

rel-(1*R*,4*R*,9*R*)-1-Acetyl-9-(azepan-1-yl)-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitrileDietrich Döpp,^a Claudia Kruse,^a
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The title molecule, C₂₁H₂₄N₂O, shows elongated C—C single bonds due to their thermal lability. In the crystal structure, the molecules are linked *via* intermolecular C—H···N hydrogen bonds, forming chains extended along [010].

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Comment

In continuation of our study of regioselective (head-to-tail) photocycloadditions of 2-aminopropenenitriles [as (II)] to triplet excited 1-acetonaphthone (I) (Döpp & Mlinaric, 1994*a,b*; Döpp *et al.*, 2006*a,b*; Döpp, 2000), we present the crystal structure of the title compound, (IV).

Key indicators

Single-crystal X-ray study

T = 150 K

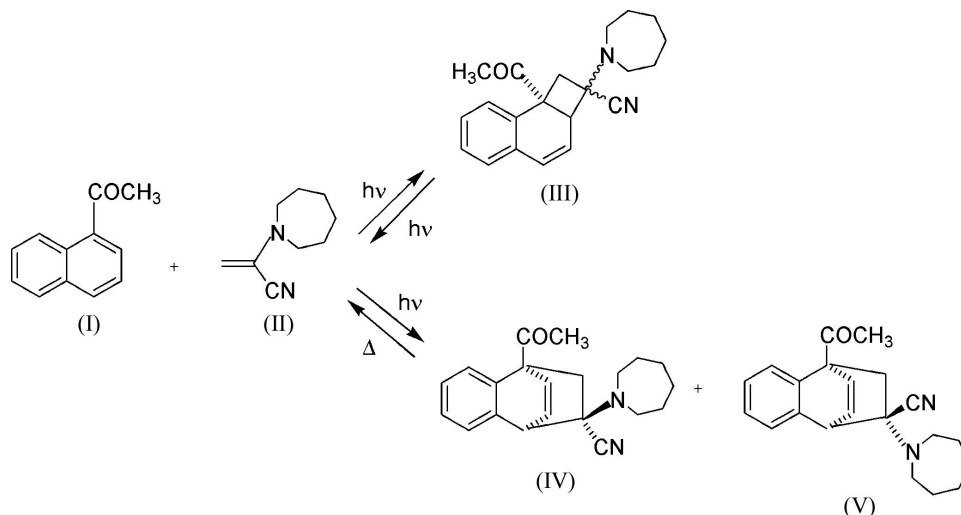
Mean $\sigma(\text{C—C}) = 0.002 \text{ \AA}$

R factor = 0.045

wR factor = 0.112

Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.



Its molecular structure (Fig. 1) is related to that of the pyrrolidinyll compound (Döpp *et al.*, 2006*a*) with azepan-1-yl instead of the pyrrolidinyll group, showing similar geometric features. The slight elongation of the highly restricted C7—C8 bond [1.577 (2) Å] in (IV) is the same as in the known piperidinyll compound (Döpp *et al.*, 2006*b*) and agrees well with the thermal lability of this bond, *e.g.* in the thermal retro-Diels–Alder reaction of compound (IV) (Kruse, 2001). In the ethanonaphthalene unit, the mean planes C7/C10–C12 (*A*), C1/C6/C7/C10 (*B*) and C7–C10 (*C*) make dihedral angles $A/B = 56.55 (8)^\circ$, $A/C = 61.11 (7)^\circ$ and $B/C = 62.34 (8)^\circ$. The methoxy group is almost coplanar with C8—C9—C10, the C9—C10—C13—O1 torsion angle being $8.8 (2)^\circ$. Weak intermolecular C—H···N hydrogen bonds (Table 1) link the molecules into chains extended along [010] (Fig. 2).

