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The Structures of 2-(2,6-Dichlorophenyl)imino-3-methylperhydro-1,3-thiazine, 2-(2,6-Dimethylphenyl)imino-3-methylperhydro-1,3-thiazine and 2-[N-(2,6-Dimethylphenyl)-N-methylamino]-4,5-dihydro-6H-1,3-thiazine

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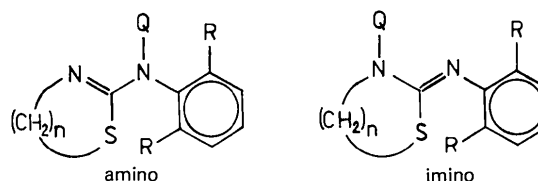
Abstract

The structures of the title compounds have been established by X-ray crystallography from diffractometer data. Crystals of the first, $C_{11}H_{12}Cl_2N_2S$ (III), are monoclinic, space group $P2_1/c$, with $a = 12.741$ (6), $b = 9.636$ (5), $c = 20.432$ (8) Å, $\beta = 96.36$ (4)°, $Z = 8$. Crystals of the second, $C_{13}H_{18}N_2S$ (IV), are orthorhombic, space group $Pna2_1$, with $a = 15.169$ (7), $b = 9.775$ (3), $c = 8.801$ (3) Å, $Z = 4$. Crystals of the third, $C_{13}H_{18}N_2S$ (V), are monoclinic, space group $P2_1/c$, with $a = 12.118$ (8), $b = 7.709$ (7), $c = 14.658$ (11) Å, $\beta = 105.76$ (9)°, $Z = 4$. The structures were refined to $R = 0.051$ for 2919 reflexions of (III), $R = 0.063$ for 1261 reflexions of (IV) and $R = 0.095$ for 1405 reflexions of (V). The characteristic features of the geometries (amino or imino form) of the cyclic amidine (thiourea) groups in 2-arylamino-1,3-thiazines and their dependence on the position of substituent (H, alkyl, acyl) are shown and discussed. The mean $S^{II}-C(sp^3)$ and $S^{II}-C(sp^2)$ lengths [1.803 (5) and 1.766 (3) Å] for the title compounds and other structures discussed indicate single bonds and agree well with expected values.

Introduction

In the course of a systematic X-ray analysis of various 2-arylamino(imino)thiazoli(d)ines ($n = 2$) (Argay,

Kálmán, Lazar, Ribár & Tóth, 1977; Kálmán & Argay, 1978*b*, and references therein) and analogous 1,3-thiazines ($n = 3$),



the structures of 2-phenyliminoperhydro-1,3-thiazine (I) and 2-(2,6-dimethylphenyl)iminoperhydro-1,3-thiazine (II) (Kálmán, Argay, Ribár & Toldy, 1977; Argay, Kálmán, Kapor & Ribár, 1977) together with two derivatives of (II) with $Q =$ methylsulphonyl [hereinafter (VI) for the *endo* and (VII) for the *exo* substituent] have been published (Kálmán & Argay, 1978*a*; Kálmán, Argay & Vassányi, 1977). Now we report the structures of three methyl derivatives ($n = 3$, $Q =$ Me) termed as (III), (IV) and (V). The differences among these three structures [(III): $R =$ Cl, Q *endo*; (IV): $R =$ Me, Q *endo*; (V): $R =$ Me, Q *exo*] allow the study of their effects upon the electronic structures (geometries) of the amidine groups. They allow us also to corroborate our conclusions that the predominant tautomeric form ($Q =$ H *endo*) of (I) and (II) and their thiazolidine analogues (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977; Argay, Kálmán, Lazar, Ribár & Tóth, 1977) could be distinguished unambiguously on the basis of five inequalities observed for the bond lengths

and angles in the cyclic amidine (thiourea) moieties (Kálmán, Argay, Ribár & Toldy, 1977).

Experimental

Compound (III), 2-(2,6-dichlorophenyl)imino-3-methylperhydro-1,3-thiazine

Crystal data. $C_{11}H_{12}Cl_2N_2S$, $M_r = 275.2$, monoclinic, $a = 12.741$ (6), $b = 9.636$ (5), $c = 20.432$ (8) Å, $\beta = 96.36$ (4)°, $V = 2493.0$ Å³, $D_c = 1.465$ Mg m⁻³, $Z = 8$ (two molecules in the asymmetric unit), $F(000) = 1136$, $\mu[\lambda(\text{Mo } K\alpha) = 0.7107 \text{ Å}] = 0.60 \text{ mm}^{-1}$, space group $P2_1/c$.

