

Substituent effects on the photoaddition reactions of 1-naphthol to benzonitriles

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ABSTRACT

Methoxy-, methyl-, and chloro-substituted benzonitriles undergo photoaddition to 1-naphthol to give the substituted addition products, 5_{c-k} , by initial attack of the cyano group on the aromatic ring of 1-naphthol. The efficiency of the photoaddition reaction varied with the position of the substituents, with the *para*-substituted benzonitriles giving the largest yield of photoproduct.

INTRODUCTION

In a previous report (Al-Jalal *et al.* 1985) we have shown that conjugated nitrile groups (e.g. acrylonitrile and benzonitrile) undergo photoaddition to benzene rings in a manner analogous to that of acetylenes (Bryce-Smith & Lodge 1963) to give azocines, as shown in Fig. 1. This facile direct access to the azacyclooctatetraene skeleton is of appreciable interest since such compounds are known to have hypnotic and anticonvulsive actions (Porter 1970), and to stimulate the central nervous system (Lien *et al.* 1971). More recently, we have shown that the nitrile group of benzonitrile readily undergoes 1,2 addition to the aromatic rings of phenol and 1-naphthol giving the substituted 1,2-dihydroazocin-2-one (Al-Jalal 1989), and the addition product 5_a , respectively (Al-Jalal *et al.* 1995). This process is also of considerable photochemical interest since cycloaddition reactions involving phenols have been previously limited to the formation of a tricycle [5.2.1.0^{2,6}] dec-7-en-10-one (Srinivasan *et al.* 1974) from cyclopentane and phenol, and the addition of acrylonitrile to 2-naphthol giving the cyclobutane (structure 2, Fig. 1) in Akhtar & McCullough 1981. The photoaddition of benzonitrile to 1-naphthol, on the other hand, represented the first reported example in which a cyano group was shown to add photochemically to the aromatic ring of a naphthalene compound yielding compound 5_a , the structure of which was unambiguously confirmed by X-ray structural analysis (Al-Jalal *et al.* 1995).

In our attempt to enhance our understanding of the factors controlling this type of addition, we have investigated the photochemical reactions of various substituted benzonitriles with 1-naphthol. We have studied the following: benzonitrile, *o*-, *m*- and *p*-hydroxybenzonitrile, *o*-, *m*- and *p*-methoxybenzonitrile, *o*-, *m*- and *p*-methylbenzonitrile, *o*-, *m*- and *p*-aminobenzonitrile, *o*-, *m*- and *p*-nitrobenzonitrile and *o*-, *m*- and

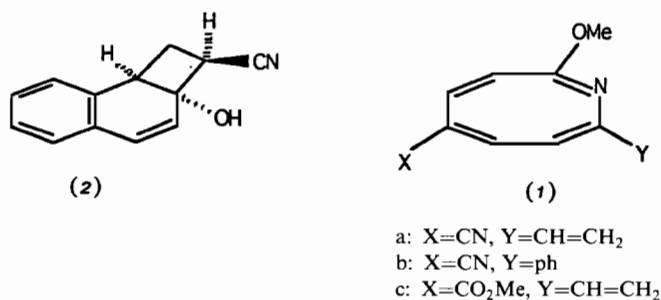


Fig. 1. Photoaddition of conjugated nitriles to substituted benzenes.

