differences from those of an ideal benzene ring. All H-atom positions (except for the hydroxyl H1O atom) were calculated using a riding model and were considered with fixed isotropic U values in all refinements. The H1O atom was located in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density and was not refined.

Data collection: *Nonius Diffractometer Control Software* (Nonius, 1993). Cell refinement: *Nonius Diffractometer Control Software*. Data reduction: *REDU*4 (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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(1*RS*,10a*RS*)-3-Imino-1-(2-thienyl)-1,2,3,9,10,10a-hexahydrophenanthrene-2,2,4-tricarbonitrile

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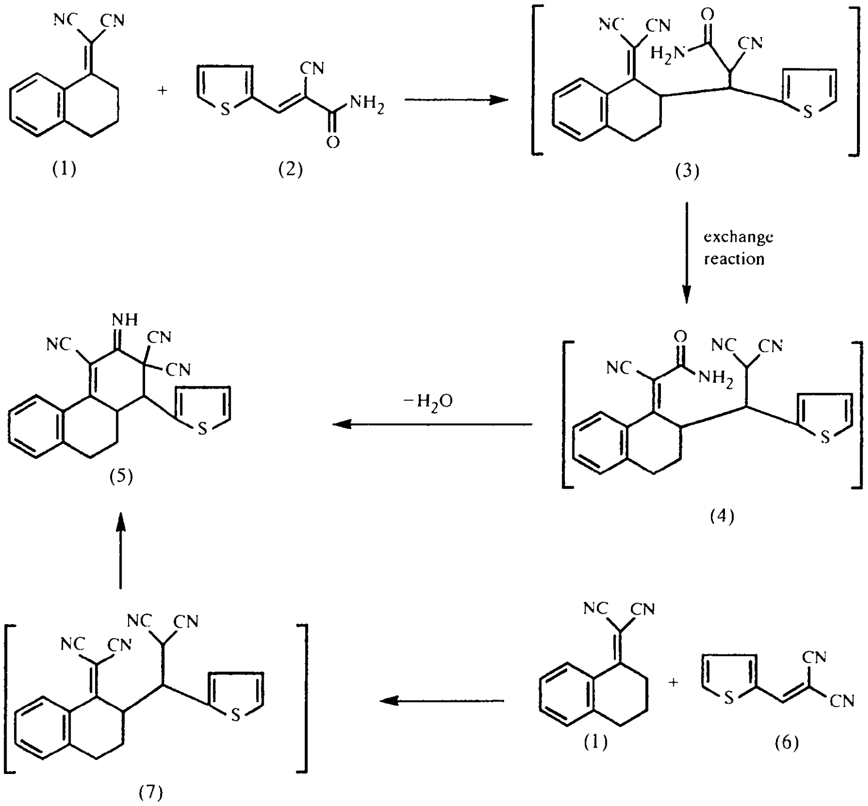
Abstract

The title compound, $C_{21}H_{14}N_4S$, involves an exocyclic imino (C=NH) bond of 1.264 (3) Å. The relative stereochemistry at the two chiral centres is (*R*,*R*). The non-aromatic rings adopt half-chair conformations. The molecules are linked in centrosymmetric pairs by C=N—H···NC hydrogen bonds.

Comment

The highly reactive α,β-unsaturated nitriles have been extensively utilized in heterocyclic synthesis (Elgemeie, Elghandour, Elzanate & Hussein, 1997; Elgemeie, Elghandour, Ali & Hussein, 1997). We now report the novel reaction of 1,2,3,4-tetrahydro-1-naphthylidenemalononitrile, (1), with β-(2-thienylmethylidene)-(cyano)acetamide, (2), to give a product identified as the unexpected phenanthrene, (5). The reaction is assumed to be initiated by an exchange process between the tetrahydronaphthylidene group of (1) and the thienylmethylidene group of (2), to give the intermediate (4), which then cyclizes *via* elimination of water to give (5). We also investigated the reaction between (1) and β-(2-thienylmethylidene)malononitrile, (6), under the same conditions. The product was identified as the same as



that obtained from the reaction of (1) and (2) (thin-layer chromatography, melting point measurement and spectral data). An X-ray structure determination was undertaken to establish the nature of the product unambiguously.

The molecule of (5) is shown in Fig. 1. Bond lengths and angles are essentially normal [*e.g.* C3=N4 1.264 (3) Å], except for a widening of the C4—C3—N4 angle at the expense of C2—C3—C4 [129.0 (2) *vs.* 114.2 (2)°]. The relative stereochemistry at the chiral centres C1 and C10a is (*R*,*R*); Fig. 1 shows the (*S*,*S*) enantiomer.

