Light-Induced [2 + 2] Cycloaddition of 2-Morpholinoacrylonitrile to 1-Naphthalenecarbonitrile

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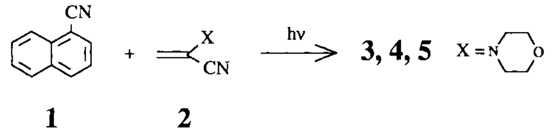
Photoexcited 1-naphthalenecarbonitrile (**1**) adds 2-morpholinoacrylonitrile (**2**) in the [2 + 2] mode both at the C(1)–C(2) and C(7)–C(8) bond unidirectionally and with the formation of only one (**3** and **4**, respectively) of the two a priori possible stereoisomers in each case. The structure of **3** has been unambiguously confirmed by an X-ray structural analysis.

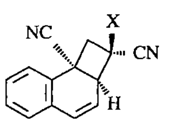
Photocycloadditions of monoolefins to various aromatics have been of interest for several years and are still under intensive investigation[1]. Such additions to the skeleton of naphthalene have been formerly reported for naphthalene itself[1], methylnaphthalenes[2], 2-naphthol[3–5] and its methyl ether[6,7], *N*-methyl-1,8-naphthalenedicarboxamide[8,9], 1-naphthalenecarbonitrile (**1**)[1,10], 2- and 4-methoxy-1-naphthalenecarbonitrile[11], 2-naphthalenecarbonitrile[1], and (1-naphthyl)ethyl vinyl ethers (intramolecularly)[12]. [2 + 2] Cycloaddition to naphthoates has been demonstrated with acetylacetone enol[13], and 1-(3-butenoxy)-2-acetonaphthones as well as their 2-(3-butenoxy) 1-isomers undergo an intramolecular [2 + 2] cycloaddition[14]. Aside from this, [2 + 2] additions of alkenes to naphthones have been rarely observed[15,16], but 1,4-additions seem to prevail with 1-acylnaphthalenes[15–19]. It should be noted that 1,4-additions to the naphthalene skeleton are more typical of 1,3-dienes (giving [4 + 4] adducts)[1] than of alkenes. Since we have previously observed successful 1,4-additions[15–20] of captodative[21] alkenes to photoexcited 1-acylnaphthalenes, and since it has also been demonstrated that the lowest excited (π,π^*) triplet state of 1-acetonaphthone[22] is the most likely candidate for the reactive state of this ketone in cycloadditions, it has been highly tempting to test captodative alkenes in light-induced cycloadditions to 1-naphthalenecarbonitrile (**1**). For this compound, *singlet* reactivity has been demonstrated in the interaction with highly alkylated ethylenes through exciplex emission in aprotic solvents[23]. A polar exciplex originating from the reaction of arylethylenes with singlet excited **1** has recently been invoked from solvent dependence, salt effect and quenching studies[10].

Irradiation ($\lambda \geqslant 280$ nm) of a cyclohexane solution containing equimolar amounts of **1** and 2-morpholinoacrylonitrile (**2**)[24] (both 0.1 M) up to 36% conversion of **1** gave a mixture of products, which was subjected to preparative layer chromatography (PLC). This method allowed the recovery of 64% of starting material **1** and yielded minor amounts of the ketone **5** (2%) as well as a mixture, which was finally separated by HPLC to give two isomeric 1:1 adducts **3** and **4**, in yields of 14% and 9%, respectively, which were demonstrated to be positional isomers. Examination of the ^{1}H-NMR spectrum of the crude photolysate did not reveal any other products.

It must be admitted, that the overall mass balance with reference to starting material **1** is at best 73% and thus not satisfactory. The chromatographic methods used, however, inevitably caused some losses due to the instability of the products **3** and **4** towards prolonged exposure to silica gel aside from the fact that unreacted olefin **2** is noticeably hydrolysed during silica gel chromatography of the crude mixture.

Ketone **5**, most likely the hydrolysis product of **4**, may be formed during workup. A corresponding hydrolysis product of adduct **3** could not be detected so far and may not be present in more than 1% based on converted **1**.

