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Key indicators

Single-crystal X-ray study

T = 150 K

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

R factor = 0.032

wR factor = 0.080

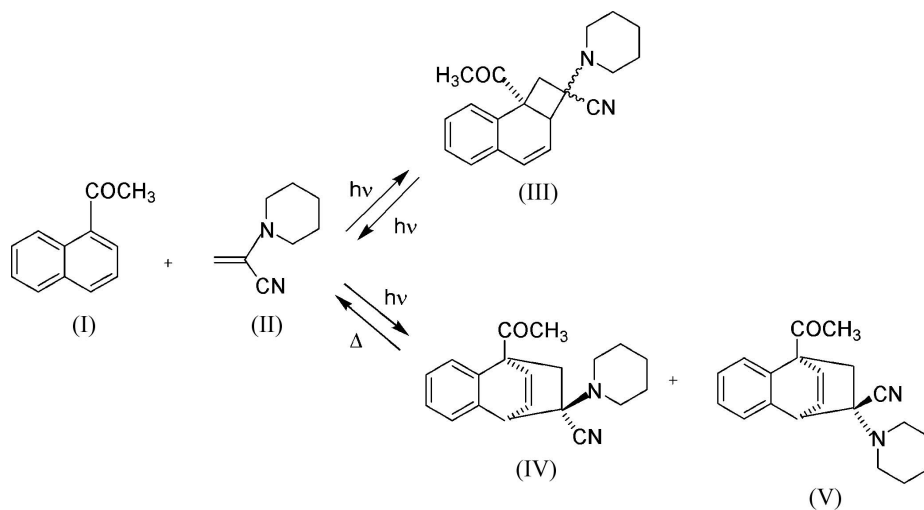
Data-to-parameter ratio = 10.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*rel*-(1*R*,4*R*,9*R*)-1-Acetyl-9-(1-piperidinyl)-1,4-di-
hydro-1,4-ethanonaphthalene-9-carbonitrile

The molecular structure of the title compound, $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}$, shows elongated C–C single bonds due to their thermal lability. The crystal packing shows molecules linked *via* intermolecular C–H \cdots O hydrogen bonds, forming infinite chains along [010].

Comment

Regioselective (head-to-tail) photocycloadditions of 2-amino-1-propenenitriles [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 [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 demonstrated. 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 VAKBAK (Döpp *et al.*, 1989; refiled in the Cambridge Structural Database; *MOGUL*, Version 1.0; Allen, 2002) with *tert*-butylthio instead of the piperidinyl group, showing similar geometric features. The slight elongation of the highly restricted C7–C8 bond [1.5777 (19) Å] in (IV) has also been observed in VAKBAK 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

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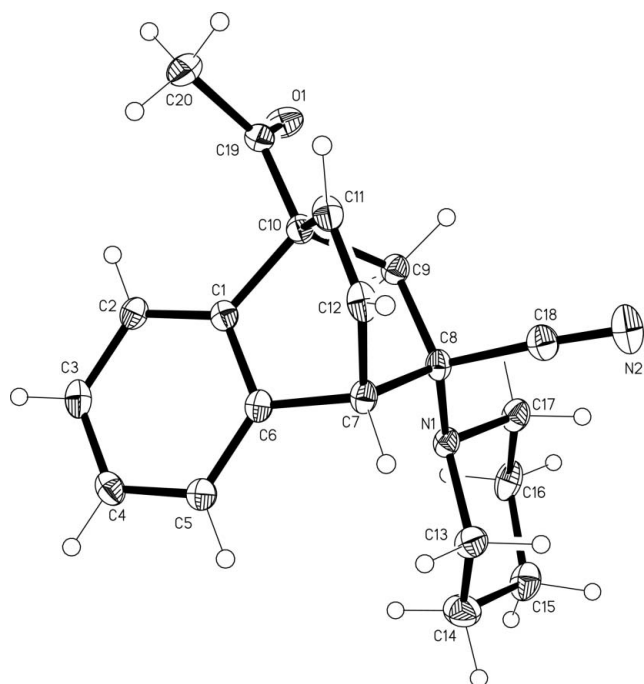


Figure 1
The molecular structure of (IV). Displacement ellipsoids are drawn at the 50% probability level.

