Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual C(sp²)—H···Cl Interaction in the Solid State: Reinvestigation of 4,6-Dimethylpyrimidine-2-thione Hydrochloride Monohydrate

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Abstract

The crystals of $C_6H_9N_2S^+.Cl^-.H_2O$ are composed of 4,6-dimethyl-2-thioxopyrimidinium cations, Cl^- anions and water molecules of crystallization. The Cl^- ion and the water $O(1W)$ atom are strongly bonded to the cation by N—H···Cl and N—H···O hydrogen bonds, forming a hydrated molecule. The cation is

almost coplanar with the Cl^- anion while the water $O(1W)$ atom deviates significantly from the plane of the cation. The molecules form stacks along the z axis with an interplanar distance of 3.62 Å. A three-dimensional network of hydrogen bonds links molecules in consecutive planes with H_2O molecules and Cl^- ions in the lattice cavities and thus stabilizes the molecular packing. The lattice exhibits an unusual $C(sp^2)$—H···Cl interaction, bridging consecutive molecular chains.

Comment

A single-crystal X-ray diffraction study of the title compound was undertaken for a critical re-examination (Battaglia, Corradi, Battistuzzi & Manfredini, 1986) of its crystal structure and also to compare it with the adduct of the same molecule and thiourea (Seth & Sur, 1995). This is important due to its antibacterial, antiviral and antimicrobial properties (Coutts & Casy, 1975; Rosenfield, Berneds, Gelmini, Stephan & Mascharak, 1987). Pyrimidinethiones are also important sulfur-containing components of minor nucleobases; 2- and 4-thiouracil and 2-thiocytosine are normal constituents of some tRNA species. As essential components, they can inhibit RNA synthesis under certain conditions, leading to antitumour and antithyroid activity (Abbot, Goodgame & Jeeves, 1978).

The present study reveals that the crystals of $C_6H_8N_2S.HCl.H_2O$ are composed of 4,6-dimethyl-pyrimidine-2-thione (dtm) cations, Cl^- anions and water molecules of crystallization. The dtm moieties are almost coplanar with the Cl^- anions [deviation 0.007 (1) Å] while the water $O(1W)$ atoms deviate considerably from these planes [-0.324 (3) Å]. The adduct is characterized by a monoprotonated pyrimidine nucleus, whereas in the present case it is protonated at both $N(1)$ and $N(2)$ rather than at the $S(1)$ atom, providing the maximum opportunity for delocalization of the resulting positive charge over almost the entire dtm ion. Thus, the pyrimidine ring of the title compound has appreciable and identical contributions from equivalent canonical structures (I) and (II).

(I)　　　　(II)
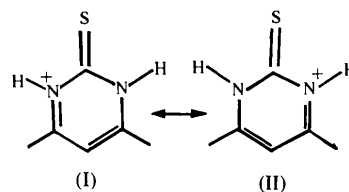
This isovalent resonance, along with the stability gained due to strong hydrogen bonding with the O atom and Cl^- anion on both sides, serve as the potential factors in directing the dtm moiety towards simultaneous thionation and protonation. In the dtm cation, the positive charges on both ring N atoms may also be

stabilized by the hyperconjugative donor effect of the 4- and 6-methyl protons.

With the exception of the C(1)—N(2) bond [1.375 (2) Å] and the C(1)—N(1)—C(2) and C(1)—N(2)—C(4) angles [125.1 (2), 123.9 (2)°], the C—N and C—C distances within the dtm ion are similar to those observed in analogous pyrimidines, their adducts and related metal complexes (Furberg & Jensen, 1970; Seth & Sur, 1995; Cartwright, Langguth & Skapski, 1979; Cotton, Niswander & Sekutowski, 1979; Seth, 1994) and are typical of C—N and C—C bonds with partial double-bond character. The C(1)—S(1) distance [1.644 (2) Å] is significantly smaller than that found in the adduct and in similar compounds (Battaglia & Corradi, 1984; Battaglia, Corradi & Nardelli, 1984; Raper, Oughtred & Nowell, 1985) indicating the strengthening of the π-bond character due to protonation, and is in good agreement with the C—S distances in other thiosubstituted pyrimidines (Saenger & Suck, 1971).
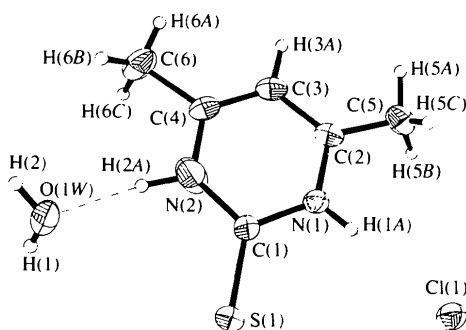
C(3)—H(3A)···Cl(1)($x - \frac{1}{2}$, $2 - y$, z) interaction along the x direction serves as a bridge between the two adjacent chains running along the y direction (Taylor & Kennard, 1982; Saenger, 1973; Jeffrey & Maluszynska, 1982). The molecular packing may also have achieved somewhat additional stability from these weak interactions, present throughout the lattice, apart from that resulting from the three-dimensional network of strong hydrogen bonds. The protonation and thionation of the pyrimidine moiety and subsequent loss of aromaticity is undoubtedly favoured by the energy of the C=S bond and probably augmented by strong hydrogen bonds with two kinds of acceptors (O and Cl⁻), and therefore packing forces are very likely to have influenced the internal geometry of the molecule, at least to some extent, as evidenced by the elongation of the C(1)—N(2) bond and a widening of the C(1)—N(2)—C(4) and C(1)—N(1)—C(2) angles.
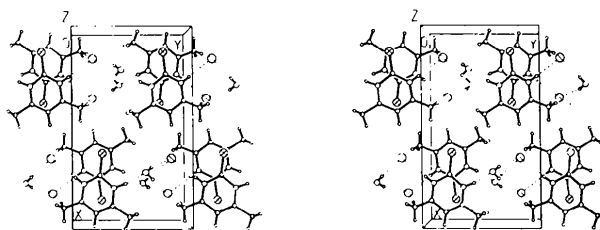

