O4—C10	1.385 (4)	C5—C6	1.374 (8)
C5—C10	1.390 (6)	C6—C7	1.358 (8)
C7—C8	1.382 (8)	C8—C9	1.403 (4)
C9—C10	1.378 (4)	C11—P19	1.781 (3)
C11—O12	1.410 (4)	O12—P13	1.589 (2)
P13—O14	1.559 (2)	P13—O15	1.554 (3)
P13—O16	1.441 (2)	O14—C17	1.444 (4)
O15—C18	1.447 (5)	P19—O20	1.567 (3)
P19—O21	1.562 (3)	P19—O22	1.455 (2)
O20—C23	1.427 (5)	O21—C24	1.445 (5)
C2—C1—C9	121.8 (3)	C2—C1—Cl1	119.6 (3)
C9—C1—Cl1	118.6 (2)	C1—C2—C3	121.3 (3)
C2—C3—O4	117.2 (3)	C2—C3—C11	126.8 (3)
C11—C3—O4	116.0 (3)	C3—O4—C10	121.3 (3)
C6—C5—C10	118.3 (5)	C5—C6—C7	120.8 (5)
C6—C7—C8	121.0 (5)	C7—C8—C9	119.8 (4)
C1—C9—C8	126.1 (3)	C1—C9—C10	116.3 (3)
C8—C9—C10	117.6 (3)	C5—C10—O4	115.6 (3)
C5—C10—C9	122.4 (3)	C9—C10—O4	122.1 (3)
C3—C11—O12	119.1 (3)	C3—C11—P19	128.2 (2)
O12—C11—P19	112.7 (2)	C11—O12—P13	125.3 (2)
O12—P13—O14	106.9 (1)	O12—P13—O15	101.3 (1)
O12—P13—O16	115.1 (1)	O14—P13—O15	102.0 (1)
O14—P13—O16	112.5 (1)	O15—P13—O16	117.6 (1)
C17—O14—P13	121.6 (2)	C18—O15—P13	120.1 (2)
C11—P19—O20	106.2 (1)	C11—P19—O21	106.8 (1)
C11—P19—O22	112.4 (1)	O20—P19—O21	95.6 (1)
O20—P19—O22	117.7 (1)	O21—P19—O22	116.3 (1)
C23—O20—P19	120.0 (3)	C24—O21—P19	119.2 (3)

The structure was solved by Patterson and direct methods using *SHELXS*86 (Sheldrick, 1985). The first *E* map revealed six atoms, three of which were Cl and P atoms. Calculation of the Fourier map with these atoms revealed all of the non-H atoms. Least-squares refinement was carried out using *SHELX*76 (Sheldrick, 1976) of the *CRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986) with isotropic and then anisotropic temperature factors. H atoms were located on a difference Fourier map and the methyl H atoms were refined as part of a rigid body.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71438 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1041]

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Structure of 5-[(1-Amidiniohydrazono)ethyl]-4-methyl-2-methylthio-3H^+-pyrimidinium Dichloride Hydrate, $C_9H_{16}N_6S^{2+}.2Cl^-.H_2O$

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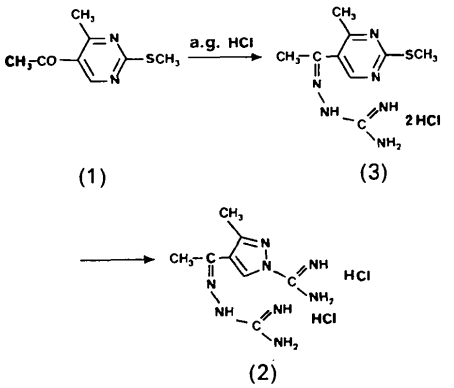
Abstract

The amidiniohydrazone group of the title compound (5-acetyl-4-methyl-2-methylthiopyrimidine amidinohydrazone dihydrochloride) has a *trans* conformation (*E*) and the (amidiniohydrazone)ethyl part of the molecule compares very well with the same chaining in mitoguazone and its analogue. Both ionic salts are stabilized by a series of hydrogen bonds to both water molecules and chlorine ions. The structure consists of stacks of parallel planes of the dipositive ion.

