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X-RAY STUDY OF THE N-MESYL DERIVATIVES OF 2-ARYLAMINO(IMINO)-THIAZOLI(DI)NES AND ANALOGOUS 1,3-THIAZINES, I.: CRYSTAL STRUCTURE OF N-(2,6-DIMETHYLPHENYL)-N-MESYL-2-AMINO-1,3-THIAZINE

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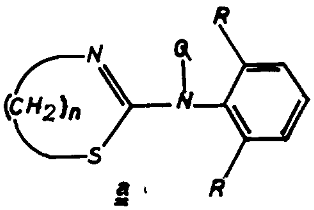
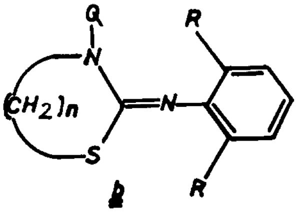
2-Arylamino(imino)-thiazoli(di)nes (n=2) and the analogous 1,3-thiazines (n=3) can exist in the tautomeric structure a and b (Q=H). These compounds and also the possible isomers of their N-substituted derivatives (Q = acyl, alkyl) have been investigated by ^{1}H n.m.r., i.r., u.v. and mass spectrometry[1-4], but the small differences in the data obtained did not allow unambiguous determination of the isomeric or tautomeric structures. To clarify the uncertainties of the spectroscopic studies, X-ray structure determinations of eleven thiazoline and thiazine derivatives (Table 1) have been performed so far.



a



b

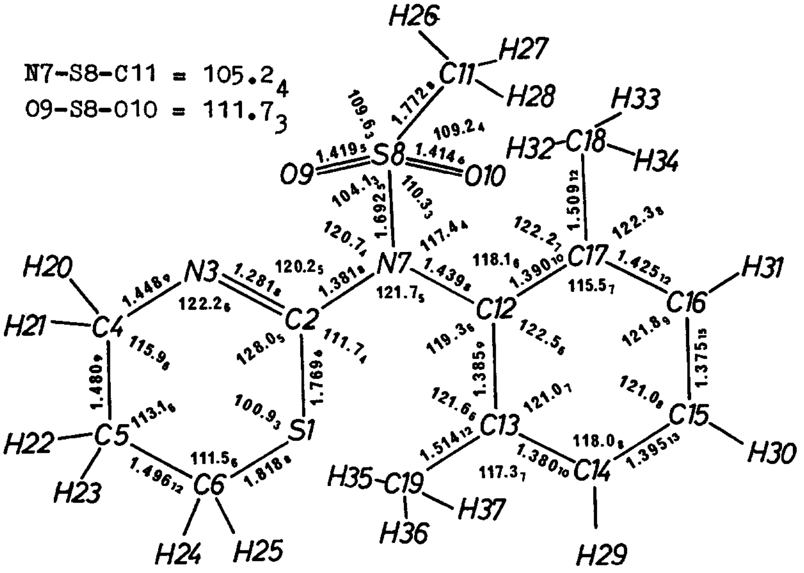
Table 1. Characteristic data of the model compounds investigated by X-ray diffraction. Column S indicates the structures suggested by the spectroscopic investigations, column F presents the structure found by X-ray analysis.

No.	S	F	n	Q	R	ref.	No.	S	F	n	Q	R	ref.
1.	a	b	2	o-Cl-Bz	Me	[5]	7.	b	a	3	Ms	Me	*
2.	a	b	2	o-Me-Bz	Me	[6]	8.	a	b	3	Ms	Me	**
3.	a	b	2	H	Me	[7]	9.	a	b	2	Ms	Me	**
4.	a	b	2	H	H	[8]	10.	b	b	2	Me	Me	**
5.	b	b	3	H	Me	[9]	11.	b	b	3	Me	Me	**
6.	b	b	3	H	H	[10]							

* present work
** to be published

First the disputed orientation of acylation with ortho-substituted benzoic acid was elucidated[5,6] and it was pointed out that the acyl group attacks only the endocyclic N atom in the circumstances applicable during these reactions. Later it was revealed that the imino form[7-10] is the predominant tautomer of both types of these cyclic amidines. Now we present evidence, that the structures inferred from ^1H n.m.r. spectra for the N-mesyl derivatives (No.7-9) are not correct. The compounds which were believed to possess an exocyclic mesyl group (Ms) turned out to have endocyclic one and *vice versa*. The ^{13}C n.m.r. reinvestigation[11] of these derivatives indicated that these observations are valid also for the tautomeric structures in solution. The title compound (m.p. 139-140°) deserves particular attention because this compound is the only one among the compounds of Table 1 to possess an amino structure.

The compound has orthorhombic space group $P2_12_12_1$ with $\underline{a} = 14.247(2)$, $\underline{b} = 10.245(3)$, $\underline{c} = 10.051(3)$ Å, $Z = 4$, $D_x = 1.327$ g.cm^{-3} and $F(000) = 362$. The structure was solved and refined with program SHELX[12] to a final $R = 0.074$ for 1392 reflexions collected on a STOE semi-automatic two-circle diffractometer using Ni-filtered $CuK\bar{\alpha}$ ($\bar{\lambda} = 1.5418$ Å) radiation. The fractional coordinates of the non-hydrogen atoms, refined anisotropically, are given in Table 2 together with the hydrogen coordinates (generated with C-H constrained to 1.08 Å). Bond distances and angles are shown in Figure 1.