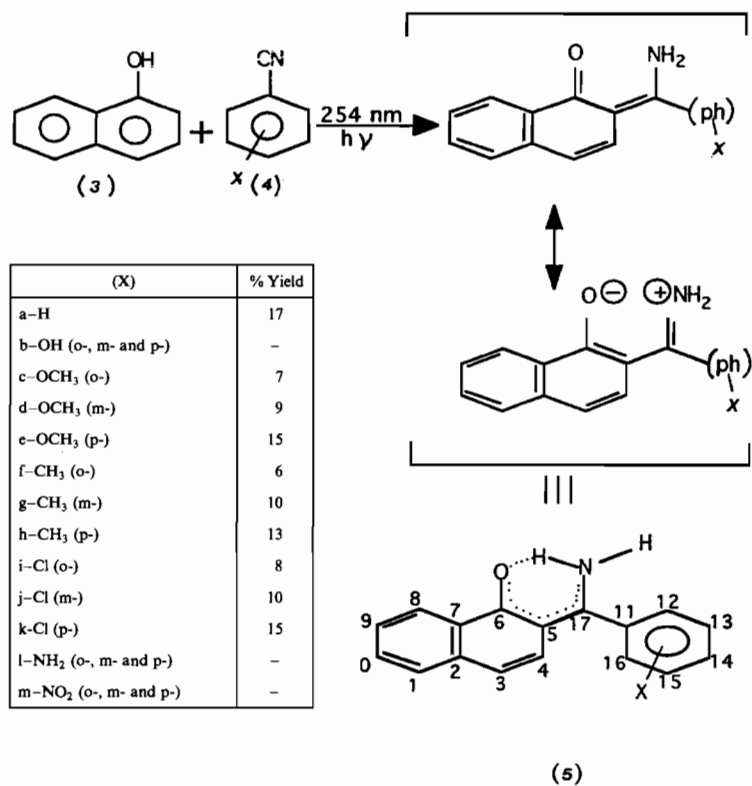


Fig. 2. Photoaddition substituted benzonitriles to 1-naphthol.

p-chlorobenzonitrile (4_{b-m}, Fig. 2). We have observed that the photolabilities of these arenes in the presence of 1-naphthol vary appreciably and we now report details of these results.

RESULTS AND DISCUSSION

Irradiation of 1-naphthol (0.17 M) and the substituted benzonitriles 4_{b-m} (2.43 M) in acetonitrile solution, produced only one major photoproduct in each system, except

for benzonitriles 4_b , 4_l and 4_m , where no photochemical reaction was observed. All photoproducts were yellow in colour and were separated with >99% purity (GC) by flash chromatography. The 300 MHz ^1H NMR spectra (Table 1) of these photoproducts showed the presence of ethenyl (2 H, 6.60 and 6.90 ppm), aromatic (7 H, 7.15–7.60 ppm) and amino protons (2 H, 6.70 ppm); a single aromatic proton at 8.50 ppm; plus methoxy or methyl protons in the case of adducts 5_{c-k} (Fig. 2). The most important feature of the ^1H NMR spectra was the presence of the ethenyl protons each as a doublet ($J = 7.0$ Hz) corresponding to 3-H and 4-H in the addition products 5_{c-k} . The presence of a single aromatic proton at 8.50 ppm, as a doublet ($J = 5.0$ Hz), must correspond to 8-H which is strongly deshielded due to the nearby carbonyl group (a similar observation has been reported for the ^1H NMR spectrum of 1,4-naphthaquinone in Williams & Fleming 1987). At 6.70 ppm, a broad peak appeared corresponding to two protons which disappeared upon shaking with D_2O , indicating that the peak must be due to the $-\text{NH}_2$ group.

The IR spectra (Table 1) confirmed the absence of the cyano group (no signal between 2000 and 2500cm^{-1}) and at the same time it showed a signal at 1635cm^{-1} corresponding to the carbonyl stretching frequency, lowered due to the presence of a stronger hydrogen bond and the involvement of the carbonyl group in the resource structure. The IR spectra also showed a band at 3050cm^{-1} corresponding to the amino group ($=\overset{+}{\text{N}}\text{H}_2$). Amino acids showing the spectrum of the zwitterionic groups display similar behavior for the primary ammonium ($-\text{NH}_3^+$) group, where the $-\text{NH}_2$ stretching appears under the peaks of the saturated C–H absorption (Williams & Fleming 1987). From the various spectroscopic data (Table 1), and most importantly, from comparison with the spectroscopic data of the addition product 5_a (Al-Jalal *et al.* 1995), the substituted addition products 5_{c-k} were assigned.

The formation of the addition products 5_{c-k} can be accounted for by the reaction sequence suggested in Fig. 3, which involves electron transfer from 1-naphthol to the substituted benzonitrile followed by attack of the benzonitrile anion radical on the aromatic ring of 1-naphthol.

