

Photodimerisation of Naphthalene-2-carbonitrile

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Summary A photodimer of naphthalene-2-carbonitrile has been isolated and found to have a 1,4-head-to-tail structure.

INVESTIGATION of the photolysis of a number of naphthalene derivatives has revealed only one type, the 2-alkoxy-naphthalenes, which form isolable photodimers.¹⁻³ Consideration of the structural and electronic effects of the 2-alkoxy-substituent provides no explanation for this seemingly unique capacity. The conversion¹⁻⁴ of these dimers into their monomers on dissolution makes it evident that crystal forces contribute significantly to their stability. This suggested that photodimers of other naphthalene derivatives would be isolable if conditions were found in which their steady-state concentration under irradiation exceeded their solubility in the medium. We report here some results with naphthalene-2-carbonitrile.

Photolysis† of concentrated (0.1–1.0M) solutions of naphthalene-2-carbonitrile in benzene, methanol, or benzene–methanol (sealed in Pyrex glass under nitrogen) gave no evidence of photodimerisation even after 15 days. However, a 15% yield of a crystalline precipitate was

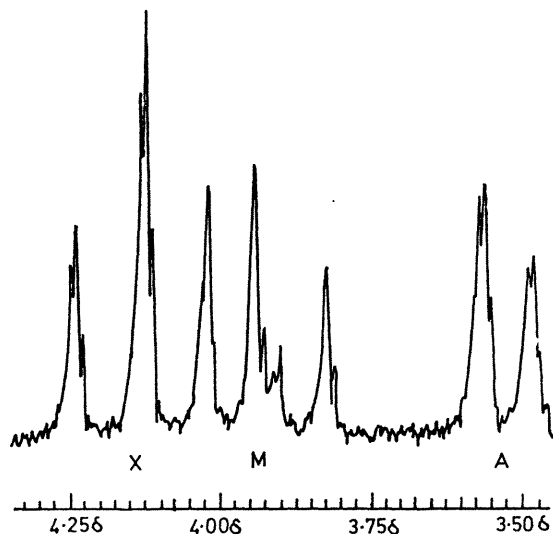
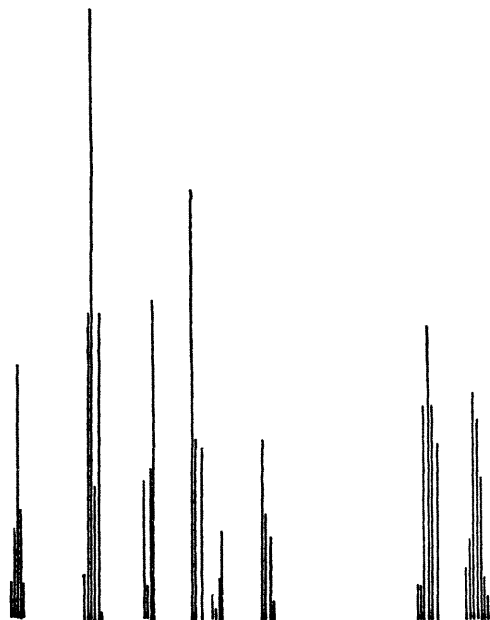
obtained after 10 days of irradiation of a saturated solution of this nitrile in n-hexane–benzene (2:1). Recrystallisation from acetone gave colourless crystals, analysing for C₁₁H₇N, which decomposed to naphthalene-2-carbonitrile without melting at *ca.* 225°. Conversion into the monomer was also readily accomplished with dilute acid. Although the most intense peak (*m/e* 153) in the mass spectrum of the photoproduct corresponded to the monomer, the highest peak at *m/e* 306 confirmed that it was dimeric.

The i.r. spectrum (mineral oil) of the photodimer displayed conjugated nitrile absorption at 2235 cm⁻¹ and bands at 805, 782, 775, and 742 cm⁻¹ consistent with a 1,2-disubstituted benzene moiety in a strained system, but not with a 1,2,4-trisubstituted benzene or naphthalene ring system. The u.v. spectrum, λ_{max} (MeOH) 264 (log ε 2.51), 269 (2.43), and 275sh nm (2.31), was also that of a 1,2-dialkyl substituted benzene derivative.