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. For non-H atoms, 50% probability ellipsoids are shown; H atoms are represented by spheres of arbitrary size.

Fig. 2. A stereoview showing the contents of one unit cell of the title compound. The dotted lines represent hydrogen-bonding interactions.

The short N(1)—H(1A)···Cl(1) distance of 3.124 (2) Å hints at strong hydrogen bonding, similar to that reported for pyrazolidinium system (Yang, Ni, Xu & Tang, 1994). The water molecule of crystallization is also strongly bound [$U_{eq} = 0.085\,(1)\,\text{Å}^2$] to the dtm ion by an N(2)—H(2A)···O(1W) hydrogen bond, thereby forming a planar dtm sheet slightly inclined to the *xy* plane. Intermolecular O(1W)—H(1)···Cl(1)(x, $y - 1$, z) and O(1W)—H(2)···Cl(1)($\frac{1}{2} - x$, $y - 1$, $z + \frac{1}{2}$) hydrogen bonds connect the planar sheets in a zigzag chain along the y direction along which the molecules form stacks, with an interplanar distance of 3.62 Å, thus producing infinite intervening channels in the z direction. Adjacent stacks are related by a glide plane so that the molecular planes are not parallel and generate another channel in the lattice. The packing throughout the crystal, therefore, resembles that reported previously (Battaglia *et al.*, 1986) and the adduct of the same molecule also reveals a zigzag channel running along the z axis throughout its lattice. A weak

Experimental

4,6-Dimethyl-2-thiopyrimidine was synthesized by the thermal acid-catalyzed cyclization of thiourea with acetylacetone (Seth, 1994). The compound was recovered from the reaction mixture as a crystalline solid which was recrystallized as acicular crystals by slow evaporation of its hot dilute aqueous solution in order to avoid adduct formation with any unreacted thiourea. Elemental analysis of the compound (observed: C 37.02, H 5.70, N 14.40, S 16.50, O 8.23, Cl 18.15%) confirms the empirical formula $C_6H_{11}N_2SOCl$, or $C_6H_8N_2S.HCl.H_2O$, indicating the formation of a hydrated hydrochloride salt of the thiopyrimidine. The IR spectrum (Dyer, 1965) of the compound (KBr) reveals notable absorptions at $1185\,\text{cm}^{-1}$ (C=S stretch), $3450\,\text{cm}^{-1}$ (N—H stretch), $3050\,\text{cm}^{-1}$ (N—H stretch, amine salts) and $2860\,\text{cm}^{-1}$ (most probably O—H stretch for bifurcated hydrogen bonds; the abnormal decrease in wave number may suggest that apart from the H atoms, the O atom is also engaged in hydrogen bonding), indicating the presence of a pyrimidine-2-thione monocation, protonated at both N atoms of the ring along with strongly hydrogen-bonded water molecules of crystallization. This is further corroborated by the ¹H NMR spectrum of the compound (DMSO-d_6 as solvent, TMS as internal standard) at pH 4 when chemical exchange is considerably retarded and separate absorptions are observed at $\delta = 4.3$ p.p.m. (protons of water molecule) and $\delta = 7.4$ p.p.m. (protons attached to the ring N atoms). The crystal density D_m was measured by flotation in xylene–CHCl₃.