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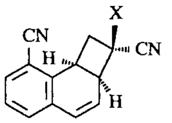
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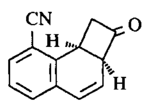
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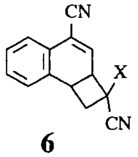
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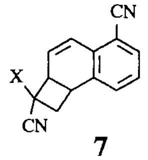
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Structure **3** has been assigned to the major component on the basis of an X-ray crystal structure analysis[25] (Figure 1), which confirms the *endo* orientation of the morpholino group and assists in the interpretation of the ^{1}H-NMR data (see Tables 1 and 2), which in turn are useful for the structural assignment of compounds **4** and **5**. In **3**, 4-H, 3-H and 2a-H form an ABX system as do 1-*exo*-H, 1-*endo*-H and 2a-H. The coupling constant $^4J_{1\text{-}exo,2a} = 4.1$ Hz is typical of a rigid W-type arrangement[26].

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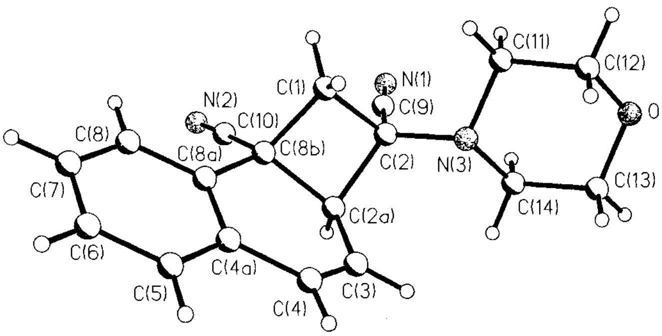

Figure 1. Molecular structure of *rel*-(2*R*,2a*S*,8b*R*)-1,2,2a,8b-tetrahydro-2-morpholinocyclobuta[a]naphthalene-2,8b-dicarbonitrile (**3**) in the crystal

All three products exhibit in their UV spectra (acetonitrile) a slightly structured maximum at similar wavelengths with similar absorbancies (**3**: 265 nm, $\log\varepsilon = 3.91$; **4**: 267, $\log\varepsilon = 3.97$; **5**: 272 and 263 nm, $\log\varepsilon = 3.87$ and 3.85). This allows the assignment of closely related chromophores, and since these data are well in accord with the UV data of related compounds[27], **4** and **5** may be well regarded as tetrahydrocyclobuta[*a*]naphthalenes.

Table 1. Structurally relevant ^{1}H chemical shifts δ [ppm] and signal multiplicity for photoproducts **3**, **4**, **5**

	3	**4**		**5**
	($CDCl_3$)	($CDCl_3$)	(C_6D_6)	($CDCl_3$)
1-H_{endo}	2.82 dd	2.45 [a]	1.84 ddd	3.40 dd
1-H_{exo}	3.08 dd	2.75 ddd	2.26 ddd	3.89 ddd
2a-H	4.09 m_c	3.70 [a]	3.07 m_c	4.41 m_c
8b-H	–	4.04 ddd	3.87 ddd	4.07 ddd
3-H	5.65 dd	5.73 dd	5.22 dd	5.87 dd
4-H	6.57 dd	6.47 dd	5.94 dd	6.50 dd

[a] Overlapped by signals due to morpholino group.

Table 2. Structurally relevant ^{1}H,^{1}H coupling constants of photoproducts **3**, **4**, **5**

	Coupling protons	*J* [Hz] for compound			
		3 ($CDCl_3$)	**4** ($CDCl_3$)	 (C_6D_6)	**5** ($CDCl_3$)
^2J	1-*endo*/*exo*	11.8	10.8	10.9	17.7
^3J	2a,8b	–	[a]	8.1	9.8
	1-*endo*, 8b	–	[a]	10.8	7.5
	1-*exo*, 8b	–	8.1	8.1	9.7
	3,4	10.1	10.0	10.0	9.7
	2a,4	4.0	3.3	3.4	4.9
^4J	1-*endo*,2a	0.5	[a]	0.9	3.1
	1-*exo*,2a	4.1	4.2	4.2	4.8
	2a,3	1.8	2.1	2.1	2.2

[a] Not determined.

As can also be seen from Tables 1 and 2, the C(1)–C(2) bond of **1** is not involved in the formation of **4** (and its presumed hydrolysis product **5**) since 2a-H and the methylene protons are coupled to an additional proton, 8b-H. The assignment of all signals and the mutual couplings have been verified by homonuclear shift correlation (COSY) experiments[28a].