Intensities of 3069 independent reflexions were collected on a Philips PW 1100 computer-controlled four-circle diffractometer equipped with a graphite monochromator. After data reduction, 2919 reflexions with $F - 5\sigma(F) > 0$ were taken as observed. No absorption correction was applied.

The structure was solved with *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) from 300 reflexions with $E \geq 1.55$. The E map revealed the positions of 22 of the 32 non-hydrogen atoms which were used to phase a Fourier synthesis ($R = 0.24$). Block-diagonal least-squares refinement of the positional parameters, and anisotropic thermal parameters for non-hydrogen atoms with Cruickshank's weighting scheme $w = (9.6 + F_o + 0.0017F_o^2)^{-1}$, reduced R to 0.06. At this stage H-atom positions were generated from assumed geometries and verified by a difference map. Introduction of the H atoms reduced R to 0.051 ($R_{\text{total}} = 0.053$ for the 3069 reflexions). Scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).

Compound (IV), 2-(2,6-dimethylphenyl)imino-3-methylperhydro-1,3-thiazine

Crystal data. $C_{13}H_{18}N_2S$, $M_r = 234.3$, orthorhombic, $a = 15.169$ (7), $b = 9.775$ (3), $c = 8.801$ (3) Å, $V = 1305.0$ Å³, $D_c = 1.192$ Mg m⁻³, $Z = 4$, $F(000) = 504$, $\mu[\lambda(\text{Mo } K\alpha) = 0.7107 \text{ Å}] = 0.18 \text{ mm}^{-1}$, space group $Pna2_1$ (from systematic absences and refinement).

Intensities of 1261 independent reflexions were collected on a Philips PW 1100 diffractometer equipped with a graphite monochromator. After data reduction 1252 reflexions with $F - 2\sigma(F) > 0$ were taken as observed. No absorption correction was performed.

The coordinates of the S atom were determined by the Patterson method. Successive cycles of structure factor and Fourier calculations revealed the positions of all non-hydrogen atoms ($R = 0.34$). The structure was refined anisotropically to $R = 0.078$ by block-

diagonal least squares with a program of Albano, Domenicano & Vaciano (1966) adapted for use on a Varian 73 computer at Novi Sad. From this stage, refinement was continued with *SHELX* (Sheldrick, 1976) adapted for use on a CDC 3300 computer in Budapest. Prior to this part of refinement, all H atoms were generated assuming staggered methyl groups and with the C-H lengths constrained to 1.08 Å. These moieties together with the phenyl group were refined as rigid groups. Blocked full-matrix refinement of the non-hydrogen atoms resulted in a final $R = 0.063$ [$R_G = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.115$] for the observed reflexions. The weights were $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where k and g refined to 1.000 and 0.0216, respectively. A bonded H-atom scattering factor was employed (Stewart, Davidson & Simpson, 1965) with complex neutral scattering factors for the remaining atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970).

Compound (V), 2-[N-(2,6-dimethylphenyl)-N-methylamino]-4,5-dihydro-6H-1,3-thiazine

Crystal data. $C_{13}H_{18}N_2S$, $M_r = 234.3$, monoclinic, $a = 12.118$ (8), $b = 7.709$ (7), $c = 14.658$ (11) Å, $\beta =$

Table 1. Fractional coordinates ($\times 10^4$) and mean temperature factors for non-hydrogen atoms of (III)

E.s.d.'s are given in parentheses.

