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Acta Cryst. (1994). C**50**, 289–291

Structure of 2-Methylthio-7,8-dihydroquinazolin-5(6*H*)-one Amidinohydrazone Hydrochloride, $C_{10}H_{15}N_6S^+.Cl^-$

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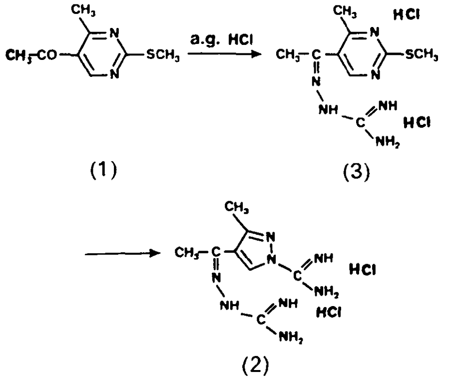
(*Received* 2 *February* 1993; *accepted* 28 *June* 1993)

Abstract

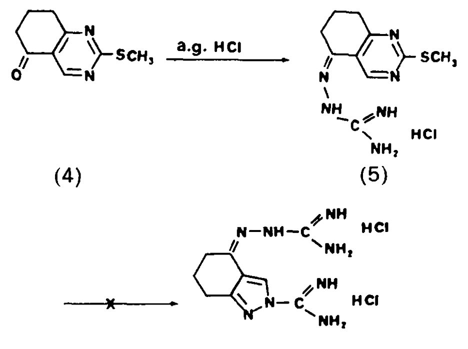
The structural differences between the title compound [3-(2-methylthio-7,8-dihydro-6*H*-quinazolin-5-ylideneamino)guanidinium chloride] and 5-acetyl-4-methyl-2-methylthiopyrimidine amidinohydrazone dihydrochloride, which are clearly apparent from this study, should help in interpreting the observed discrepancies between their chemical properties.

Comment

Under the action of aminoguanidine hydrochloride (a.g. HCl) in acidic boiling methanol, 5-acetyl-4-methyl-2-methylthiopyrimidine, (1), is regiospecifically transformed into 4-acetyl-1-amidino-3-methylpyrazole amidinohydrazone dihydrochloride (2) through formation of the intermediary 5-acetyl-4-methyl-2-methylthiopyrimidine amidinohydrazone dihydrochloride (3) [the structure of the free base of (3) has been determined and compared with that of the dihydrochloride (3) by Cousson, Nectoux, Bachet, Kokel & Hubert-Habart (1993)].



Although 2-methylthio-7,8-dihydroquinazolin-5(6*H*)-one (4) could be considered as a 5-acylpyrimidine, when submitted to the action of aminoguanidine hydrochloride it did not lead to the expected pyrazole-like derivative 2-amidino-2,5,6,7-tetrahydroindazol-4-one amidinohydrazone dihydrochloride, but only to 2-methylthio-7,8-dihydroquinazolin-5(6*H*)-one amidinohydrazone hydrochloride (5) (Bajnati, Kokel & Hubert-Habart, 1987).



In order to understand better this difference in reactivity between compounds (3) and (5), the crystal structure of the latter has been determined by X-ray diffraction and compared to that of the former which we have described previously (Cousson, Nectoux, Bachet, Kokel & Hubert-Habart, 1994) (Fig. 1).

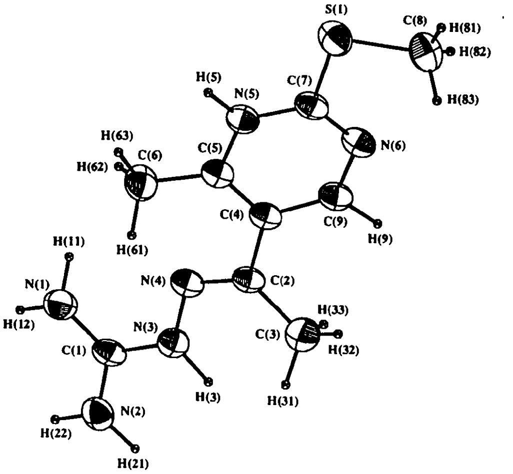


Fig. 1. *ORTEP* (Johnson, 1965) plot of (3).

The intermolecular relationship in the crystal of compound (5) appears as stacks of parallel planes of the molecules, linked to each other by the Cl^- anion located in the mean plane of these molecules (Fig. 1) and van der Waals contacts along the *b* axis. In two neighbouring planes, the molecules are piled up head to tail (Fig. 2). Two different molecules are bound to the Cl^- anion, on one hand Cl(1)···H(11) [2.293 (1) Å] and Cl(1)···H(3) [2.329 (1) Å], and on the other hand Cl(1)···H(21) [2.174 (1) Å] and Cl(1)···H(12) [2.426 Å]. Other bonds involving Cl are larger [Cl(1)···H(32) 2.874 (1), Cl(1)···H(31) 2.882 (1) Å].