Structures **6**[29] and **7** as well as their 1,1-disubstituted isomers could be ruled out on the basis of the following arguments: Only one low-field olefinic proton should be found for **6** instead of two, and for **7** the chemical shift of 4-H should be strongly influenced by the *peri* CN group. No indication for this is given by the data of Table 1, which agree well with published chemical shifts and coupling constants for related systems[27]. All further spectroscopic evidence is in agreement with structures **4** and **5**. Especially, the similar vicinal coupling constants found for the interaction of both 1-H_{endo} and 1-H_{exo} with 8b-H and the typical W-type coupling ^4J constants for 1-H_{exo} with 2a-H rule out the 1,1-disubstituted isomer of **4** and the 1-oxo isomer of **5**. Also, the *endo* orientation of the morpholino group in **4** is confirmed by a NOE intensity difference experiment[28b]: Irradiation at the frequency of the $N(CH_2)_2$ multiplet enhances the intensity of the 3-H signal in both **3** and **4**.

The results demonstrate unidirectional and highly stereoselective [2 + 2] photoaddition of the captodative olefin 2-morpholinoacrylonitrile to two sites of 1-naphthalenecarbonitrile (**1**). So far, we have not found any indication of 1,4-adducts. It should also be noted that the direction of the addition of **2** to **1** is opposite to that of various enol ethers[27e].

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Experimental

Melting points (uncorrected): Kofler micro hot stage apparatus. – Elemental analyses: Carlo Erba 1106 CHN-analyzer. – IR: Perkin-Elmer spectrometer 283. Band intensities: w weak, m medium, s strong. – 300-MHz ^{1}H and 75-MHz ^{13}C NMR: Bruker WM 300, TMS as internal standard. ^{13}C assignments were corroborated by DEPT spectra[28c] and heteronuclear shift correlations[28d]. – MS (70 eV, EI mode, temp. of inlet system given): MAT 311 A. – UV spectra: Perkin-Elmer 554 (sh = shoulder).

Irradiation of **1** *in Solution in the Presence of* **2**: A solution of 1.53 g (10 mmol) of **1** and 1.38 g (10 mmol) of **2** in 100 ml of dry cyclohexane was purged with dry argon and irradiated for 48 h with a Philips HPK 125-W high-pressure mercury vapor burner through a water-jacketed immersion well made of Duran glass ($\lambda \geqslant 280$ nm). The residue obtained upon concentration of the solution was subjected to preparative layer chromatography by using 10 glass plates each 48 cm wide and 20 cm high covered with a 1 mm thick layer of slurry-applied and air-dried silica gel Merck PF_{254} as well as a mixture of hexane/chloroform/ethyl acetate (2:1:0.3) for developing. From the fastest moving zone, 982 mg of **1** could be recovered, thus maximally 0.548 g (3.58 mmol) had been consumed during irradiation. Aside from a few minor zones, which did not warrant recovery, from a zone at $R_f = 0.15$, 15 mg (2% based on starting material not recovered) of compound **5** could be collected as colorless crystals, m.p. 115°C (from methanol). The main fraction consisted of 240 mg of a 3:2 mixture of two isomeric adducts, **3** (14%) and **4** (9%). This mixture was successfully separated by HPLC on a 250 mm long and 10 mm wide column charged with 5 μ silica particles with a phenylsilane bonded phase. Eluent: hexane/ethyl acetate (3:1), flow rate 3 ml/min at 15 bar. Compound **3** was eluted first.

rel-(2R,2aS,8bR)-1,2,2a,8b-Tetrahydro-2-morpholino-cyclobuta[a]naphthalene-2,8b-dicarbonitrile (**3**): M.p. 149–150°C (methanol). – IR (KBr): $\tilde{\nu}$ = 2238 m (CN), 2220 w (CN) cm^{-1}. – ^{1}H NMR ($CDCl_3$): See Tables 1 and 2; δ = 2.42–2.58 [m, 4H, $N(CH_2)_2$], 3.64–3.76 [m, 4H, $O(CH_2)_2$], 7.10, 7.29 and 7.42 (three m$_c$, 1H, 2H and 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 44.13 (C-1), 48.02 [$N(CH_2)_2$], 49.38 (C-2a), 63.52 (C-2), 66.08 [C-8b and $O(CH_2)_2$], 117.40 (CN), 119.26 (C-3), 122.02 (CN), 126.09 (C-8), 128.35 (C-5), 128.98 (C-4a), 129.28 (C-8a), 129.37 (C-6), 129.45 (C-4), 129.46 (C-7). – UV (CH_3CN): λ [nm] (logε) = 298 (sh, 3.23), 290 (sh, 3.48), 265 (structured max., 3.91), 235 (min., 3.51), 223 (max., 4.41), 217 (max., 4.51). – MS (70 eV, 143°C): *m/z* (%) = 291 (0.7) [M$^+$], 264 (12) [M – 27], 263 (15) [M – 28], 233 (4), 205 (4), 178 (9), 166 (6), 153 (100) [represents **1**], 138 (56) [represents **2**], 126 (26), 80 (50), 69 (58).

