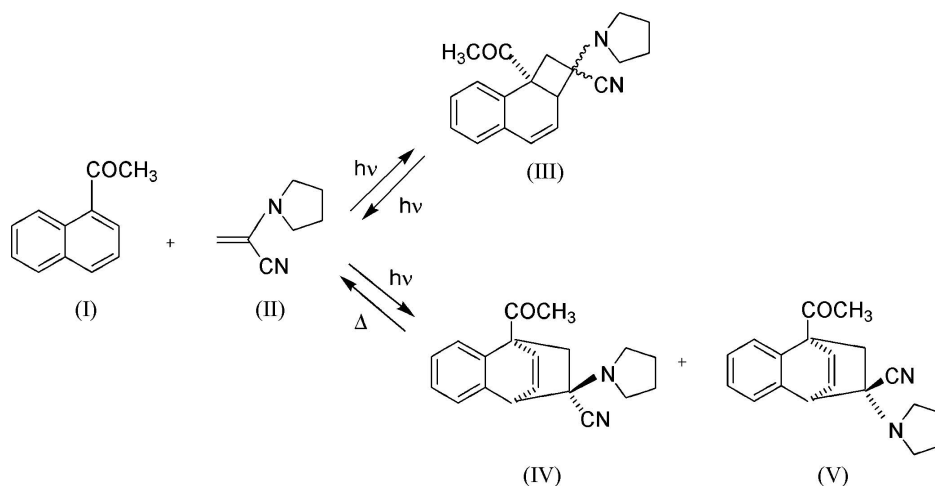


***rel*-(1*R*,4*R*,9*R*)-1-Acetyl-9-(1-pyrrolidinyl)-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitrile: the major [4+2]-photocycloadduct of 1-acetonaphthone with 2-(1-pyrrolidinyl)propenenitrile**Dietrich Döpp,^a Claudia Kruse,^a
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Key indicatorsSingle-crystal X-ray study
T = 150 K
Mean σ (C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.095
Data-to-parameter ratio = 16.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The molecular structure of the title compound, C₁₉H₂₀N₂O, shows elongated C–C single bonds due to their thermal lability. The methyl group forms an intermolecular C–H···N hydrogen bond.Received 26 June 2006
Accepted 4 July 2006**Comment**Regioselective (head-to-tail) photocycloadditions of 2-aminopropenenitriles [such as (II)] to triplet excited 1-acetonaphthone (I) occur in both the [2 + 2] and [4 + 2] modes (Döpp, 2000). Usually, the faster but photoreversible [2 + 2]-addition giving rise to cyclobuta[*a*]naphthalenes [such as (III)] precedes the photo-irreversible (but thermally reversible) [4 + 2]-addition leading to (IV) (major product) and (V) (minor isomer, see scheme). In the [4 + 2]-cycloadduct *rel*-(1*R*,4*R*,9*R*)-(IV), the generally observed (Döpp, 2000) preferential *endo* orientation of the cyclic amino group is once more exhibited. The percentage of any amino-*exo*-oriented C9-epimer of (IV), namely *rel*-(1*R*,4*R*,9*S*)-(V), never exceeds 6% of the total yield of [4 + 2]-adducts (Döpp *et al.*, 1994*a,b*; Döpp, 2000; Pies, 1988).The molecular structure of (IV) (Fig. 1) is related to that of *rel*-(1*R*,4*R*,9*R*)-1-acetyl-9-(*tert*-butylthio)-9-cyano-1,4-dihydro-1,4-ethanonaphthalene, (VI) (Döpp *et al.*, 1989), with *tert*-butylthio instead of the pyrrolidinyl group, showing similar geometric features. The slight elongation of the highly overcrowded C2–C3 bond [1.5801 (15) Å] in (VI) has also been observed in (VA) and agrees well with the thermal lability of this bond, *e.g.* in the thermal retro-Diels–Alder reaction of compound (IV) (Kruse, 2001). The orientation of the pyrrolidine ring is nearly perpendicular to the aromatic C7–C12 plane. The three dihedral angles within the