	x	y	z	B_i (Å ²)
S(1)	5684 (1)	5498 (2)	4264 (1)	4.6 (1)
C(2)	6623 (4)	4829 (5)	3776 (2)	3.1 (2)
N(3)	7491 (3)	5560 (4)	3674 (2)	3.9 (2)
C(4)	7712 (5)	6971 (6)	3922 (4)	5.6 (3)
C(5)	6803 (7)	7812 (7)	4014 (5)	7.7 (4)
C(6)	6047 (6)	7291 (8)	4423 (4)	7.3 (4)
N(7)	6482 (3)	3600 (4)	3537 (2)	5.9 (3)
C(8)	8237 (4)	4935 (7)	3269 (3)	3.9 (2)
C(9)	5533 (4)	2904 (5)	3571 (3)	3.6 (2)
C(10)	4657 (4)	3126 (5)	3105 (3)	4.2 (2)
C(11)	3715 (5)	2393 (7)	3089 (3)	5.2 (3)
C(12)	3656 (5)	1363 (6)	3569 (3)	5.7 (3)
C(13)	4492 (5)	1105 (6)	4041 (3)	5.4 (3)
C(14)	5420 (4)	1877 (5)	4036 (3)	4.2 (2)
Cl(15)	6459 (1)	1578 (2)	4647 (1)	5.7 (1)
Cl(16)	4743 (1)	4406 (2)	2517 (1)	5.4 (1)
S(17)	10668 (1)	6906 (2)	4238 (1)	4.6 (1)
C(18)	11576 (4)	7592 (5)	3727 (3)	3.3 (2)
N(19)	12465 (3)	6883 (5)	3636 (2)	4.0 (2)
C(20)	12808 (5)	5595 (6)	3965 (3)	5.2 (3)
C(21)	11924 (6)	4655 (7)	4087 (4)	7.0 (4)
C(22)	11216 (7)	5260 (8)	4524 (4)	9.2 (4)
N(23)	11386 (3)	8771 (5)	3450 (2)	5.7 (3)
C(24)	13195 (4)	7514 (7)	3214 (3)	4.0 (2)
C(25)	10425 (4)	9449 (5)	3488 (3)	3.6 (2)
C(26)	10285 (4)	10449 (6)	3958 (3)	4.4 (2)
C(27)	9350 (5)	11201 (6)	3971 (3)	5.2 (3)
C(28)	8524 (5)	10951 (6)	3482 (3)	5.5 (3)
C(29)	8626 (4)	9956 (6)	2993 (3)	4.8 (2)
C(30)	9571 (4)	9229 (5)	3014 (3)	3.9 (2)
Cl(31)	9671 (1)	7964 (2)	2420 (1)	5.3 (1)
Cl(32)	11311 (2)	10770 (2)	4570 (1)	6.5 (1)

Table 2. Fractional coordinates ($\times 10^4$) and mean temperature factors for non-hydrogen atoms of (IV)

E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	B_i (\AA^2)
S(1)	1514 (1)	1266 (1)	0	5.6 (1)
C(2)	431 (3)	1927 (4)	16 (12)	4.1 (2)
N(3)	-282 (3)	1085 (4)	58 (16)	5.5 (2)
C(4)	-255 (4)	-414 (5)	101 (23)	5.1 (3)
C(5)	550 (6)	-1065 (7)	424 (18)	8.7 (7)
C(6)	1381 (5)	-554 (6)	-85 (29)	10.6 (6)
N(7)	313 (2)	3228 (3)	-33 (11)	4.2 (1)
C(8)	-1151 (3)	1732 (6)	84 (25)	7.5 (3)
C(9)	1031 (2)	4155 (3)	28 (9)	3.6 (1)
C(10)	1356 (4)	4659 (8)	1400 (8)	4.0 (3)
C(11)	1994 (6)	5675 (9)	1349 (13)	6.0 (5)
C(12)	2285 (3)	6217 (4)	-16 (14)	6.4 (3)
C(13)	1967 (5)	5704 (8)	-1378 (13)	5.8 (4)
C(14)	1347 (5)	4653 (7)	-1353 (8)	4.9 (4)
C(15)	1022 (7)	4127 (13)	-2866 (9)	6.9 (5)
C(16)	1030 (8)	4068 (12)	2880 (12)	7.2 (6)

Table 3. Fractional coordinates ($\times 10^4$) and mean temperature factors for non-hydrogen atoms of (V)