$C_{18}H_{17}N_3O$ (291.3)	Calcd.	C 74.20	H 5.88	N 14.42
3:	Found	C 74.23	H 5.85	N 14.36
4:	Found	C 74.11	H 5.86	N 14.51

rel-(2R,2aS,8bS)-1,2,2a,8b-Tetrahydro-2-morholino-cyclobuta[a]naphthalene-2,8-dicarbonitrile (**4**): M.p. 144–145°C (from ethanol). – IR (KBr): $\tilde{\nu}$ = 2228 m (CN), 2212 w cm^{-1} (CN). – ^{1}H NMR (see Tables 1 and 2), ($CDCl_3$): δ = 2.37–2.60 [m, 5H, $N(CH_2)_2$ and 1-H$_{endo}$], 3.70 [m$_c$, 5H, $O(CH_2)_2$ and 2a-H], 7.18 (m$_c$, 2H, aromatic H), 7.38 (m$_c$, 1H, aromatic H). – (C_6D_6): δ = 1.95 and 2.06 [two m$_c$, 2H each, $N(CH_2)_2$)], 3.38 (m$_c$, 4H, $O(CH_2)_2$], 6.51 (m$_c$, 2H) and 6.85 (m$_c$, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.20 (C-8b), 38.01 (C-1), 44.23 (C-2a), 47.78 [$N(CH_3)_2$], 64.61 (C-2), 66.20 [$O(CH_2)_2$], 111.10, 116.82 (CN), 118.71 (CN), 124.09 (C-3), 128.13 and 128.18 (C-4 and aromatic C); 131.41, 131.68, 132.22 and 137.07 (aromatic). – (C_6D_6): δ = 28.37 (C-8b), 37.88 (C-1), 44.17 (C-2a), 47.87 [$N(CH_2)_2$], 64.63 (C-1), 66.14 [$O(CH_2)$], 111.76 (C-8), 116.81 (CN), 118.45 (CN), 124.59 (C-3), 127.11 (C-4); 127.54, 130.81, 131.42, 132.24 and 137.43 (aromatic C). – UV (CH_3CN): λ (logε) = 318 (sh, 3.19), 267 (max., 3.97), 248 (min., 3.79), 226 (max., 4.45). – MS (70 eV, 135°C dec.): *m/z* (%) = 291 (0.75) [M$^+$], 276 (2), 264 (11), 263 (19), 233 (3), 206 (2), 205 (4), 178 (6), 166 (5), 153 (100) [represents **1**], 138 (74) [represents **2**], 126 (27), 80 (36), 69 (52).

1,2,2a,8b-Tetrahydro-2-oxocyclobuta[a]naphthalene-8-carbonitrile (**5**): Colorless crystals, m.p. 115°C. IR (KBr): $\tilde{\nu}$ = 2220 m cm^{-1} (CN), 1775 s (C=O). – ^{1}H NMR ($CDCl_3$): See Tables 1 and 2; δ = 7.31 (m$_c$, 2H) and 7.51 (m$_c$, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 24.91 (C-8b), 59.32 (C-2), 61.48 (C-2a), 117.18 (CN), 120.91 (C-3), 126.30 (C-4); 112.22 (C-8), 131.83 and 138.63 (quaternary aromatic C); 127.77, 131.55 and 131.77 (aromatic CH); 203.83 (C=O). – UV (CH_3CN): λ [nm] (logε) = 300 (sh, 3.33), 272 (max., 3.87), 263 (max., 3.87), 263 (max., 3.85), 253 (min., 3.71), 226 (max., 4.21). – MS (70 eV, 96°C): *m/z* (%) = 195 (1.1) [M$^+$], 194 (0.9), 180 (2), 166 (32), 154 (78), 153 (100) [represents **1**], 152 (32), 140 (23), 139 (19), 126 (65), 63 (21).