Solvent polarity studies have shown that the photoproduct formation is doubled upon change of solvent from cyclohexane to acetonitrile, but the effect is only evident for nitrogen degassed solution (See Experimental Section). The results, which are summarized in Fig. 2, clearly indicate that the formation of the addition products 5_{c-k} depends on the type and position of the substituents on the benzonitrile. In general, all substituted benzonitriles are less productive than benzonitrile itself. The *para*-substituted compounds give the largest amount of photoproduct of the substituted benzonitriles.

These results indicate that the addend requirements for this novel addition process are still not clear. But evidently polar factors are important since the rate of reaction in all cases is markedly increased with the increase in solvent polarity. These observations are quite similar to the ones we have earlier reported for the “phenol-benzonitrile” systems (Al-Jalal 1989, 1990), and do strengthen our earlier suggestion (Al-Jalal 1989), that the reaction may proceed by photo-induced electron transfer from the 1-naphthol to the cyano compound and that the radical-ion species thus formed may either undergo addition or react with oxygen.

Table 1. The mass spectra, infrared, electronic and nuclear magnetic resonance spectral data of compounds S_{c-k} .

Compound	Infrared Spectra (potassium bromide)		Electronic Spectra (Acetonitrile)		NMR (Deuteriochloroform)			MS (70 eV) M ⁺
	Cm ⁻¹	ν	λ max (nm)	ϵ	δ (ppm)	(No. of protons)	Assignment	
S_c	1635 (s)	C=O	273	6740	3.85 (s)	(3)	OCH ₃	277 m.u.
	3050 (m)	=NH ₂ ⁺	320	1535	6.60 (d)	(1)	4-H	
			430	2502	6.70 (broad s)	(2)	-NH ₂	
					7.05 (d)	(1)	3-H	
					7.20-7.35 (m)	(4)	Ar-H	
					7.40-7.65 (m)	(3)	Ar-H	
S_d	1635 (s)	C=O	272	6695	3.85 (s)	(3)	OCH ₃	277 m.u.
	3050 (m)	=NH ₂ ⁺	320	1518	6.60 (d)	(1)	4-H	
			428	2485	6.70 (broad s)	(2)	-NH ₂	
					7.05 (d)	(1)	3-H	
					7.25-7.35 (m)	(4)	Ar-H	
					7.45-7.60 (m)	(3)	Ar-H	
S_e	1635 (s)	C=O	272	6720	3.80 (s)	(3)	OCH ₃	277 m.u.
	3050 (m)	=NH ₂ ⁺	318	1524	6.60 (d)	(1)	4-H	
			428	2497	6.70 (broad s)	(2)	-NH ₂	
					7.05 (d)	(1)	3-H	
					7.20-7.35 (m)	(4)	Ar-H	
					7.40-7.60 (m)	(3)	Ar-H	
S_f	1635 (s)	C=O	270	6547	2.22 (s)	(3)	CH ₃	261 m.u.
	3050 (m)	=NH ₂ ⁺	319	1378	6.55 (d)	(1)	4-H	
			428	2353	6.80 (broad s)	(2)	-NH ₂	
					7.00 (d)	(1)	3-H	
					7.15-7.30 (m)	(4)	Ar-H	
					7.40-7.55 (m)	(3)	Ar-H	
S_g	1635 (s)	C=O	270	6539	2.20 (s)	(3)	CH ₃	261 m.u.
	3050 (m)	=NH ₂ ⁺	320	1364	6.55 (d)	(1)	4-H	
			430	2302	6.80 (broad s)	(2)	-NH ₂	
					7.00 (d)	(1)	3-H	
					7.20-7.35 (m)	(4)	Ar-H	
					7.40-7.60 (m)	(3)	Ar-H	
S_h	1635 (s)	C=O	270	6518	2.20 (s)	(3)	CH ₃	261 m.u.
	3050 (m)	=NH ₂ ⁺	318	1368	6.55 (d)	(1)	4-H	
			430	2315	6.80 (broad s)	(2)	-NH ₂	
					7.00 (d)	(1)	3-H	
					7.15-7.35 (m)	(4)	Ar-H	
					7.40-7.60 (m)	(3)	Ar-H	
S_i	1635 (s)	C=O	268	6443	6.60 (d)	(1)	4-H	281.5 m.u.
	3060 (m)	=NH ₂ ⁺	318	1358	6.85 (broad s)	(2)	-NH ₂	
			430	2312	7.05 (d)	(1)	3-H	
					7.15-7.25 (m)	(4)	Ar-H	

Table 1. Continued.

