (7) were approximately 5%, 10%, and 85%, respectively, as determined from the p,m.r. spectrum of the mixture. After ten hours at 124° (5) could not be detected and (3) and (7) accounted for ca. 20% and 75% respectively. (7) is conveniently prepared by heating a solution of (5) (0.25g) in dimethylformamide (2.5 ml) for twelve minutes by immersion in boiling dimethylformamide. After the addition of water the products were extracted with carbon tetrachloride and crystallised from methanol to give colourless prisms (0.18g), m.p. 190.5-192° of the dimer (7)[8]. The mass spectra of (7) and (5) are virtually identical but the comparison of the ultraviolet spectrum of (7) [shoulder at 3.5 nm (ε3,200)] reveals the presence of additional conjugation in (7). The p.m.r. spectrum[9] of (7) exhibits four three-proton singlets at δ3.42, 3.55, 3.63, and 3.68, which account for the four (non-equivalent) ester groups. Other signals, their assignments, on the basis of structure (7),and their relative $Eu(dpm)_3$-induced shifts[10] are as follows: dt, 3.40(1H; $J_{2,3}$ 3 Hz; $J_{3,4} = J_{3,6} = 9$ Hz; H-3; 2%); dd 3.87 (1H; $J_{3,6}$ 9 Hz; $J_{6,7}$ 6 Hz; H-6; 39%); dd*, 5.15(1H; $J_{2,4}$ 1 Hz; $J_{3,4}$

9 Hz; H-4; 100%); dd, 5.77 (1H; $J_{6,7}$ 6 Hz; $J_{7,8}$ 10 Hz; H-7; 5%); d, 6.52 (1H; $J_{7,8}$ 10 Hz; H-8; 15%); dd, 6.97 (1H; $J_{2,3}$ 3 Hz; $J_{2,4}$ 1 Hz; H-2; 24%); m, 7.0-7.7 (6H; ArH). Dreiding models show that the cyclobutane ring of (7) can adopt two conformations and the p.m.r. spectrum fits only that conformer in which the C(5)-COOMe group is in the pseudoequatorial orientation. Thus, $J_{2,3}$ is smaller than $J_{6,7}$ and coupling is observed only between H-2 and H-4, and not between H-6 and H-8. The pseudoequatorial orientation of the C(5)- COOMe group accounts also for the observation that one of the ester groups in (7) is shifted farther by $Eu(dpm)_3$ than the others (i.e., 78%, 25%, 23%, and 20% for the peaks originally at δ3.68, 3.63, 3.42, and 3.55, respectively) and accordingly, the signals of the protons next to the C(5)-COOMe group undergo the largest induced shifts in (7). In agreement with the structure (7) the dimer is quantitatively converted to the monomer at temperatures near its melting point. This occurs also on irradiation of (7) under the conditions used in the preparation of (5) from (3) and thus the intermediacy of (7) in the photodimerisation of (3) appears to be ruled out.

Attempts to isolate a photodimer from methyl naphthalene-1-carboxylate have failed but irradiation of the 2-isomer under the conditions described above gave a photodimer in ca. 50% yield. This compound[8] separates from ethanol or acetone in colourless needles, m.p. ca. 212° with decomposition. Its mass spectrum confirms its molecular weight (372) and its ultra-violet spectrum is typical for a 1,2-dialkylbenzene [λ_{max}^{EtOH} (ε) at 275(300), 265(410), and 258 nm (390); sh. at 270 nm (320)]. The p.m.r. spectrum[9] shows the presence of two equivalent ester groups and of eight aromatic and six non-aromatic protons [s, 3.73 (6H; OMe); m, 3.7-3.9 (2H); m, 4.15-4.65 (4H); s, 6.93 (8H; ArH)]. The spectrum of the non-aromatic protons was analysed by examination of the changes which occurred on the gradual addition of $Eu(dpm)_3$. The following chemical shifts and relative induced shifts[10] were obtained [numbering as in structure (6)]: two ester groups at 3.73 (75%); H-3 and H-7, 3.82(100%); H-4 and H-8, 4.35(30%); and H-1 and H-5, 4.50(82%); the major coupling constants in the presence of $Eu(dpm)_3$ are: $J_{1,8} = J_{4,5} = 12$ Hz; $J_{3,4} = J_{7,8} = 8$ Hz.[10] These spectra strongly suggest that the photodimer of (4) has the structure (6), analogous to the photodimer of (3). In support of this proposal this dimer does not add hydrogen in the presence of various heterogeneous and homogeneous metal catalysts, nor does it add bromine or potassium permanganate. The dimer (6) was recovered quantitatively after being heated at 124° in tetrachloroethylene for seven hours but above 200° the monomer (4) is formed exclusively; no evidence for the formation of a dimer corresponding to (7) was found between 124 and 200°.

As the ultraviolet spectra and the p.m.r. parameters of the diester (6) closely resemble those reported for the dimer of 2-naphthonitrile[6] we suggest that this compound has in fact the structure (8). The only published item of evidence that might contradict this proposal is the infrared frequency of the nitrile groups. This is reported to occur at 2335 cm^{-1}, 5 cm^{-1} below the lower limit of the range commonly quoted for non-conjugated nitriles.[11] On the basis of structure (8) this difference might be explained by the difference in hybridisation of a cyclobutyl carbon atom and that of an unstrained sp^3-hybridised carbon atom, as the CN stretching frequency is known to respond strongly to changes in the force constants of the adjacent carbon-carbon bond (i.e. C-CN).[12]

The structures now proposed for photodimers of substituted naphthalenes are in excellent agreement with theoretical models of excimers in which the two molecules of the monomer are arranged in eclipsed sandwich structures, and dipole-dipole interactions within such excimers could account for the orientation of the substituents in dimers such as (6) and (8). The preference for bond formation between the substituted rings is reminiscent of the trend observed in the photoaddition of diarylacetylenes to substituted naphthalenes.[13,14]

The formation and structures of other photodimers of substituted naphthalenes will be described elsewhere.

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10. The induced shift of each proton is expressed in percent relative to the largest induced shift observed in this compound. The coupling constants obtained from the spectra recorded in the presence of $Eu(dpm)_3$ satisfactorily reproduce the experimental spectra using the LAOCOON II program. Some line broadening due to the shift reagent occurred and could have masked couplings smaller than 1-2 Hz.
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