$C_{13}H_9NO$ (195.2)	Calcd.	C 79.98	H 4.65	N 7.17
	Found	C 79.79	H 4.68	N 7.02

X-ray Structure Determination: A colorless crystal of **3** (0.25 × 0.22 × 0.18 mm) suitable for X-ray diffraction was mounted in a glass capillary. The orientation matrix and the unit cell dimensions were obtained by a least-squares fit of the setting angles of 18 centered reflections in the range 20° < 2Θ < 30°.

Crystallographic details: Empirical formula $C_{18}H_{17}N_3O$, molecular mass 291.35, monoclinic, space group $P2_1/n$, a = 11.991(6), b = 9.633(6), c = 13.408(7), β = 99.47°, V = 1528 Å^3, Z = 4, D_x = 1.267 gcm^{-3}, μ(MoK_α) = 0.08 mm^{-1}.

Data collection: Siemens P4RA four-circle diffractometer, rotating anode generator, MoK_α radiation (λ = 0.71073 Å), graphite monochromator, scintillation counter, ω-scan (2 check reflections), 4° < 2Θ < 54° (+h, +k, ±l), 3327 unique reflections, empirical absorption corrections (Ψ-scan), transmission range 0.787–0.762.

Structure solution and refinement: All calculations including data reduction (Lorentz and polarization corrections) and empirical absorption corrections were done by using the SHELXTL PLUS program package[30] on an MS-DOS personal computer equipped with an Intel 80486 microprocessor. The structure was solved by direct methods (all non-hydrogen atoms, hydrogen atoms calculated at idealized positions) and refined to $R = (\Sigma \| F_o | - | F_c \|)/\Sigma | F_o |$ = 0.0474 and $R_w = [\Sigma w (| F_o | - | F_c |)^2/\Sigma w F_o^2]^{1/2}$ = 0.480 [full matrix least squares, 200 variables, 2329 observed reflections with $I > 2 \cdot \sigma(I)$]. Atomic scattering factors were taken from standard sources[31]. Both the f' and f'' components of the anomalous dispersion were included for all non-hydrogen atoms. The non-hydrogen atoms were refined with anisotropic temperature factors. For hydrogen, a common isotropic temperature factor was refined. Atomic coordinates of the nonhydrogen atoms are listed in Table 3.

Table 3. $C_{18}H_{17}N_3O$: Atomic coordinates and coefficients of the equivalent isotropic temperature factors (without H atoms)[a]

atom	x	y	z	U
C(1)	0.6068(1)	0.0401(2)	0.1767(1)	0.034(1)
C(2a)	0.6235(2)	-0.1647(2)	0.2443(1)	0.037(1)
C(2)	0.5238(2)	-0.0583(2)	0.2185(1)	0.035(1)
C(3)	0.6860(1)	-0.1530(1)	0.3496(1)	0.043(1)
C(4)	0.7915(1)	-0.1093(1)	0.3726(1)	0.046(1)
C(4a)	0.8602(2)	-0.0669(2)	0.2970(1)	0.040(1)
C(5)	0.9745(2)	-0.0358(2)	0.3240(2)	0.052(1)
C(6)	1.0386(2)	0.0019(2)	0.2513(2)	0.058(1)
C(7)	0.9901(2)	0.0077(2)	0.1521(2)	0.056(1)
C(8)	0.8770(2)	-0.0236(2)	0.1231(2)	0.046(1)
C(8a)	0.8115(2)	-0.0605(2)	0.1949(1)	0.036(1)
C(8b)	0.6854(2)	-0.0866(2)	0.1662(1)	0.034(1)
C(9)	0.4367(2)	-0.1097(2)	0.1343(2)	0.043(1)
N(1)	0.3654(2)	-0.1439(2)	0.0719(1)	0.064(1)
C(10)	0.6598(2)	-0.1536(2)	0.0665(1)	0.041(1)
N(2)	0.6397(2)	-0.2095(2)	-0.0089(1)	0.064(1)
N(3)	0.4718(1)	-0.0067(2)	0.3017(1)	0.035(1)
C(11)	0.4108(2)	0.1238(2)	0.2767(1)	0.044(1)
C(12)	0.3634(2)	0.1742(2)	0.3679(2)	0.049(1)
O	0.2888(1)	0.0744(2)	0.3992(1)	0.054(1)
C(13)	0.3461(2)	-0.0522(2)	0.4249(2)	0.049(1)
C(14)	0.3966(2)	-0.1092(2)	0.3372(2)	0.046(1)

[a] The equivalent isotopic temperature factor is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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