E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	B_i (\AA^2)
S(1)	857 (1)	1848 (3)	4957 (1)	5.9 (1)
C(2)	2055 (5)	2920 (8)	4727 (4)	3.7 (2)
N(3)	2045 (5)	4137 (8)	4157 (4)	5.7 (3)
C(4)	977 (7)	4854 (12)	3535 (6)	7.3 (4)
C(5)	48 (9)	3591 (14)	3266 (6)	8.1 (5)
C(6)	-322 (7)	2777 (14)	4028 (7)	7.7 (4)
N(7)	3060 (4)	2329 (7)	5296 (3)	4.2 (2)
C(8)	4128 (6)	3050 (9)	5209 (5)	5.1 (3)
C(9)	3139 (5)	836 (7)	5893 (4)	3.9 (2)
C(10)	3254 (6)	1054 (8)	6857 (4)	4.4 (2)
C(11)	3395 (6)	-406 (10)	7438 (4)	5.4 (3)
C(12)	3424 (6)	-2079 (10)	7051 (5)	5.6 (3)
C(13)	3294 (6)	-2287 (10)	6105 (5)	5.5 (3)
C(14)	3146 (5)	-859 (9)	5501 (4)	4.5 (3)
C(15)	2991 (7)	-1106 (10)	4469 (5)	6.0 (3)
C(16)	3220 (8)	2848 (10)	7273 (5)	6.7 (3)

Table 4. Fractional coordinates ($\times 10^3$) for H atoms of (III)

The e.s.d.'s are identical to those of the C atoms to which they are constrained.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(41)	816	750	358	H(201)	1325	585	443
H(42)	819	689	439	H(202)	1332	505	366
H(51)	639	799	353	H(211)	1225	371	431
H(52)	709	879	422	H(212)	1147	442	362
H(61)	638	738	493	H(221)	1057	454	456
H(62)	534	792	434	H(222)	1165	541	500
H(81)	853	398	349	H(241)	1279	767	273
H(82)	784	473	278	H(242)	1347	850	342
H(83)	889	564	323	H(243)	1386	684	319
H(11)	306	261	272	H(27)	927	1196	435
H(12)	294	76	357	H(28)	780	1153	348
H(13)	443	32	441	H(29)	799	976	261

Table 5. Fractional coordinates ($\times 10^3$) for H atoms of (IV)

The e.s.d.'s are identical to those of the C atoms to which they are constrained.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(41)	-46	-77	-101	H(11)	226	607	240
H(42)	-73	-74	94	H(12)	276	704	-2
H(51)	60	-108	165	H(13)	222	611	-244
H(52)	49	-210	1	H(151)	43	353	-281
H(61)	190	-103	57	H(152)	155	350	-330
H(62)	144	-84	-126	H(153)	92	499	-361
H(81)	-157	84	16	H(161)	51	336	257
H(82)	-128	226	-97	H(162)	77	482	366
H(83)	-129	241	103	H(163)	156	351	342

Table 6. Fractional coordinates ($\times 10^3$) for H atoms of (V)

E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
H(41)	57 (12)	577 (17)	380 (8)
H(42)	119 (7)	572 (11)	304 (5)
H(51)	30 (7)	258 (11)	284 (5)
H(52)	-58 (9)	428 (13)	282 (7)
H(61)	-71 (8)	372 (13)	432 (6)
H(62)	-83 (8)	190 (11)	395 (6)
H(11)	348 (7)	-30 (11)	816 (6)
H(12)	345 (5)	-302 (8)	753 (4)
H(13)	318 (5)	-351 (9)	581 (4)
H(81)	414 (6)	421 (9)	508 (4)
H(82)	430 (5)	247 (9)	470 (4)
H(83)	466 (6)	343 (10)	580 (5)
H(151)	294 (7)	-226 (11)	427 (6)
H(152)	222 (6)	-51 (10)	408 (5)
H(153)	353 (6)	-34 (10)	423 (5)
H(161)	316 (7)	280 (11)	790 (5)
H(162)	331 (7)	369 (11)	692 (5)
H(163)	233 (7)	319 (11)	684 (5)

105.76 (9) $^\circ$, $V = 1317.6$ \AA^3 , $D_c = 1.181$ Mg m^{-3} , $Z = 4$, $F(000) = 504$, $\mu[\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}] = 0.18$ mm^{-1} , space group $P2_1/c$.

Intensities of 1593 independent reflexions were measured on a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer equipped with a graphite monochromator. After data reduction, 1405 reflexions with $F - 3\sigma(F) > 0$ were considered as observed. No absorption correction was applied.

