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Azinyl sulfides. L.[1] 14-Methyl-1,4-thiazino[2,3-*c*;6,5-*c*′]diquinoline

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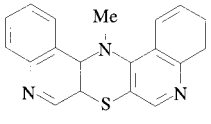
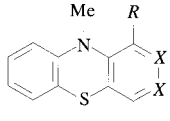
The title compound, $C_{19}H_{13}N_3S$, is folded, with the central ring in a boat conformation. The folding angle between the two quinoline rings is 150.2 (1)°. The 14-methyl substituent is in a quasi-axial orientation with respect to the thiazine ring. The S···N—C_{methyl} angle is 120.1 (1)°.

Comment

Quinolines condensed with certain heterocycles have recently become important compounds because of their affinity to the benzodiazepine receptors (Moreau *et al.*, 1988; Anzini *et al.*, 1990). On the other hand, tricyclic phenothiazines and azaphenothiazines constitute a major class of pharmaceutical agents with beneficial antipsychotic, central nervous system antidepressant and antihistaminic properties (Reynolds, 1989; Horn, 1990). These compounds are of interest in determining the constitution (synthesis with or without the Smiles rearrangement stage) and the effects of the nature and position of the substituents on the conformation and configuration (a rigid orientation of the 10-substituent) of the tricyclic ring system, and on the pharmaceutical activity (Sainsbury, 1978; Andreetti *et al.*, 1980; de Meester *et al.*, 1985; Baranski *et al.*, 1990). The purpose of this study of 14-methyl-1,4-thiazino-[2,3-*c*;6,5-*c*′]diquinoline, (I), is to determine the effect of two additional benzene rings on the configuration and conformation of pentacyclic dibenzoazaphenothiazine and to compare the results with the structures of the related tricyclic phenothiazines, (II)–(IV).



(I)



(II) X = CH, R = H
(III) X = N, R = H
(IV) X = N, R = Cl

The configuration of the molecule of (I) and the atom-numbering scheme are shown in the *ORTEP*II (Johnson, 1976) drawing in Fig. 1. The molecule as a whole is not planar and the butterfly angle between two quinoline planes is 150.2 (1)°. The central thiazine ring has a boat conformation, with N3 and S1 0.352 (1) and 0.519 (1) Å, respectively, out of the basal plane formed by C3, C4, C13 and C14. The dihedral angle between the planes determined by the atoms of the two halves of the thiazine ring (*i.e.* S1/C3/C4/N3 and S1/C13/C14/-N3) is 142.8 (7)°.

The thiazine N atom N3 shows pyramidality. It is worth noting that the quinoline rings are non-planar, with dihedral angles between the pyridine and benzene rings of 3.5 (1) and 3.7 (1)°, respectively.

Selected bond lengths and angles are given in Table 1. Whereas the N3—C4 and N3—C14 bond lengths are very similar to those found in other *N*-methylphenothiazine and *N*-methylazaphenothiazines, (II)–(IV), the N3—C_{methyl} bond lengths are different regardless of the type of aromatic ring or the C—N—C and dihedral angles [1.474 (2) *versus* 1.455 in (II), 1.490 in (III) and 1.385 Å in (IV)]. The C3—S1—C13 and C4—N3—C14 bond angles do not differ from the values found in the tricyclic *N*-methylarenothiazines (II)–(IV) (Andreetti *et al.*, 1974, 1980; Chu & van der Helm, 1974).

The most unexpected molecular feature of (I) is the orientation of the methyl substituent. In contrast to all known *N*-substituted phenothiazines and azaphenothiazines, the methyl substituent is here in a quasi-axial orientation with the respect to the thiazine ring, with torsion angles C3—C4—N3—C21 and C13—C14—N3—C21 of −114.1 (2) and 113.2 (2)°, respectively. The S···N—C_{methyl} angle is 120.1 (1)°, which is significantly smaller than values found in *N*-methylarenothiazines (153.7–168.1°; Andreetti *et al.*, 1974, 1980; Chu & van der Helm, 1974).