Compound	Infrared Spectra (potassium bromide)		Electronic Spectra (Acetonitrile)		NMR (Deuteriochloroform)		MS (70 eV) M ⁺	
	Cm ⁻¹	ν	λ max (nm)	ϵ	δ (ppm)	(No. of protons) Assignment		
5 _j	1635 (s) 3060 (m)	C=O =NH ₂ ⁺	268 320 430	6468 1362 2322	7.30–7.45 (m)	(3)	Ar-H	281.5 m.u.
					8.40 (d)	(1)	8-H	
					6.60 (d)	(1)	4-H	
					6.85 (broad s)	(2)	–NH ₂	
					7.05 (d)	(1)	3-H	
					7.20–7.35 (m)	(4)	Ar-H	
5 _k	1635 (s) 3060 (m)	C=O =NH ₂ ⁺	268 318 428	6508 1371 2295	7.20–7.35 (m)	(4)	Ar-H	281.5 m.u.
					7.40–7.60 (d)	(3)	Ar-H	
					8.45 (d)	(1)	8-H	
					6.60 (d)	(1)	4-H	
					6.85 (broad s)	(2)	–NH ₂	
					7.05 (d)	(1)	3-H	
7.10–7.50 (m)	(4)	Ar-H	7.30–7.50 (m)	(3)	Ar-H			
8.40 (d)	(1)	8-H						

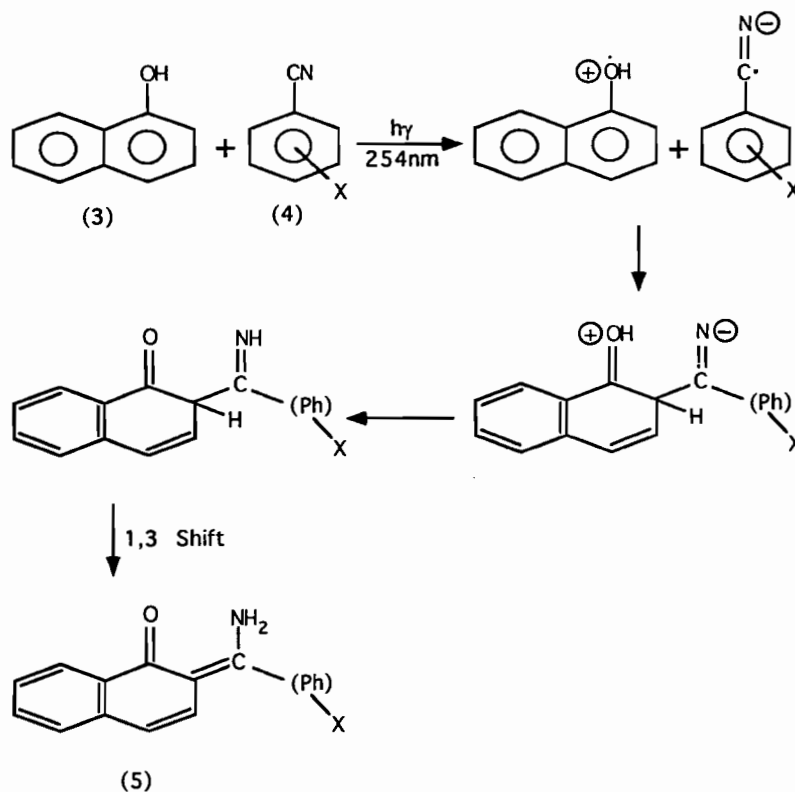


Fig. 3. Mechanism for the formation of the addition product (5).