N7-S8-C11 = 105.2_4
O9-S8-O10 = 111.7_3

Figure 1.

The planar amidine [-N=C(S)-N(Ms)-] moiety in accordance with the amino structure displays a short endocyclic C=N double bond and a long exocyclic C-N multiple bond accompanied by a S(II)-C(sp^2) single bond[6]. Short endocyclic C=N double bonds are not observed in the known 2-amino-thiazolin-4-ones structures (cf. Table 2 in ref. 7) presumably because of the conjugation between C=N and the neighbouring C=O group. The six-membered hetero-ring is non planar and has a *quasi*-sofa form puckered at C(5) with an asymmetry parameter[13] of $\Delta C_s = 3.4^\circ$. The two C-C distances are in the range of the C(sp^3)-C(sp^3) single bonds if their e.s.d.'s and thermal corrections are taken into account. The bond angles at C(2) and N(3) show characteristic differences from the corresponding values in the 2-arylimino-1,3-thiazine structures, and so they provide valuable evidence for the final discussion of the tautomerism of these compounds (see the following paper under ref. 10). The dihedral angle between the best plane [$9.352X + 7.864Y + 0.101Z - 3.370 = 0$] of the amidine group and that of the nearly planar atomic moiety $\mathrm{C(2)\text{-}N(7)}<^{\mathrm{S(8)}}_{\mathrm{C(12)}}$ [$10.258X + 7.116Y + 1.263Z - 3.739 = 0$] is only 8.6°. The central atom N(7) of this moiety is involved in two C-N multiple bonds with a total π-bond order of 0.6 as well as in a long S-N bond towards the mesyl group. That is perhaps the reason why the S-N bond length of 1.692(5) Å is 0.037 Å longer than that expected on the basis of a linear regression analysis of S-N distances against mean S-O bond lengths for the known crystal structures with mesylamino groups[14]. However, the conformation of the N-mesyl group in the title compound, as shown by the Newman projection perpendicular to the S-N bond (Figure 2a), is similar to those observed in the other structures.[14] It resembles especially that of 5-mesylamino-2*H*-1,2,3-triazole-4-carbonitrile monohydrate[15] (Figure 2b) which possesses at least one strong C-N multiple bond with a π-bond order of 0.45. Because of the steric hindrance of the *ortho*-*ortho*' methyl groups, the least-squares plane of the phenyl ring [$10.582X - 6.947Y - 0.656Z + 1.430 = 0$] is nearly orthogonal

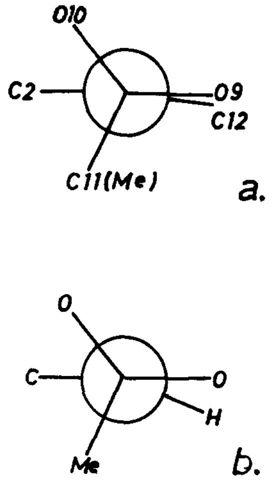


Figure 2.

(90.9°) to that of the amidine group.

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Table 2. Atomic coordinates (x10^4 for non-hydrogen atoms and x10^3 for hydrogen atoms) with their e.s.d.'s in parentheses.

	x	y	z		x	y	z		x	y	z
S(1)	2351(1)	1429(2)	4458(2)	C(14)	308(5)	1819(9)	7527(8)	H(25)	374(1)	42(1)	368(1)
C(2)	1595(4)	2357(6)	3417(6)	C(15)	862(7)	2601(12)	8335(9)	H(26)	-93(1)	267(1)	276(1)
N(3)	1560(3)	2397(6)	2175(6)	C(16)	1449(6)	3507(11)	7793(9)	H(27)	-16(1)	305(1)	144(1)
C(4)	2217(4)	1700(9)	1346(7)	C(17)	1488(5)	3731(8)	6395(8)	H(28)	-81(1)	427(1)	224(1)
C(5)	3133(5)	1394(9)	1963(8)	C(18)	2102(5)	4759(9)	5794(10)	H(29)	-13(1)	109(1)	796(1)
C(6)	3045(5)	609(10)	3212(8)	C(19)	-259(7)	1153(10)	5307(10)	H(30)	83(1)	250(1)	940(1)
N(7)	974(3)	3070(4)	4198(4)					H(31)	189(1)	406(1)	844(1)
S(8)	301(1)	4214(2)	3482(2)					H(32)	249(1)	516(1)	662(1)
O(9)	-229(3)	4726(6)	4552(5)	H(20)	189(1)	81(1)	106(2)	H(33)	175(1)	552(1)	526(1)
O(10)	865(3)	5072(5)	2741(6)	H(21)	235(1)	227(1)	47(1)	H(34)	258(1)	427(1)	513(1)
C(11)	-453(5)	3376(9)	2382(8)	H(22)	355(1)	86(1)	125(1)	H(35)	-16(1)	131(1)	425(1)
C(12)	922(4)	2941(7)	5623(6)	H(23)	349(1)	228(1)	221(1)	H(36)	-94(1)	146(1)	561(1)
C(13)	353(4)	2000(7)	6168(7)	H(24)	271(1)	-28(1)	296(1)	H(37)	-17(1)	14(1)	553(1)