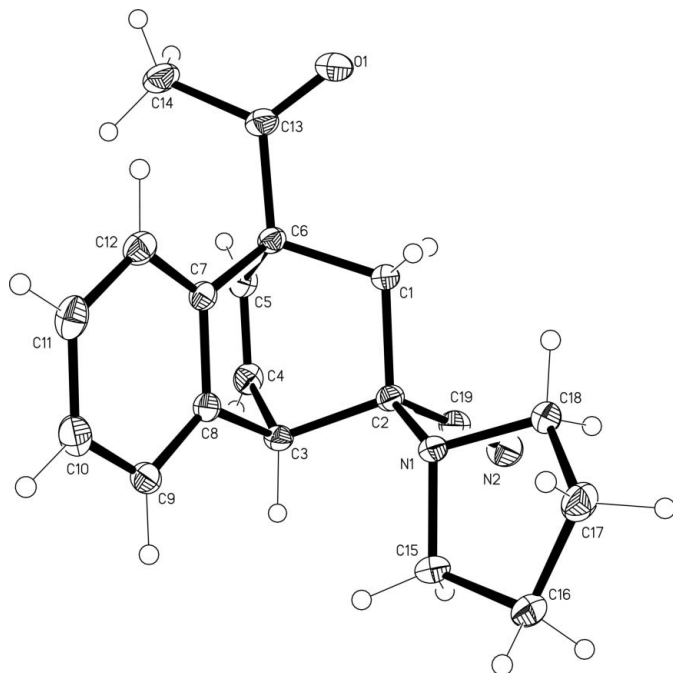


Figure 1
The molecular structure of (IV). Displacement ellipsoids are drawn at the 50% probability level.

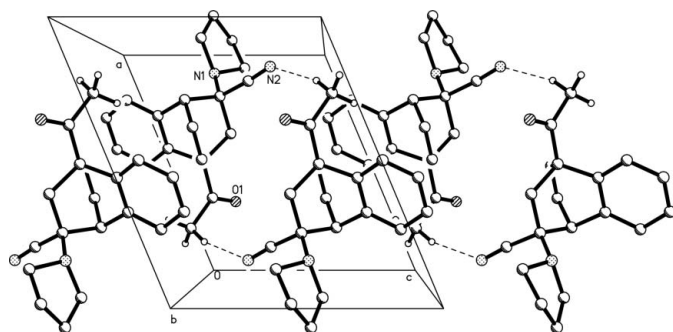


Figure 2
The packing viewed along [010], with intermolecular hydrogen bonds indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

ethanonaphthalene unit are $C3, C4, C7, C8 / C3, C4, C5, C6 = 55.75 (7)$, $C3, C4, C5, C6 / C3, C2, C1, C6 = 61.34 (6)$ and $C3, C4, C7, C8 / C3, C2, C1, C6 = 62.92 (5)^\circ$. The acetyl group is coplanar with $C2-C1-C6$; the relevant torsion angle $C1-C6-C13-O1$ is $-8.58 (15)^\circ$. The crystal packing (Fig. 2) shows only one intermolecular hydrogen bond from the methyl group $C14$, forming a $C14-H14C \cdots N2(-x+1, -y+2, -z)$ bridge, with $H \cdots N = 2.47 \text{ \AA}$ and $C-H \cdots N = 164^\circ$.

Experimental

A solution containing 17.0 mmol each of 1-acetonaphthone [(I), 2.890 g] and 2-(1-pyrrolidinyl)propenenitrile [(II), 2.074 g] in 170 ml of cyclohexane was irradiated with a 125 W Philips HPK high pressure mercury lamp through a water-cooled immersion sleeve ($\lambda = 280 \text{ nm}$) with stirring and continuous argon purging to achieve 44% conversion after 9 h of irradiation. The oily residue resulting from

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

$C_{19}H_{20}N_2O$
 $M_r = 292.37$
Monoclinic, $P2_1/c$
 $a = 9.910 (2) \text{ \AA}$
 $b = 19.443 (3) \text{ \AA}$
 $c = 8.557 (2) \text{ \AA}$
 $\beta = 112.80 (1)^\circ$
 $V = 1519.9 (5) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.278 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 150 (2) \text{ K}$
Prism, colourless
 $0.50 \times 0.25 \times 0.22 \text{ mm}$

Data collection

Siemens P4 diffractometer
 ω scans
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{\min} = 0.961$, $T_{\max} = 0.981$
5650 measured reflections
3319 independent reflections

2964 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 27.0^\circ$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.06$
3319 reflections
202 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.57P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: $0.0073 (14)$

H atoms were located in difference Fourier maps, idealized, and refined as riding on the C atoms ($C-H = 0.95-0.99 \text{ \AA}$) with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{methyl C})$.

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*.

DD is indebted to Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for their generous support.

References

- Bruker (2002). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Döpp, D. (2000). *Organic, Physical and Materials Photochemistry (Molecular and Supramolecular Photochemistry, Vol. 6)*, edited by V. Ramamurthy & K. S. Schanze, pp. 101–148. New York: Marcel Dekker.
Döpp, D., Memarian, H. R., Krüger, C. & Raabe, E. (1989). *Chem. Ber.* **122**, 585–588.
Döpp, D. & Mlinaric, B. (1994a). *ACH - Models in Chemistry*, **131**, 377–381.
Döpp, D. & Mlinaric, B. (1994b). *Bull. Soc. Chim. Belg.* **103**, 449–452.
Kruse, C. (2001). PhD thesis, Duisburg University, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Pies, M. (1988). PhD thesis, Duisburg University, Germany.
Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.