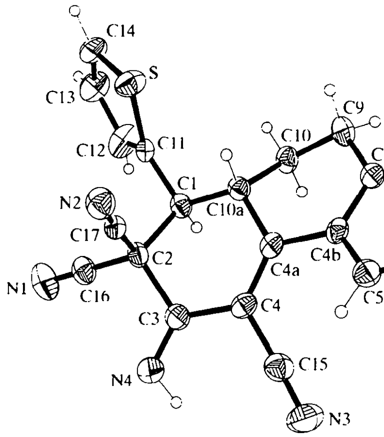


Fig. 1. The molecule of the title compound, (5), in the crystal. Displacement ellipsoids represent 50% probability levels. H-atom radii are arbitrary. Only one position of the disordered thienyl ring is shown (see text).

The non-aromatic rings both adopt a half-chair conformation (about C4b—C8a and C4—C4a, respectively), although the ring bearing the cyano groups is less ideal and is further flattened by the additional (exocyclic) double bond.

The molecules are linked in centrosymmetric pairs by weak hydrogen bonds, N4—H04···N3 (1 − *x*, 1 − *y*, −*z*), with N—H 0.85 (2), H···N 2.43 (3) and N···N 3.120 (4) Å, and N—H···N 139 (2)°.

Experimental

To a mixture of (1) and (2), or (1) and (6) [0.01 mol of each, in 50 ml ethanol] piperidine (0.5 ml) was added. The reaction mixture was stirred at room temperature until reaction was complete (thin-layer chromatography) and then set aside overnight. The resultant precipitate was filtered off and crystallized from ethanol (m.p. 506 K, yield 80%).

Crystal data

$C_{21}H_{14}N_4S$
M_r = 354.42
Mo *K*α radiation
λ = 0.71073 Å

Monoclinic
$P2_1/c$
$a = 14.131\,(3)$ Å
$b = 8.281\,(2)$ Å
$c = 15.473\,(3)$ Å
$\beta = 108.36\,(2)^\circ$
$V = 1718.3\,(6)$ Å^3
$Z = 4$
$D_x = 1.370$ Mg m^{-3}
D_m not measured

Cell parameters from 59 reflections
$\theta = 2.5$–12.0°
$\mu = 0.200$ mm^{-1}
$T = 173\,(2)$ K
Tablet
$0.6 \times 0.3 \times 0.1$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3015 measured reflections
3005 independent reflections
1515 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.009$

$\theta_{\rm max} = 25^\circ$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 17$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.078$
$S = 0.791$
3005 reflections
260 parameters
H-atom treatment: see below
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.002$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—C10a	1.537 (3)	C4a—C4b	1.479 (3)
C1—C2	1.571 (3)	C4a—C10a	1.510 (3)
C2—C3	1.540 (3)	C4b—C8a	1.404 (3)
C3—N4	1.264 (3)	C8a—C9	1.508 (3)
C3—C4	1.477 (3)	C9—C10	1.517 (3)
C4—C4a	1.355 (3)	C10—C10a	1.538 (3)
N4—C3—C4	129.0 (2)	C4—C3—C2	114.2 (2)
N4—C3—C2	116.8 (2)		
C10a—C1—C2—C3	−60.9 (2)	C4b—C8a—C9—C10	−17.1 (3)
C1—C2—C3—C4	45.0 (3)	C8a—C9—C10—C10a	47.4 (3)
C2—C3—C4—C4a	−8.4 (4)	C4—C4a—C10a—C1	−5.1 (3)
C3—C4—C4a—C10a	−13.3 (4)	C4b—C4a—C10a—C10	49.9 (3)
C10a—C4a—C4b—C8a	−20.7 (3)	C2—C1—C10a—C4a	41.9 (3)
C4a—C4b—C8a—C9	3.1 (4)	C9—C10—C10a—C4a	−63.7 (3)

The thienyl ring is disordered over two positions (rotated by *ca* 180° about the C4—C11 bond), with occupancies of 0.831 (3) and 0.169 (3). The atoms of the minor component were refined with isotropic displacement parameters. An extensive system of similarity restraints was employed; the final instruction file, including full details of the restraints, is included in the supplementary material. The weak diffraction is accounted for by the disorder. The H atom on N4 was located on a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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3,3′-[Ethane-1,2-diylbis(aminomethylene)]-bis(pentane-2,4-dione) and the Nickel(II) Complex of a Condensation Product

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Abstract

3,3′-[Ethane-1,2-diylbis(aminomethylene)]bis(pentane-2,4-dione) [$C_{14}H_{20}N_2O_4$, (1)] displays crystallographic twofold symmetry. The N—H function forms the donor part of a three-centre hydrogen bond, with two oxygen acceptors. [6,13-Diacetyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2−)-κ^4N]-nickel(II) bis(deuterochloroform) solvate {[Ni($C_{16}H_{22}$-N_4O_2)].2$CDCl_3$, (2)} is a nickel complex of a condensation product of (1). It displays non-crystallographic inversion symmetry, with square-planar geometry at nickel and Ni—N bond lengths of 1.881 (3) and 1.882 (3) Å to N1 and N8 (with a neighbouring α-methyl group), respectively, and bond lengths of