Comment

The hydrochloride salt of the amidinohydrazone of 5-acetyl-4-methyl-2-methylthiopyrimidine (3) is the likely intermediary in the reaction of transformation of 5-acetyl-4-methyl-2-methylthiopyrimidine (1) into 4-acetyl-1-amidino-3-methylpyrazole amidinohydrazone dihydrochloride (2) by action of aminoguanidine hydrochloride (a.g. HCl) in acidic boiling methanol (Menichi, Naciri, Kokel & Hubert-Habart, 1984; Menichi, Boutar, Kokel, Takagi & Hubert-Habart, 1986; Bajnati & Hubert-Habart, 1988).



(1) (3) (2)

We isolated compound (3) in order to study its structure in detail for comparison with our previous observations on molecules possessing an amidinohydrazone substituent (Cousson, Robert & Hubert-Habart, 1991; Cousson, Bachet, Kokel & Hubert-Habart, 1991) and to try to understand why pyrimidine (1) is more sensitive than other 5-acylpyrimidines to this type of ring contraction (Bajnati & Hubert-Habart, 1988; Bajnati, Kokel & Hubert-Habart, 1987; Takagi, Bajnati & Hubert-Habart, 1990).

The crystal structure of molecule (3) exhibits the following characteristics: it is a dihydrochloride and not a monohydrochloride as would have been expected from the published description of 5-acetyl-2-amino-4-methylpyrimidine amidinohydrazone hydrochloride (Arya, David, Grewal, Marathe & Patil, 1977), and the two H atoms supplied by the acid have become attached to the imino group of the terminal amidino function and to the N(5) atom of the pyrimidine ring, the positive charges being centred at C(1) and N(5) (Fig. 1).

The amidiniohydrazone group has a *trans* conformation (*E*) and the C(3)—C(2)—N(4)—N(3)—C(1)—$(NH_2)_2$ part of the molecule compares very well with the same chaining in methyl GAG (mitoguazone) (Hamilton & La Placa, 1968), dimethyl GAG (Edmonds & Hamilton, 1972) and analogues of methyl GAG that we have recently described, such as pyrazole (2) (Cousson, Robert & Hubert-Habart, 1991; Cousson, Bachet, Kokel & Hubert-Habart, 1991). The C(2)—N(4) bond [1.293 (6) Å] is almost a pure double bond, while in the three C—N bonds surrounding C(1) we see that there is approximately 50% double-bond character. The slight difference between C(1)—N(1) [1.310 (7) Å] and C(1)—N(2) [1.319 (6) Å] within the $C(NH_2)_2^+$ group may be due to short interactions between parallel stacking molecules. In the pyrimidine ring, the C(7)—N(6) bond [1.319 (7) Å] is shorter than C(7)—N(5) [1.353 (7) Å], as is S(1)—C(7) [1.726 (5) Å] compared to S(1)—C(8) [1.781 (6) Å]. This could be a result of the quartenary nature of N(5) and packing effects. This ionic salt is stabilized by a series of hydrogen bonds to both H_2O and Cl^-, as was observed in methyl GAG and dimethyl GAG (Hamilton & La Placa, 1968; Edmonds & Hamilton, 1972). Cl(1) is bonded to two water molecules and to one molecule of (3) through the positive terminal group C—$(NH_2)_2$, while Cl(2) is bonded to two adjacent molecules. The structure is made of stacks of parallel planes of the dipositive ions (Fig. 2). The shortest distance between two adjacent molecules is at C(1)···N(6) [3.237 (6) Å]. This value is comparable to that found for methyl GAG (3.15 Å). The main difference with previous studies is that the diionic molecule studied here is less planar than methyl GAG and dimethyl GAG. Not considering the methyl groups and the S atom, deviations from the mean plane range from −0.35 Å for C(5) to 0.34 Å for N(6), and from 0.61 Å for H(11) to −0.41 Å for H(21). The presence of a pyrimidine group certainly leads to an increase in rigidity of the molecule but surprisingly to a decrease in planarity.

In order to lead to the formation of pyrazole, the intermediary (3) must undergo two rotations of the C(4)—C(2) bond to bring N(3) and C(9) closer to each other.