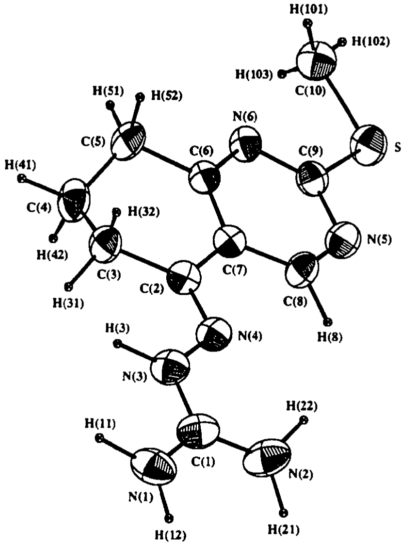


Fig. 2. *ORTEP* (Johnson, 1965) plot of the title molecule.

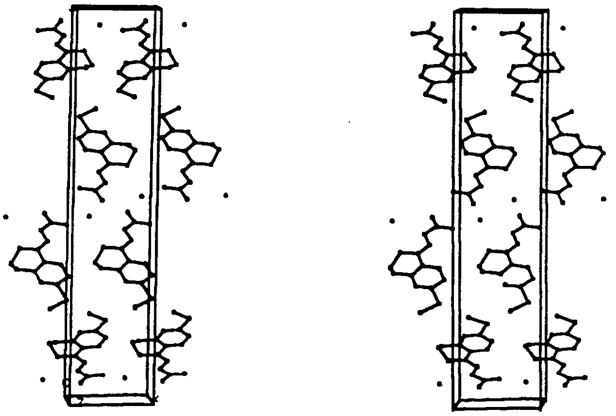


Fig. 3. *PLUTO* (Motherwell & Clegg, 1976) stereoview of the title compound.

The structure of quinazolinone derivative (5) differs from that of pyrimidine (3) in many aspects: it is a monochloride and not a dichloride; its N atom N(5) does not bear an H atom as in pyrimidine (3); its S(1)—C(10) bond is oriented in the opposite direction to the corresponding S(1)—C(8) in molecule (3), as is the case with C(2)—N(4) when compared with C(2)—N(4) in molecule (3); the C(2)—C(7) bond which is part of a ring structure in compound (5) cannot rotate, unlike the corresponding C(4)—C(2) bond in pyrimidine (3). However, as in pyrimidine (3), the N(4)—C(2) bond [1.281 (5) Å] is almost a pure double bond with a *trans* conformational (*E*) environment.

The obvious differences between the structures of pyrimidine (3) and quinazoline (5), as revealed by X-ray diffraction, should help in understanding why the former can undertake an intramolecular ring contraction while the latter cannot.

Experimental

Crystal data

$C_{10}H_{15}N_6S^+.Cl^-$
$M_r = 286.79$
Monoclinic
$P2_1/n$
$a = 7.302$ (4) Å
$b = 32.43$ (1) Å
$c = 5.666$ (4) Å
$\beta = 103.43$ (2)°
$V = 1305$ (4) Å^3
$Z = 4$

$D_x = 1.459$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 18$–$26°$
$\mu = 0.44$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.15 × 0.15 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω-2θ step scans

1960 observed reflections [$I \geq 3\sigma(I)$]
$\theta_{\max} = 66°$

Absorption correction: empirical
$T_{\min}$ = 0.830, $T_{\max}$ = 1.465
2563 measured reflections
2563 independent reflections
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 38$
$l = 0 \rightarrow 6$
3 standard reflections
frequency: 60 min
intensity variation: <1.5%

Refinement

Refinement on F
R = 0.0514
wR = 0.0525
S = 3.1
1960 reflections
165 parameters
Only H-atom U's refined (one U_{eq} for all H atoms)
Unit weights applied
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.2 e Å^{-3}
$\Delta\rho_{\min}$ = −0.3 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 6 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99-101)