The phases for 241 reflexions having $E \geq 1.2$ were obtained with *SHELX* (CDC 3300 computer, Budapest) which gave $R = 0.22$ for the non-hydrogen atoms. The structure was then refined anisotropically to $R = 0.095$ by block-diagonal least squares on the Varian 73 computer (Novi Sad). The final coefficients in the Cruickshank weighting scheme were $a = 7.5$ and $c = 0.0058$. The H-atom positions were generated from assumed geometries and included in the final structure factor calculations. Scattering factors were from *International Tables for X-ray Crystallography* (1962).

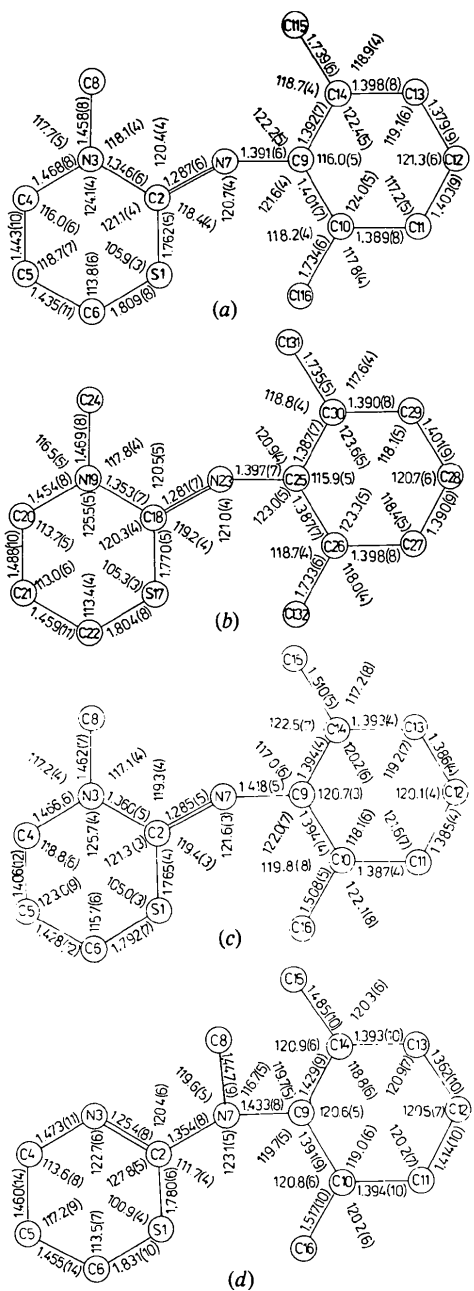


Fig. 1. Atomic numbering, bond distances (Å) and angles (°) with their e.s.d.'s for (a) and (b) the symmetry-independent molecules of (III), (c) (IV) and (d) (V).

The final coordinates for the non-hydrogen atoms of (III), (IV) and (V) are given in Tables 1–3, the parameters of the H atoms in Tables 4–6, and the bond distances and angles in Fig. 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34827 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

As shown by the least-squares planes (Table 7), in each molecule [(IIIa), (IIIb), (IV) and (V)] the thiourea group is fairly planar and makes a dihedral angle with the phenyl ring of about 88°. The thiazine rings themselves are non-planar (*cf.* torsion angles in Table 8) and their conformations (quasi sofa) can be characterized by the asymmetry parameters suggested by Duax, Weeks & Rohrer (1976):

	ΔC_s	at	ΔC_2	at
(IIIa)	10.6°	C(5)	17.2°	S(1)—C(2)
(IIIb)	7.8	C(5)	20.5	S(1)—C(2)
(IV)	5.9	C(5)	12.0	S(1)—C(2)
(V)	9.1	C(5)	20.6	S(1)—C(2)

The bond lengths and angles involving C(2), N(3) and N(7) agree well in (III) and (IV) but differ significantly from the corresponding ones in (V) in accordance with the different location of *Q* = Me. The two so-called *Q*-position-dependent bond lengths and the three angles of (III) and (IV) resemble those in (I) and (II), where *Q* = H and is claimed to be in an *endo* position (Table 9). The mean values of these bond lengths and angles for the seven symmetry-independent molecules possessing the imino form differ characteristically from the corresponding average values for (V) and (VII) which

Table 7. Equations of planes in the form $AX + BY + CZ = D$, where *X*, *Y* and *Z* are orthogonal coordinates (Å) related to *a**, *b* and *c*

Deviations (Å × 10³) of relevant atoms from the planes are given in square brackets in the same order as the equations are presented [(IIIa), (IIIb), (IV) and (V)].