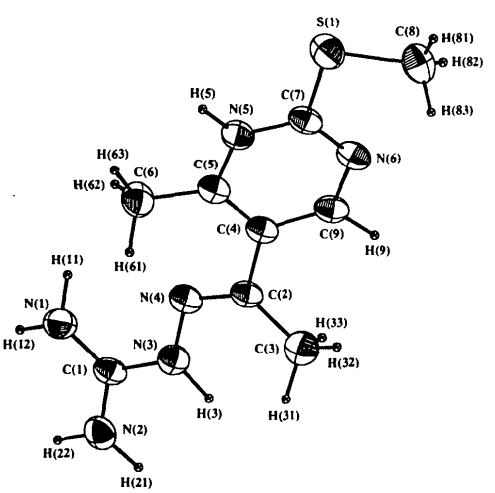


Fig. 1. *ORTEP* (Johnson, 1965) plot of the diionic molecule.

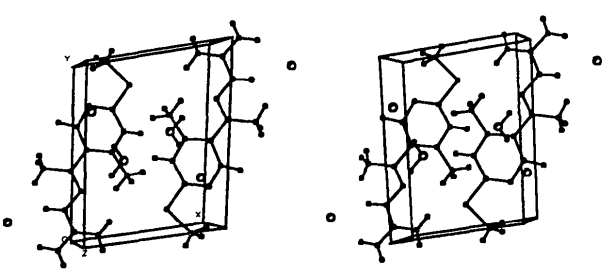


Fig. 2. *PLUTO* (Motherwell & Clegg, 1976) stereoview of the title compound.

Experimental

Crystal data

$C_9H_{16}N_6S^{2+}.2Cl^-.H_2O$
M_r = 329.25
Triclinic
$P\bar{1}$
a = 7.652 (7) Å
b = 10.481 (5) Å
c = 11.076 (6) Å
α = 67.37 (4)°
β = 71.67 (6)°
γ = 75.93 (6)°
V = 771 (1) Å^3
Z = 2
D_x = 1.42 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 25.04–27.61°
μ = 5.1 mm^{-1}
T = 293 K
Prism
0.45 × 0.30 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.591, T_{max} = 1.698
2694 measured reflections
2685 independent reflections
2431 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.016
θ_{max} = 66°
h = −8 → 9
k = −11 → 12
l = 0 → 13
2 standard reflections
frequency: 60 min
intensity variation: <1.2%

Refinement

Refinement on F
R = 0.073
wR = 0.079
S = 0.92
2431 reflections
174 parameters
Only H-atom U's refined (one U_{eq} for all H atoms)
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.11
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 15.9 (9)
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)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl(1)	0.0531 (2)	0.7328 (1)	0.8661 (2)	0.0528
Cl(2)	−0.5251 (2)	0.1886 (2)	0.6046 (2)	0.0513
S(1)	0.4216 (2)	0.8511 (2)	−0.0067 (2)	0.0444
C(1)	−0.0373 (7)	0.0812 (5)	0.6153 (5)	0.0291
C(2)	−0.0467 (7)	0.4202 (5)	0.3828 (5)	0.0286
C(3)	−0.2458 (9)	0.4585 (6)	0.3825 (7)	0.0500
C(4)	0.0816 (7)	0.5226 (5)	0.2935 (5)	0.0275
C(5)	0.2704 (7)	0.4898 (5)	0.2407 (5)	0.0296
C(6)	0.3812 (8)	0.3480 (6)	0.2681 (6)	0.0428
C(7)	0.2829 (7)	0.7303 (5)	0.1144 (5)	0.0318
C(8)	0.2493 (9)	0.9977 (6)	−0.0497 (6)	0.0475
C(9)	0.0089 (7)	0.6646 (5)	0.2522 (5)	0.0331
N(1)	0.1375 (7)	0.0443 (5)	0.6196 (5)	0.0404
N(2)	−0.1614 (7)	−0.0056 (5)	0.6836 (5)	0.0406
N(3)	−0.0995 (6)	0.2094 (4)	0.5379 (4)	0.0334
N(4)	0.0239 (6)	0.3023 (4)	0.4573 (4)	0.0303
N(5)	0.3655 (6)	0.5964 (4)	0.1534 (4)	0.0336
N(6)	0.1056 (6)	0.7674 (4)	0.1650 (4)	0.0341
O(1)	0.7243 (6)	0.5540 (5)	0.0331 (5)	0.0574