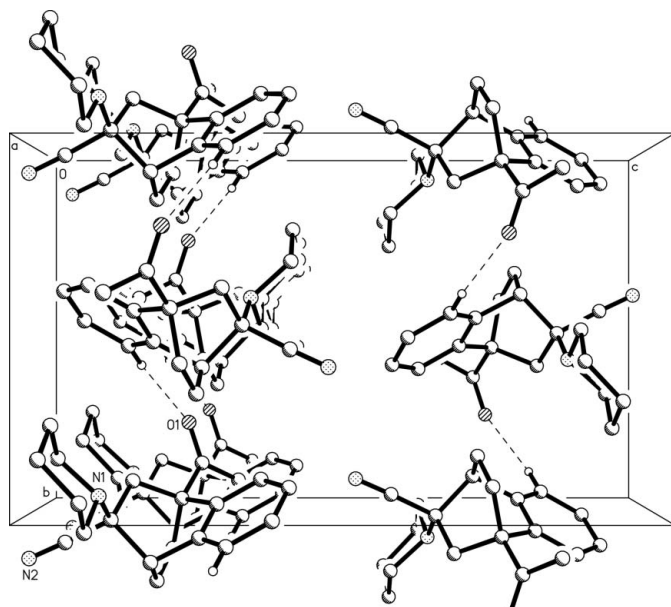


Figure 2
Crystal packing, viewed along [100], with the intermolecular hydrogen-bonding pattern indicated by dashed lines. H atoms not involved have been omitted.

the piperidine ring is nearly perpendicular to the aromatic C1–C6 plane. The three dihedral angles within the ethanonaphthalene unit are 56.00 (7), 61.0 (1) and 62.77 (6)°. The methoxy group is almost coplanar with C8–C9–C10; the relevant torsion angle C1–C6–C13–O1 measures 18.6 (2)°. The crystal packing (Fig. 2) shows a prominent intermolecular hydrogen bond C5–H5A···O1(–x, y + ½, –z + ½), with

H···O = 2.48 Å and C–H···O = 163° that gives rise to infinite chains of molecules along [010].

Experimental

A solution containing 17.0 mmol each of 1-acetonaphthone [(I); 2.890 g] and 2-(1-piperidiny)propenenitrile [(II); 2.312 g] in 170 ml of cyclohexane was irradiated with a 125 W Philips HPK high pressure mercury lamp through a water-cooled immersion sleeve ($\lambda = 280$ nm) with stirring and continuous argon purging to achieve 42% conversions after 8 h of irradiation. The oily residue resulting from concentration was vigorously stirred with hexane under ice cooling to precipitate all photoadducts while 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

$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}$
 $M_r = 306.40$
Orthorhombic, $P2_12_12_1$
 $a = 8.869$ (2) Å
 $b = 10.552$ (2) Å
 $c = 17.902$ (4) Å
 $V = 1675.4$ (6) Å³

$Z = 4$
 $D_x = 1.215$ Mg m^{–3}
Mo $K\alpha$ radiation
 $\mu = 0.08$ mm^{–1}
 $T = 150$ (2) K
Prism, colourless
 $0.59 \times 0.22 \times 0.22$ mm

Data collection

Siemens P4 rotating-anode diffractometer
 ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.961$, $T_{\max} = 0.981$
3963 measured reflections

2103 independent reflections
1923 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 27.0^\circ$
3 standard reflections every 100 reflections
intensity decay: <0.01%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.080$
 $S = 1.02$
2103 reflections
209 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.3818P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22$ e Å^{–3}
 $\Delta\rho_{\min} = -0.16$ e Å^{–3}
Extinction correction: SHELXL97
Extinction coefficient: 0.045 (2)

Table 1

Selected geometric parameters (Å, °).

N1–C8	1.4739 (18)	C8–C9	1.565 (2)
C1–C10	1.5385 (19)	C9–C10	1.5623 (19)
C6–C7	1.5158 (19)	C10–C19	1.525 (2)
C7–C12	1.516 (2)	C10–C11	1.525 (2)
C7–C8	1.5777 (19)	C11–C12	1.322 (2)
C8–C18	1.503 (2)		
C6–C7–C12	108.42 (11)	C10–C9–C8	110.66 (11)
C6–C7–C8	106.49 (11)	C19–C10–C11	115.09 (12)
C12–C7–C8	105.35 (11)	C19–C10–C1	110.12 (11)
N1–C8–C18	110.12 (12)	C11–C10–C1	107.25 (11)
N1–C8–C9	109.95 (11)	C19–C10–C9	111.91 (12)
C18–C8–C9	109.70 (12)	C11–C10–C9	106.96 (11)
N1–C8–C7	112.40 (11)	C1–C10–C9	104.91 (11)
C18–C8–C7	107.34 (11)	C12–C11–C10	113.86 (13)
C9–C8–C7	107.25 (11)	C11–C12–C7	115.28 (13)

H atoms were located in difference Fourier maps and refined at idealized positions ($C-H = 0.95-1.00 \text{ \AA}$) riding on the C atoms with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ and $1.5U_{\text{eq}}(\text{methyl C})$. Methyl H atoms were allowed to rotate but not to tip. The title compound crystallizes in the non-centrosymmetric space group $P2_12_12_1$; however, in the absence of significant anomalous scattering effects, the Flack (1983) parameter is essentially meaningless. Accordingly, Friedel pairs were merged.

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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