Plane (1): S(1), C(2), N(3) and N(7)

(IIIa)	$0.502X - 0.396Y + 0.769Z = 7.597$	(r.m.s.d. = 0.008)
(IIIb)	$0.488X + 0.460Y + 0.742Z = 14.960$	(r.m.s.d. = 0.002)
(IV)	$0.017X + 0.031Y + 0.999Z = 0.078$	(r.m.s.d. = 0.003)
(V)	$-0.032X + 0.678Y + 0.735Z = 6.059$	(r.m.s.d. = 0.010)

IS(1) 4 (1), 1 (2), -1 (2), 5 (2); C(2) -14 (5), -3 (5), 5 (6), -18 (6); N(3) 5 (4), 1 (4), -2 (5), 7 (6); N(7) 5 (4), 1 (4), -2 (5), 6 (5); C(4) -27 (6), 106 (6), -9 (8), 10 (9); C(5) -682 (8), -580 (7), 277 (9), -680 (10); C(6) -239 (8), -13 (8), -134 (9), -181 (10); C(8) 0 (6), 16 (6), 18 (7), -10 (7); C(9) -176 (5), -134 (5), 98 (6), -154 (6)

Plane (2): C(9)—C(14)

(IIIa)	$-0.352X + 0.678Y + 0.646Z = 3.641$	(r.m.s.d. = 0.003)
(IIIb)	$0.355X + 0.700Y - 0.620Z = 7.550$	(r.m.s.d. = 0.004)
(IV)	$0.727X - 0.687Y - 0.011Z = -1.640$	(r.m.s.d. = 0.012)
(V)	$0.991X + 0.066Y - 0.113Z = 2.807$	(r.m.s.d. = 0.006)

IC(9) -2 (5), 1 (5), -12 (6), 8 (6); C(10) -1 (5), 5 (6), -5 (6), -3 (6); C(11) 4 (6), -6 (6), 17 (7), -5 (7); C(12) -4 (6), 1 (6), -12 (7), 8 (7); C(13) 1 (6), 4 (6), -5 (7), -2 (7); C(14) 2 (5), -6 (5), 17 (6), -6 (6); Cl(15) 55 (2), -53 (2), -, -; Cl(16) 13 (2), -3 (2), -, -; C(15) -, -, 26 (8), -33 (8); C(16) -, -, 17 (8), -20 (8); N(7) -100 (4), 107 (4), -180 (5), 89 (5)

Angles between planes (1) and (2): 87.0, 88.0, 86.0 and 88.8°. (E.s.d.'s are between 0.6 and 1.4°.)

represent the amino form (Table 10). The parameters of (VI), owing to the strong interaction between the methylsulphonyl (*Q*) group and the thiazine ring, as shown by the strong S—N (1.653 Å) multiple bond, are omitted from this study. In (VII), the electron-withdrawing effect of the *exo* methylsulphonyl (*Q*) group on the geometry of the thiourea moiety is less pronounced; therefore its five characteristic parameters could be used along with those of (V) to represent the rare amino form (Table 10). A protonated form of (II) described by Carpy, Gadret & Leger (1979) displays intermediate values for the five *Q*-position-dependent parameters indicating the simultaneous effects of the *endo* and *exo* H atoms on the electronic structure of the sensitive thiourea moiety.

The bond lengths and angles involving the S atoms seem to be independent of both the nature and position of *Q*, within experimental error. The S^{II}—C(*sp*³) and S^{II}—C(*sp*²) mean bond lengths [1.803 (5) and 1.766 (3) Å] agree well with expected values (Argay, Kálmán, Nahlovski & Ribár, 1975) and are accompanied by a mean C—S—C angle of 103.0 (6)°. Comparison of the geometries of (III) and (IV) shows that *R* (Cl or Me) has no significant effect upon the structures of these molecules.