There are very close contacts between the methyl group and the H6(—C6) and H16(—C16) atoms. The C21···H6 and C21···H16 distances are 2.76 Å, which is less than the sum of the van der Waals radii of the CH_3 and H atoms (3.20 Å; Pauling, 1960). These steric interactions cause deshielding of the H6, H16 and CH_3 protons, as shown in the ^{1}H NMR spectrum by values of 0.26–0.38 p.p.m., in comparison with the

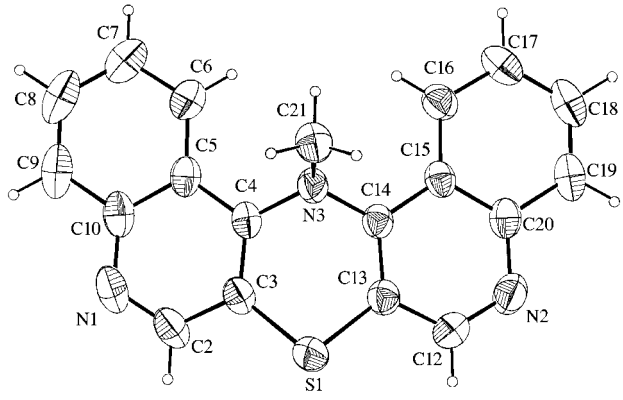


Figure 1
An *ORTEP*II (Johnson, 1976) view of the molecule of compound (I) with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

[1] Part XLIX: Skrzypek & Maslankiewicz (1997).

analogous protons in the 4-methylaminoquinoline derivatives (Maślankiewicz & Skrzypek, 1994; Skrzypek, 1997, unpublished data).

Experimental

Compound (I) was synthesized and purified as reported previously by Pluta (1997). Single crystals suitable for X-ray data collection were obtained on slow evaporation from an *N*,*N*-dimethylformamide solution.

Crystal data

$C_{19}H_{13}N_3S$
M_r = 315.38
Monoclinic, $P2_1/c$
a = 11.848 (3) Å
b = 11.015 (4) Å
c = 12.313 (4) Å
β = 109.01 (3)°
V = 1519.3 (8) Å^3
Z = 4
D_x = 1.379 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 6–14°
μ = 0.215 mm^{-1}
T = 293 (2) K
Prism, yellow
0.82 × 0.28 × 0.21 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4597 measured reflections
4409 independent reflections
3052 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 30.04°
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.109
S = 1.140
4315 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.0125P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0118 (18)

All of the H atoms were treated as riding on their parent C atom, with $U_{iso}(H) = 1.2U_{eq}(C)$ except for the methyl-H atoms where $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP-Plus* (Frenz, 1985); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1091). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

S1—C13	1.7608 (15)	N2—C12	1.311 (2)
S1—C3	1.766 (2)	N2—C20	1.369 (2)
N1—C2	1.314 (2)	C14—N3	1.415 (2)
N1—C10	1.364 (2)	N3—C21	1.474 (2)
C4—N3	1.413 (2)		
C13—S1—C3	97.79 (7)	N2—C12—C13	124.11 (14)
C2—N1—C10	117.66 (13)	C14—C13—S1	120.96 (10)
N1—C2—C3	123.8 (2)	C12—C13—S1	119.19 (11)
C4—C3—S1	121.44 (10)	C13—C14—N3	122.43 (12)
C2—C3—S1	118.86 (12)	N3—C14—C15	119.45 (12)
C3—C4—N3	121.93 (12)	N2—C20—C19	118.12 (13)
N3—C4—C5	119.64 (12)	N2—C20—C15	123.03 (13)
N1—C10—C5	123.09 (14)	C4—N3—C14	117.15 (11)
N1—C10—C9	118.65 (14)	C4—N3—C21	117.82 (11)
C12—N2—C20	117.24 (12)	C14—N3—C21	116.82 (11)
C13—S1—C3—C4	−32.09 (13)	C3—C4—N3—C21	−114.07 (15)
S1—C3—C4—N3	4.1 (2)	C5—C4—N3—C21	68.2 (2)
C3—S1—C13—C14	30.91 (12)	C13—C14—N3—C4	−34.7 (2)
S1—C13—C14—N3	−2.1 (2)	C13—C14—N3—C21	113.16 (15)
C3—C4—N3—C14	33.5 (2)		

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