EXPERIMENTAL

APPARATUS AND MATERIALS

An annular photoreactor model APQ 40 (Applied Photophysics Limited) fitted with a 16W low pressure mercury arc lamp was used for the irradiations. NMR spectra were recorded on a Bruker 300 MHz spectrometer using tetramethylsilane as the internal standard. IR and UV spectra were taken with a Perkin-Elmer 580 B IR' spectrometer and a Shimadzu UV-visible recording spectrometer (UV 160). Mass spectra were recorded on a Ribermag R10-10 (NERMAG). Gas chromatography (GC) was performed with a Varian 3300 instrument fitted with a flame ionization detector and 12m DB1-15W (OV 17 equivalent) bonded phase capillary column. Melting points (m.p.) were measured on a BUCHI 510 melting point apparatus. Microanalysis was performed on a Leco Model CHNS-932.

Benzonitrile and all of the substituted benzonitriles were from Aldrich and were used without further purification. 1-Naphthol was also from Aldrich, and was purified by crystallization from ethanol before use. Ethyl acetate and acetonitrile were purified by distillation before use. The photoproducts were isolated by flash chromatography using the method of Still *et al.* (1978) using silica gel (E. Merck No. 9385, 40–60 μm) eluted with a mixture of ethylacetate: petroleum ether (2:5 V/V). Chromatography was monitored with TLC sheet no. 60 (silica gel). The solutions were degassed by bubbling nitrogen for one hour before irradiation. The substituted addition products S_{c-k} (Fig. 2) were identified from their spectroscopic data and by comparison with the spectroscopic data reported earlier for the addition product S_a (Al-Jalal *et al.* 1995).

PHOTOCHEMICALS REACTION OF 1-NAPHTHOL AND THE SUBSTITUTED BENZONITRILES

Photoreaction of 1-naphthol (0.17 M) and the substituted benzonitriles (2.43 M) in acetonitrile (20 ml) for 24 hours gave in each case where there is a photochemical reaction, the corresponding acyclic addition products (yellow in color) which were isolated pure (GC, TLC one spot) by flash chromatography using 2:5 V/V mixture of ethyl acetate and petroleum ether (40–60°C) as eluting solvent. In all cases, only 25% of the starting 1-naphthol was converted to the photoproducts as indicated by GC.

Table 2. Melting points and elemental analysis of compounds S_{c-k} .

Compound No.	MP °C	Formula	Calcd. %				Found %			
			C	H	N	Cl	C	H	N	Cl
S_c	142–144	$C_{18}H_{15}NO_2$	77.95	5.45	5.05	–	78.21	5.61	5.18	–
S_d	140–142	$C_{18}H_{15}NO_2$	77.95	5.45	5.05	–	78.24	5.52	5.21	–
S_e	147–149	$C_{18}H_{15}NO_2$	77.95	5.45	5.05	–	78.15	5.58	5.14	–
S_f	169–171	$C_{18}H_{15}NO$	82.73	5.78	5.35	–	82.62	5.91	5.23	–
S_g	168–170	$C_{18}H_{15}NO$	82.73	5.78	5.35	–	82.57	5.86	5.25	–
S_h	172–174	$C_{18}H_{15}NO$	82.73	5.78	5.35	–	82.51	5.88	5.19	–
S_i	194–196	$C_{17}H_{12}ClNO$	72.47	4.29	4.97	12.58	72.61	4.35	5.21	12.39
S_j	192–194	$C_{17}H_{12}ClNO$	72.47	4.29	4.97	12.58	72.33	4.34	5.18	12.37
S_k	197–199	$C_{17}H_{12}ClNO$	72.47	4.29	4.97	12.58	72.28	4.42	5.16	12.45

The analytical results are reported in Tables 1 and 2, except for compound 5_a, since its spectroscopic properties have been reported elsewhere (Al-Jalal *et al.* 1995).

SOLVENT POLARITY STUDIES

A merry-go-round apparatus fitted with a low pressure mercury arc lamp used for the solvent polarity studies using 1-naphthol (0.17 M) and all substituted benzonitriles (2.43 M) in four different solvents (acetonitrile, methanol, ethyl acetate and cyclohexane) which were placed in quartz tables. The products were analyzed by GC and the results indicated that the amount of addition products 5_{c-k} doubled upon changing from a non-polar to a polar solvent.

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