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6-Methyl-11*a*,12-dihydro-6*H*-quino-[3,2-*b*][1,4]benzothiazine: an amidine formed under unusual conditions

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.041
wR factor = 0.099
Data-to-parameter ratio = 7.1

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

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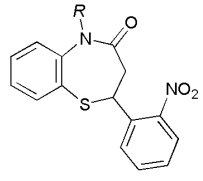
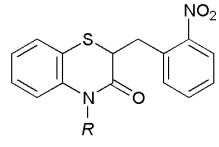
The crystal structure determination of the title compound, $C_{16}H_{14}N_2S$, confirms the amidine nature of this reaction product. In *N*,*N*′-diphenylamidines both phenyl groups are nearly orthogonal with the N—C(—C)=N grouping, whereas in this constrained amidine the benzene groups are substantially less twisted [C—C—N—C torsion angles = −17.2 (7) and 38.1 (6)°]. The result is a slightly cupped molecule with the ring-fused benzene rings appearing like the extended wings of a butterfly. The S—C distances of 1.807 (4) and 1.760 (5) Å are significantly different, with the shorter distance representing the S—C bond to a benzene ring.

Comment

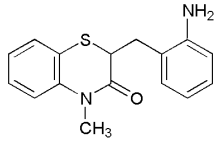
A literature procedure (Levai, 1980) reporting formation of (1*a*) as the sole product gave, in our hands, two products (1*a*) and (2*a*), whose ratio varied with reaction time and conditions. Subsequent treatment of (2*b*), obtained by methylation of (2*a*) (Gaino *et al.*, 1983), with excess tin(II) chloride (in ethanol, under reflux), did not produce the expected aniline derivative, (3). Instead, based on spectroscopic data, amidine (4) was proposed as the product (Bates & Li, 2002). In view of the possibility of equilibration between skeletons (1) and (2) and the unprecedented formation of an amidine under the conditions of the reaction, it was concluded that structural confirmation of (4) *via* an X-ray diffraction study was warranted. The four fused rings in (4) are loosely arranged along the *c* axis, with the benzene rings at the ends oriented towards the −*b* axis (Fig. 2).



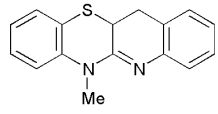
(1*a*) *R* = H
(1*b*) *R* = Me



(2*a*) *R* = H
(2*b*) *R* = Me



(3)



(4)

Experimental

The crystal was obtained by placing a test tube of a solution of the compound in ethyl acetate in a sealed chamber containing *n*-hexane and leaving the system undisturbed at room temperature until the crystal formed.

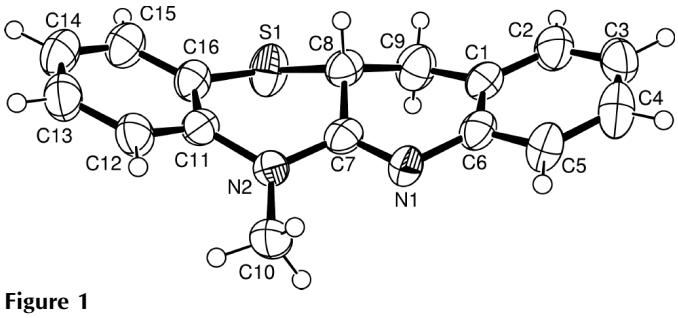


Figure 1
View of (4), with displacement ellipsoids shown at the 50% probability level.

Crystal data

$C_{16}H_{14}N_2S$
$M_r = 266.35$
Orthorhombic, $Pca2_1$
$a = 22.775$ (4) Å
$b = 5.381$ (1) Å
$c = 10.587$ (2) Å
$V = 1297.5$ (4) Å^3
$Z = 4$
$D_x = 1.364$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–25°
$\mu = 0.24$ mm^{-1}
$T = 293$ (2) K
Irregular, white
0.40 × 0.30 × 0.08 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.954$, $T_{max} = 0.977$
1274 measured reflections
1214 independent reflections
844 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.0^\circ$
$h = -1 \rightarrow 27$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.099$
$S = 1.07$
1214 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

H atoms were positioned geometrically and allowed to ride on their respective atoms. Not enough Friedel pairs were measured to determine a reasonable Flack (1983) parameter.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

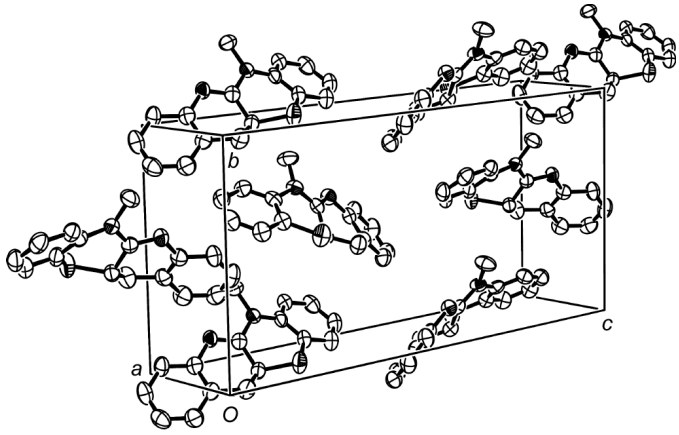


Figure 2
Packing diagram for (4). H atoms have been omitted.

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