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

S(1)—C(7)	1.726 (5)	C(4)—C(5)	1.389 (7)
S(1)—C(8)	1.781 (6)	C(4)—C(9)	1.403 (7)
C(1)—N(1)	1.310 (7)	C(5)—C(6)	1.491 (7)
C(1)—N(2)	1.319 (6)	C(5)—N(5)	1.354 (6)
C(1)—N(3)	1.351 (6)	C(7)—N(5)	1.353 (7)
C(2)—C(3)	1.479 (8)	C(7)—N(6)	1.319 (7)
C(2)—C(4)	1.476 (7)	C(9)—N(6)	1.333 (6)
C(2)—N(4)	1.293 (6)	N(3)—N(4)	1.373 (6)
C(8)—S(1)—C(7)	100.3 (3)	N(5)—C(5)—C(4)	117.5 (5)
N(2)—C(1)—N(1)	121.9 (5)	N(5)—C(5)—C(6)	115.7 (4)
N(3)—C(1)—N(1)	121.8 (5)	N(5)—C(7)—S(1)	116.5 (4)
N(3)—C(1)—N(2)	116.3 (5)	N(6)—C(7)—S(1)	121.4 (4)
C(4)—C(2)—C(3)	118.6 (5)	N(6)—C(7)—N(5)	122.2 (5)
N(4)—C(2)—C(3)	124.4 (5)	N(6)—C(9)—C(4)	125.1 (5)
N(4)—C(2)—C(4)	117.1 (5)	N(4)—N(3)—C(1)	119.6 (4)
C(5)—C(4)—C(2)	125.2 (5)	N(3)—N(4)—C(2)	115.3 (4)
C(9)—C(4)—C(2)	118.5 (5)	C(7)—N(5)—C(5)	122.6 (4)
C(9)—C(4)—C(5)	116.2 (4)	C(9)—N(6)—C(7)	116.4 (4)
C(6)—C(5)—C(4)	126.9 (5)		

Molecule (3) was prepared by leaving a mixture of 1.82 g (0.01 mol) of 5-acetyl-4-methyl-2-methylthiopyrimidine and an excess of amidinohydrazine hydrogencarbonate (3 g) in ethanol solution, acidified to a pH of between 2 and 3 with concentrated hydrochloride acid, at room temperature for a week. Removal of the solvent at room temperature and crystallization of the residual solid in ethanol yielded 2 g of crude compound (3) which was then recrystallized in absolute ethanol. The size and shape of some of the crystals formed allowed an X-ray study of them. Elemental analysis calculated for $C_9H_{14}N_6S.2HCl.H_2O$, with the observed values in parentheses: C 32.83 (33.04), H 5.51 (5.45), N 25.52 (24.99), S 9.74 (10.01), Cl 21.53 (21.18). NMR ^{1}H (DMSO-d_6): 11.5 (*s*, 1H, ech.), 8.55 [*s*, 1H, H(6)], 7.8 (*s*, 3H, ech.), 6.2 (*s*, 4H, ech.), 2.5 (*s*, 6H, $2CH_3$), 2.3 (*s*, 3H, $1CH_3$). IR: 3073 (NH, NH_2), 1680 cm^{-1} (C=N).

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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 71439 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1034]

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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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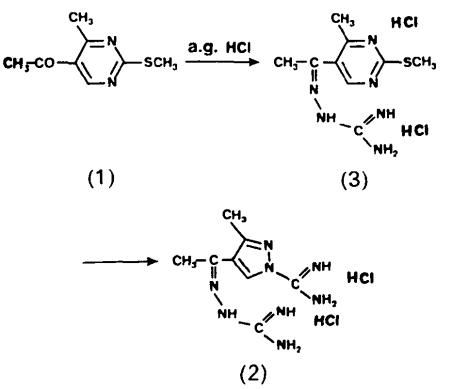
Abstract

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.

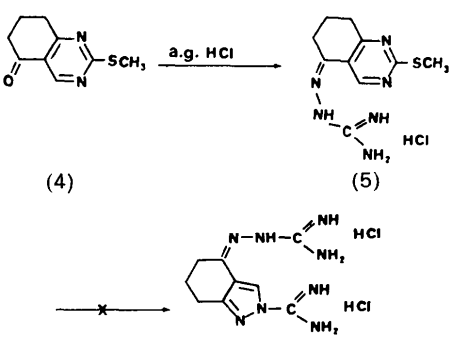
Comment

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)].



(1) (3) (2)

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).



(4) (5)

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