As can be seen from Table 11, the C(*sp*³)—C(*sp*³) single bonds in the non-planar thiazine rings puckered

approximately at C(5) are subject to smaller or greater shortenings, which are presumably due to the vigorous thermal motions of C(5) and C(6). A correction of such a shortening has been attempted in the refinement of (II) without success (Argay, Kálmán, Kapor & Ribár, 1977). Nevertheless, the different methods of data collection (four different diffractometers were used) and numbers of observed reflexions per parameter refined (6–10) suggest that a systematic error in the structure analyses is highly improbable. In order to throw light upon these phenomena, data collection for at least one of these structures [(I)–(VIII)] would have to be performed at low temperature.

The exocyclic C=N double bond in (III) and (IV), in principle, permits the formation of two geometrical isomers: *syn* (*Z*) and *anti* (*E*). However, steric hindrance between the *N*-methyl group and phenyl ring seems to account for the exclusion of the *E* form as shown by the torsion angles S(1)—C(2)—N(7)—C(9) (Table 8).

Table 10. *Five inequalities between the characteristic (i.e. the Q-position-dependent) bond lengths and angles of the amino and imino forms of 2-arylamino-1,3-thiazines*

The corresponding parameters of a protonated form of (II) (Carpy, Gadret & Leger, 1979) are also presented for comparison.

Parameters	Imino form*	Amino form†	Protonated (II)
C(2)—N(3)	1.352 (3) Å	≥ 1.268 (8) Å	1.323 (3) Å
C(2)—N(7)	1.283 (3)	≤ 1.368 (8)	1.322 (3)
S(1)—C(2)—N(3)	120.1 (6)°	≤ 127.9 (5)°	124.2 (2)°
S(1)—C(2)—N(7)	120.2 (5)	≥ 111.7 (4)	116.3 (2)
C(2)—N(3)—C(4)	126.5 (7)	> 122.5 (6)	125.5 (2)

* Mean values for (I)–(IV).

† Mean values for (V) and (VII).

Table 8. *The relevant torsion angles (°) for thiazine rings in (IIIa), (IIIb), (IV) and (V)*

	(IIIa)	(IIIb)	(IV)	(V)
S(1)—C(2)—N(3)—C(4)	−3.1 (6)	−4.6 (8)	0.3 (6)	−2.4 (13)
C(2)—N(3)—C(4)—C(5)	−27.9 (8)	35.1 (8)	13.4 (16)	−29.9 (18)
N(3)—C(4)—C(5)—C(6)	55.2 (9)	−62.5 (8)	−35.9 (16)	59.2 (17)
C(4)—C(5)—C(6)—S(1)	−45.6 (9)	56.1 (9)	39.9 (16)	−51.2 (15)
S(1)—C(2)—N(7)—C(9)	13.5 (7)	−24.5 (8)	−21.8 (13)	17.5 (12)
C(6)—S(1)—C(2)—N(3)	9.4 (5)	−0.8 (5)	3.9 (10)	8.1 (16)
C(6)—S(1)—C(2)—N(7)	−173.1 (5)	179.8 (3)	−175.2 (9)	−175.3 (13)
S(1)—C(2)—N(7)—C(9)	10.3 (6)	−6.9 (7)	−5.3 (8)	9.4 (19)

Table 9. *Bond lengths (Å) and angles (°) in the thiourea moieties of seven different 2-arylamino-1,3-thiazines*

Notations: *Q*, amino, imino and *R* refer to the formulae given in the text.