Experimental

A solution containing 17.0 mmol each of 1-acetonaphthone [(I), 2.890 g] and 2-hexamethyleneiminopropenenitrile [(II), 2.550 g] in

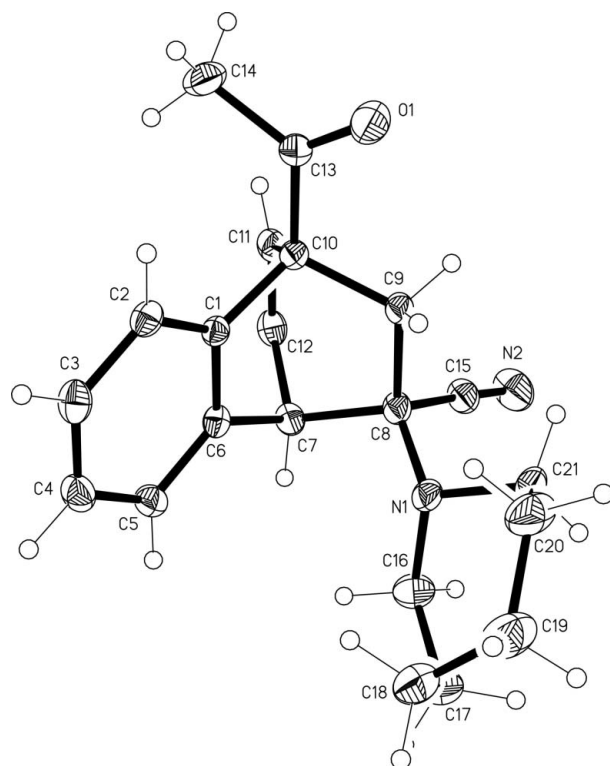


Figure 1
The molecular structure of (IV). Displacement ellipsoids are drawn at the 50% probability level.

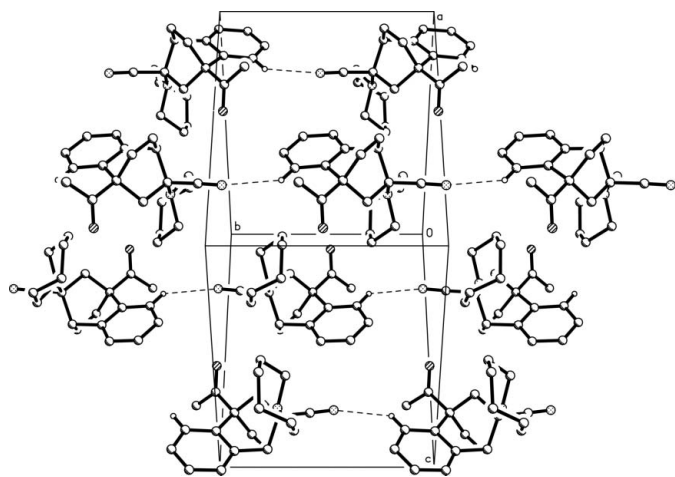


Figure 2
The crystal packing of (IV), viewed along [101], with intermolecular hydrogen bonds indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

170 ml of cyclohexane was irradiated with a 125 W Philips HPK high-pressure mercury lamp through a water-cooled immersion sleeve ($\lambda = 280$ nm) with stirring and continuous argon purging to achieve 45% conversion after 8 h of irradiation. The oily residue obtained by concentration was vigorously stirred with hexane under ice cooling to precipitate all photoadducts while the residual starting materials remained dissolved in the mother liquor. The precipitate was analysed by ^1H NMR spectroscopy and repeatedly crystallized from ethyl acetate/hexane (1:1) with cooling (ice/salt bath) to recover the main photoproduct (IV) (Kruse, 2001).

Crystal data

$\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}$
 $M_r = 320.42$
 Monoclinic, $P2_1/c$
 $a = 13.362$ (4) Å
 $b = 9.718$ (2) Å
 $c = 13.757$ (4) Å
 $\beta = 99.72$ (1)°
 $V = 1760.7$ (8) Å³

$Z = 4$
 $D_x = 1.209$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 150$ (2) K
 Prism, colourless
 $0.56 \times 0.49 \times 0.46$ mm

Data collection

Siemens P4 rotating-anode diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.940$, $T_{\max} = 0.967$
 4023 measured reflections

3860 independent reflections
 2987 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 27.0^\circ$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.112$
 $S = 1.02$
 3860 reflections
 219 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.704P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0034 (9)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{N2}^i$	0.95	2.61	3.358 (2)	136

Symmetry code: (i) $x, y - 1, z$.

H atoms were located in difference Fourier maps and refined at idealized positions riding on the C atoms ($\text{C}-\text{H} = 0.95\text{--}0.99$ Å), with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{methyl C})$. Methyl H atoms were allowed to rotate but not to tip.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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