Unlike the 2-alkoxynaphthalene photodimers¹⁻⁴ this material was sufficiently soluble and stable in several solvents so that satisfactory n.m.r. spectra could be obtained. In dichloromethane, the 100 MHz spectrum showed absorption near δ 7.0 (aromatic) and 3.4–4.5 p.p.m. (aliphatic and olefinic) with an intensity ratio of 4:3. A

† The photolyses were carried out in a Rayonet fitted with RPR 3600 lamps.

concentrated solution in $[^2\text{H}_6]\text{C}_6\text{H}_6-[^2\text{H}_6]\text{Me}_2\text{SO}$ resulted in separation of the latter absorption into three equally intense signals (see Figure). Two of the three expected couplings of an AMX system were readily discernible, but many extra weaker lines were also present. These could have arisen from the additional couplings of an XMAA'M'X' proton arrangement demanded by a dimeric structure. Trial spectra were computed with the LAOCN3 program into which were inserted various estimates of the coupling constants not directly measurable from the observed spectrum together with all possible permutations of sign. A good simulation of the olefinic and aliphatic proton.



FIGURE

region of the spectrum (Figure) was computed using the chemical shifts and coupling constants in the Table. Decoupling of the aromatic region sharpened the M and X

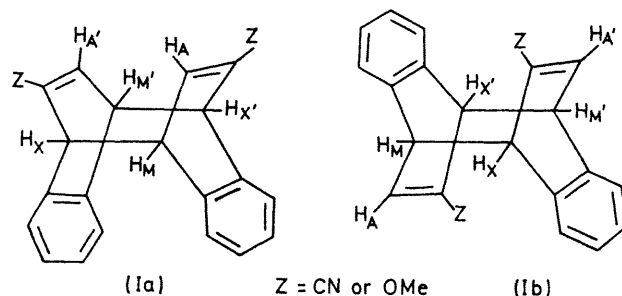
TABLE

Chemical shifts and coupling constants for protons of the naphthalene-2-carbonitrile dimer

	H_X	H_M	H_A	$H_{A'}$	$H_{M'}$	H_X	H_{ar}
H_m	4.17	11.7	b	1.0	b	b	a
H_M	11.7	3.94	8.0	-1.0	c	b	a
H_A	b	8.0	3.53	1.0	-1.0	1.0	
$H_{A'}$	1.0	-1.0	1.0	3.53	8.0	b	
$H_{M'}$	b	c	-1.0	8.0	3.94	11.7	a
H_m'	b	b	1.0	b	11.7	4.17	a
H_{ar}	a	a			a	a	7.05

^a Although no coupling was employed in the simulated spectrum, a small coupling is indicated since decoupling of H_{ar} sharpens H_X and H_M . ^b No significant value of $J_{XX'}$, J_{XA} , $J_{X'A'}$, $J_{XM'}$, or J_{XM} was needed to simulate the spectrum. ^c $J_{MM'} = \text{Hz}$ can be substituted for $J_{AA'}$ without significantly changing the spectrum.

proton regions but did not affect the A proton region indicating that only the former are adjacent to the aromatic ring.



Consideration of the structure of all possible dimers leads to the conclusion that only the two resulting from 1-4', 4-1' coupling, (Ia) and (Ib) ($Z = \text{CN}$), are consistent with the spectral data. It was proposed that the photodimer of 2-methoxynaphthalene was *alpha* to the *substituted* rather than the unsubstituted ring, and a comparison of its i.r. spectrum with that of the photodimer of naphthalene-2-carbonitrile militates for a similar structure. In addition to an almost identical aromatic overtone pattern ($2000-1800\text{ cm}^{-1}$), a close similarity is observed in both the intensity and the position of the aromatic ring stretching bands at $1600-1450\text{ cm}^{-1}$ as well as in the unusually complex absorption between 700 and 800 cm^{-1} . Furthermore, the spectrum of the methoxynaphthalene dimer contains an intense band at 1650 cm^{-1} which demands the methyl vinyl ether of structure (I; $Z = \text{OMe}$) rather than the alternative alkyl substituted double bond.

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