The structure was solved using direct methods and successive Fourier maps (*SHELXS*86; Sheldrick, 1986), and refined using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). H atoms were located from difference Fourier syntheses.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.4028 (2)	0.21970 (4)	0.1531 (2)	0.0537
Cl(1)	−0.2507 (2)	0.03670 (4)	−0.3126 (2)	0.0587
C(1)	0.2760 (6)	0.0488 (1)	−1.0692 (8)	0.0484
C(2)	0.0993 (5)	0.1104 (1)	−0.6721 (7)	0.0393
C(3)	−0.1115 (5)	0.1075 (1)	−0.7666 (8)	0.0476
C(4)	−0.2128 (6)	0.1438 (1)	−0.6933 (9)	0.0545
C(5)	−0.1580 (5)	0.1526 (1)	−0.4277 (9)	0.0499
C(6)	0.0519 (5)	0.1572 (1)	−0.3426 (7)	0.0377
C(7)	0.1707 (5)	0.1368 (1)	−0.4607 (7)	0.0365
C(8)	0.3635 (5)	0.1428 (1)	−0.3656 (8)	0.0474
C(9)	0.3019 (5)	0.1863 (1)	−0.0823 (7)	0.0405
C(10)	0.2044 (6)	0.2379 (1)	0.2547 (9)	0.0536
N(1)	0.2083 (6)	0.0276 (1)	−1.2702 (7)	0.0592
N(2)	0.4583 (5)	0.0534 (1)	−0.9780 (8)	0.0616
N(3)	0.1512 (5)	0.0666 (1)	−0.9619 (6)	0.0475
N(4)	0.2208 (4)	0.09129 (9)	−0.7617 (6)	0.0431
N(5)	0.4306 (5)	0.1677 (1)	−0.1799 (7)	0.0513
N(6)	0.1161 (4)	0.18181 (9)	−0.1501 (6)	0.0405

Table 2. *Geometric parameters* (Å, °)

S(1)—C(9)	1.742 (4)	C(4)—C(5)	1.492 (6)
S(1)—C(10)	1.779 (5)	C(5)—C(6)	1.503 (5)
C(1)—N(1)	1.325 (5)	C(6)—C(7)	1.382 (5)
C(1)—N(2)	1.320 (5)	C(6)—N(6)	1.345 (5)
C(1)—N(3)	1.338 (5)	C(7)—C(8)	1.399 (5)
C(2)—C(3)	1.510 (5)	C(8)—N(5)	1.327 (5)
C(2)—C(7)	1.464 (5)	C(9)—N(5)	1.340 (5)
C(2)—N(4)	1.281 (5)	C(9)—N(6)	1.329 (4)
C(3)—C(4)	1.500 (6)	N(3)—N(4)	1.385 (4)
C(10)—S(1)—C(9)	102.9 (2)	N(6)—C(6)—C(7)	122.5 (3)
N(2)—C(1)—N(1)	122.4 (4)	C(6)—C(7)—C(2)	122.1 (3)
N(3)—C(1)—N(1)	117.2 (4)	C(8)—C(7)—C(2)	122.1 (3)
N(3)—C(1)—N(2)	120.4 (4)	C(8)—C(7)—C(6)	115.8 (3)
C(7)—C(2)—C(3)	117.8 (3)	N(5)—C(8)—C(7)	122.9 (4)
N(4)—C(2)—C(3)	124.8 (3)	N(5)—C(9)—S(1)	112.6 (3)
N(4)—C(2)—C(7)	117.3 (3)	N(6)—C(9)—S(1)	120.8 (3)
C(4)—C(3)—C(2)	112.3 (3)	N(6)—C(9)—N(5)	126.7 (3)
C(5)—C(4)—C(3)	113.2 (4)	N(4)—N(3)—C(1)	117.5 (3)
C(6)—C(5)—C(4)	110.9 (3)	N(3)—N(4)—C(2)	116.7 (3)
C(7)—C(6)—C(5)	120.3 (3)	C(9)—N(5)—C(8)	115.9 (3)
N(6)—C(6)—C(5)	117.2 (3)	C(9)—N(6)—C(6)	116.1 (3)

Molecule (5) was prepared according to a published procedure (Bajnati, Kokel & Hubert-Habart, 1987). 0.5 g of (5) was dissolved in 50 ml of boiling methanol and left to stand at room temperature for 6 d, during which time large crystals formed.

This work was supported by a grant (Contrat Coopératif, Décision 90-24) from the Institut Curie.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71434 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1043]

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Acta Cryst. (1994). C**50**, 291–294

Structure of a Modified Nucleoside, 3′α-Diethylphosphono-3′β-hydroxy-5′-*O*-tritylthymidine

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(*Received* 28 *May* 1993; *accepted* 16 *August* 1993)

Abstract

The modified nucleoside of the title was synthesized by nucleophilic addition of lithium diethyl phosphite to the corresponding 3′-keto nucleoside under basic conditions. C—P bond formation resulted from attack on the α face, *trans* to C(5′) and the thymine ring. One molecule of