<i>Q</i>	Isomer	<i>R</i>	C(2)—N(3)	C(2)—N(7)	S(1)—C(2)—N(3)	S(1)—C(2)—N(7)	C(2)—N(3)—C(4)	S(1)—C(6)	S(1)—C(2)	C(2)—S(1)—C(6)	
(Ia)	H	imino	H	1.350 (6)	1.267 (5)	116.6 (3)	122.2 (3)	125.9 (4)	1.771 (7)	1.787 (4)	105.2 (3)
(Ib)	H	imino	H	1.347 (5)	1.283 (5)	119.3 (3)	121.4 (3)	127.9 (4)	1.792 (6)	1.763 (4)	103.4 (2)
(IIa)	H	imino	Me	1.360 (6)	1.283 (6)	120.3 (4)	120.6 (4)	129.1 (4)	1.815 (6)	1.764 (6)	102.4 (3)
(IIb)	H	imino	Me	1.349 (6)	1.295 (6)	121.5 (3)	119.9 (3)	127.7 (4)	1.801 (7)	1.762 (4)	102.8 (3)
(IIIa)	Me	imino	Cl	1.346 (6)	1.287 (6)	121.1 (4)	118.4 (4)	124.1 (4)	1.809 (8)	1.762 (5)	105.9 (3)
(IIIb)	Me	imino	Cl	1.353 (7)	1.281 (7)	120.3 (4)	119.2 (4)	125.5 (5)	1.804 (8)	1.770 (5)	105.3 (3)
(IV)	Me	imino	Me	1.360 (5)	1.285 (5)	121.3 (3)	119.4 (3)	125.7 (4)	1.792 (7)	1.765 (4)	105.0 (3)
(V)	Me	amino	Me	1.254 (8)	1.354 (8)	127.8 (5)	111.7 (4)	122.7 (6)	1.831 (10)	1.780 (6)	100.9 (4)
(VIa)	CH ₃ SO ₂	imino	Me	1.414 (6)	1.263 (8)	114.0 (4)	124.6 (4)	115.9 (4)	1.808 (7)	1.758 (5)	99.5 (2)
(VIb)	CH ₃ SO ₂	imino	Me	1.403 (6)	1.270 (7)	115.9 (4)	123.1 (4)	116.7 (5)	1.791 (8)	1.754 (6)	101.7 (3)
(VII)	CH ₃ SO ₂	amino	Me	1.281 (8)	1.381 (8)	128.0 (5)	111.7 (4)	122.2 (6)	1.818 (8)	1.769 (6)	100.9 (3)

(I) 2-Phenylimino-perhydro-1,3-thiazine (Kálmán, Argay, Ribár & Toldy, 1977); (II) 2-(2,6-dimethylphenyl)imino-perhydro-1,3-thiazine (Argay, Kálmán, Kapor & Ribár, 1977); (III), (IV), (V) present work; (VI) 2-(2,6-dimethylphenyl)imino-3-mesylperhydro-1,3-thiazine (Kálmán & Argay, 1978a); (VII) 2-[N-(2,6-dimethylphenyl)-N-mesylamino]-4,5-dihydro-6*H*-1,3-thiazine (Kálmán, Argay & Vassányi, 1977).

Table 11. The C(sp³)-C(sp³) distances and C-C-C bond angle at C(5) in the non-planar thiazine rings with the indication of maximum puckering at C(5)

Some information concerning the data collection and refinement is also presented.

Compound	C(4)-C(5)	C(5)-C(6)	C(4)-C(5)-C(6)	ΔC(5)	Diffractometer	Radiation	R	Number of reflections/parameter
(Ia)	1.48 (1) Å	1.46 (1) Å	113 (1)°	0.87	Syntex P2 ₁	Mo Kα	0.04	6
(Ib)	1.38 (1)	1.34 (1)	128 (1)	0.40				
(IIa)	1.52 (1)	1.49 (1)	111 (1)	0.81	Philips	Cu Kα	0.05	7
(IIb)	1.46 (1)	1.40 (1)	120 (1)	0.54				
(IIIa)	1.44 (1)	1.44 (1)	114 (1)	0.68	Philips	Mo Kα	0.05	10
(IIIb)	1.49 (1)	1.46 (1)	113 (1)	0.58				
(IV)	1.41 (1)	1.43 (1)	123 (1)	0.28	Philips	Mo Kα	0.06	9
(V)	1.46 (1)	1.46 (1)	114 (1)	0.68	Syntex P1	Mo Kα	0.09	10
(VIa)	1.49 (1)	1.50 (1)	114 (1)	0.64	Syntex P2 ₁	Mo Kα	0.05	7
(VIb)	1.45 (1)	1.41 (1)	118 (1)	0.57				
(VII)	1.48 (1)	1.50 (1)	113 (1)	0.67	Stoe two-circle	Cu Kα	0.07	8

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The Structure of 2,3,4aβ,6,7β,8aβ-Hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract

Crystals of 2,3,4aβ,6,7β,8aβ-hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone are monoclinic, $a = 6.865$ (1), $b = 16.043$ (2), $c = 13.166$ (2) Å, $\beta = 99.57$ (1)°, space group $P2_1/c$, $Z = 4$. The structure

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was refined to $R = 0.047$ for 1862 independent observed reflections. The crystal structure consists of well separated molecules with the two fused six-membered rings in distorted half-chair conformations and twisted with respect to each other. A comparison with *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone and

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