Crystal data

$C_6H_9N_2S^+.Cl^-.H_2O$	Mo $K\alpha$ radiation
$M_r = 194.68$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 72
$Pca2_1$	reflections
$a = 14.8793\,(7)$ Å	$\theta = 3-15°$
$b = 8.9205\,(6)$ Å	$\mu = 0.562$ mm⁻¹
$c = 7.2837\,(4)$ Å	$T = 294$ K
$V = 966.77\,(10)$ Å³	Prismatic
$Z = 4$	$0.20 \times 0.10 \times 0.10$ mm
$D_x = 1.338$ Mg m⁻³	Yellow
$D_m = 1.35$ Mg m⁻³	

Data collection

Rigaku RAXIS-II diffractometer	$R_{int} = 0.019$
Imaging plate	$\theta_{max} = 27.5°$
Absorption correction:	$h = -18 \to 18$
none	$k = 0 \to 11$
3051 measured reflections	$l = -9 \to 9$
1900 independent reflections	3 standard reflections
1888 observed reflections	monitored every 100
$[F > 4\sigma(F)]$	reflections
	intensity decay: 2.6%

Refinement

Refinement on F	$\Delta\rho_{max} = 0.19$ e Å⁻³
$R = 0.034$	$\Delta\rho_{min} = -0.25$ e Å⁻³
$wR = 0.037$	Extinction correction:
$S = 1.116$	SHELX76 (Sheldrick,
1888 reflections	1976)
144 parameters	Extinction coefficient:
All H-atom parameters	0.048 (6)
refined	Atomic scattering factors
$w = 3.4954/[\sigma^2(F_o)$	from International Tables
$+ 0.000135F_o^2]$	for X-ray Crystallography
$(\Delta/\sigma)_{max} = 0.30$	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
S(1)	0.37359 (3)	0.75001 (7)	1/2	0.0620 (2)
Cl(1)	0.34597 (4)	1.17639 (7)	0.35463 (16)	0.0702 (2)
N(1)	0.2228 (1)	0.9031 (2)	0.4472 (3)	0.0505 (5)
N(2)	0.2054 (1)	0.6558 (2)	0.5295 (3)	0.0546 (5)
C(1)	0.2639 (1)	0.7710 (2)	0.4915 (3)	0.0482 (5)
C(2)	0.1332 (1)	0.9236 (3)	0.4347 (3)	0.0562 (6)
C(3)	0.0780 (2)	0.8032 (3)	0.4726 (4)	0.0648 (7)
C(4)	0.1153 (2)	0.6682 (3)	0.5198 (4)	0.0606 (7)
C(5)	0.1000 (2)	1.0722 (4)	0.3755 (6)	0.0783 (10)
C(6)	0.0631 (2)	0.5287 (5)	0.5586 (6)	0.0936 (14)
O(1W)	0.2817 (2)	0.4029 (3)	0.6603 (4)	0.0853 (9)

Table 2. *Selected geometric parameters (Å, °)*

S(1)—C(1)	1.644 (2)	N(1)—C(1)		1.366 (3)
N(1)—C(2)	1.349 (2)	N(2)—C(1)		1.375 (2)
N(2)—C(4)	1.347 (3)	C(2)—C(3)		1.380 (4)
C(2)—C(5)	1.479 (4)	C(3)—C(4)		1.370 (4)
C(4)—C(6)	1.494 (5)			
C(1)—N(1)—C(2)	125.1 (2)	C(1)—N(2)—C(4)		123.9 (2)
N(1)—C(1)—N(2)	114.1 (2)	S(1)—C(1)—N(2)		122.4 (1)
S(1)—C(1)—N(1)	123.5 (1)	N(1)—C(2)—C(5)		118.1 (2)
N(1)—C(2)—C(3)	118.0 (2)	C(3)—C(2)—C(5)		123.9 (3)
C(2)—C(3)—C(4)	119.6 (3)	N(2)—C(4)—C(3)		119.3 (3)
C(3)—C(4)—C(6)	124.7 (3)	N(2)—C(4)—C(6)		116.1 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N(1)—H(1A)⋯Cl(1)	0.79 (3)	2.33 (3)	3.124 (2)	176 (3)
N(2)—H(2A)⋯O(1W)	0.91 (4)	1.80 (4)	2.699 (3)	170 (3)
O(1W)—H(1)⋯Cl(1ⁱ)	0.80 (4)	2.37 (4)	3.155 (4)	168 (4)
O(1W)—H(2)⋯Cl(1ⁱⁱ)	0.76 (5)	2.35 (5)	3.114 (4)	174 (5)
C(3)—H(3A)⋯Cl(1ⁱⁱⁱ)	0.95 (4)	2.63 (4)	3.562 (3)	165 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{1}{2} - x, y - 1, \frac{1}{2} + z$; (iii) $x - \frac{1}{2}, 2 - y, z$.

For the crystal structure solution, the approximate positions of the S atom and Cl⁻ anion were obtained from a Patterson function while successive weighted Fourier syntheses yielded the positions of the remaining non-H atoms. Anisotropic thermal parameters were adjusted for all the non-H atoms; all the H atoms were then located in a difference map and finally refined isotropically. Full-matrix least-squares refinement of the enantiomer gave $R = 0.0336$. Computations were carried out on a MicroVAX II platform at the Distributed Information Centre, Bose Institute, Calcutta, India.

Data collection: *SHELXTL-Plus* (Sheldrick, 1987). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *XRAYARC* (Vickery, Bright & Mallinson, 1971) for Patterson syntheses, *NORMAL*, *EXFFT* and *SEARCH* sequences of *MULTAN78* (Main *et al.*, 1978) for weighted Fourier syntheses. Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Structures of Five ω-Phthalimidoaliphatic Carboxylic Acids†

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Abstract

The crystal structures of five ω-phthalimidoaliphatic carboxylic acids are reported: 2-phthalimidoethanoic acid, $C_{10}H_7NO_4$ (I), 3-phthalimidopropanoic acid, $C_{11}H_9NO_4$ (II), 4-phthalimidobutanoic acid, $C_{12}H_{11}NO_4$ (III), 5-phthalimidopentanoic acid, $C_{13}H_{13}NO_4$ (IV), and 6-phthalimidohexanoic acid, $C_{14}H_{15}NO_4$ (V). Hydrogen bonding within the crystal structures of (I) and (II) produces chains of molecules. In (IV) carboxylic acid dimers are formed through hydrogen bonding between centrosymmetric pairs. The structures of (III) and (V) show a similar motif to (IV) except that the hydrogen bonds are between symmetry-independent molecules.

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† It should be noted that the delay in publication of this paper was not due to problems with the structures, or to the slow response of the authors.

Comment

As part of a general study on the stability of organic peracids and peracid salts (Kariuki & Jones, 1990), and in particular the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the crystal structures of five ω-phthalimidoaliphatic carboxylic acids.
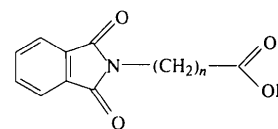
(I) $n = 1$
(II) $n = 2$
(III) $n = 3$
(IV) $n = 4$
(V) $n = 5$

The bond distances and angles observed for all five structures are similar to those reported for phthalimide (Matzat, 1972), *N*-(4-bromophenyl)phthalimide (Ribar, Stankovic & Halasi, 1976) and *N*-(4-iodophenyl)phthalimide (Ribar, Stankovic, Herak, Halasi & Djuric, 1974). In addition, this last structure is isostructural with (I).

The two symmetry-independent molecules in (III) and (V) have similar bond distances and angles, and differ only in their conformation. Also for these structures long C=O and short C—O bonds are observed suggesting a disordered model for the carboxyl groups (Leiserowitz, 1976). No such disorder is seen for (I), (II) and (IV).

The molecules of (I) and (II) contain two planar groups. The phthalimido moiety *A*, N(1),C(8),O(8),C(7), O(7),C(6)–C(1), is planar to within 0.052 Å for (I) and 0.042 Å for (II); the aliphatic acid group *B* in (I), H(101),O(101),C(10),O(100),C(9), is planar to within 0.007 Å. In (II) the aliphatic acid group *B*, H(111),O(111),C(11),O(110),C(10), is planar to within 0.089 Å and the group, N(1),C(9),C(10),C(11), is planar to within 0.093 Å. Table 4 gives details of the *AB* dihedral angles. Molecules of (III), (IV) and (V) on the other hand may be considered as consisting of three moieties. The phthalimido moiety *A* is again planar to within 0.030 and 0.044 Å for molecules 1 and 2 of (III), 0.023 Å for (IV), and 0.016 and 0.032 Å for molecules 1 and 2 of (V), respectively. The second group is the alkyl chain *C*, planar to within 0.003 Å for (IV), and 0.039 and 0.067 Å for molecules 1 and 2 of (V), respectively. The dihedral angles are summarized in Table 4 along with the angles made between these two groups and the COO group, *D*. The group consisting of the alkyl chain, N atom and carboxyl C atom is planar to within 0.404 and 0.416 Å for molecules 1 and 2 of (III), 0.133 Å for (IV) and 0.126 and 0.115 Å for molecules 1 and 2 of (V), respectively.

Fig. 2 is a *PLUTO* (Motherwell & Clegg, 1978) plot of a partial packing diagram for (I). The diagram illustrates that molecules related by a twofold-