Table 1. *Final atomic coordinates and U_{eq} values*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}(Å^2)
C(11)	0	0·0227 (2)	0·25	0·077 (1)
C(12)	0·29282 (6)	0·0533 (1)	0·1991 (1)	0·081 (1)
N(1)	−0·1337 (2)	0·0277 (4)	0·1335 (3)	0·057 (2)
N(2)	−0·2201 (1)	−0·0111 (4)	0·0295 (3)	0·053 (2)
N(3)	−0·1612 (2)	0·1572 (4)	−0·0143 (3)	0·054 (2)
N(4)	−0·1094 (1)	0·2301 (4)	0·0157 (3)	0·052 (2)
C(1)	−0·1710 (2)	0·0623 (5)	0·0481 (3)	0·049 (3)
C(2)	−0·1581 (2)	−0·0845 (6)	0·1794 (4)	0·071 (3)
C(3)	−0·2173 (2)	−0·1111 (5)	0·1080 (4)	0·065 (3)
C(4)	−0·1024 (2)	0·3249 (5)	−0·0442 (4)	0·052 (3)
C(5)	−0·0740 (2)	0·8393 (6)	−0·0500 (4)	0·075 (4)
C(6)	−0·0184 (2)	0·7885 (5)	−0·0192 (4)	0·064 (3)
C(7)	−0·0077 (2)	0·6449 (4)	−0·0100 (3)	0·050 (3)
C(8)	−0·0493 (2)	0·4118 (4)	−0·0201 (3)	0·046 (3)
C(9)	−0·0576 (2)	0·5545 (4)	−0·0309 (3)	0·045 (3)
C(10)	−0·1147 (2)	0·6138 (5)	−0·0624 (4)	0·062 (3)
C(11)	−0·1224 (2)	0·7516 (5)	−0·0729 (4)	0·071 (3)
O(1)	0·2434 (2)	0·2481 (4)	0·3381 (3)	0·084 (3)
N(5)	0	0·3341 (7)	0·25	0·081 (5)
C(12)	0·0522 (3)	0·3998 (8)	0·2735 (4)	0·089 (5)
C(13)	0·0528 (3)	0·5425 (8)	0·2745 (4)	0·099 (6)
C(14)	0	0·613 (1)	0·25	0·098 (7)

Table 2. *Bond lengths* (Å) *and angles* (°) *for bisantrenium pyridinium chloride*

N(1)–C(1)	1·316 (5)	N(1)–C(2)	1·445 (6)
N(2)–C(1)	1·320 (5)	N(2)–C(3)	1·440 (6)
N(3)–N(4)	1·373 (5)	N(3)–C(1)	1·317 (5)
N(4)–C(4)	1·272 (5)	C(2)–C(3)	1·503 (6)
C(4)–C(8)	1·467 (6)	C(5)–C(6)	1·356 (7)
C(5)–C(11)	1·386 (7)	C(6)–C(7)	1·415 (6)
C(7)–C(9)	1·428 (6)	C(8)–C(9)	1·400 (6)
C(9)–C(10)	1·418 (6)	C(10)–C(11)	1·351 (7)
N(5)–C(12)	1·342 (7)	C(12)–C(13)	1·384 (9)
C(13)–C(14)	1·380 (8)	C(7)–C(8)	1·405 (6)

C(2)–N(1)–C(1)	109·6 (4)	C(3)–N(2)–C(1)	110·3 (3)
C(1)–N(3)–N(4)	116·8 (4)	C(4)–N(4)–N(3)	115·3 (4)
N(2)–C(1)–N(1)	112·4 (4)	N(3)–C(1)–N(1)	125·0 (4)
N(3)–C(1)–N(2)	122·6 (4)	C(3)–C(2)–N(1)	104·2 (4)
C(2)–C(3)–N(2)	103·5 (4)	C(8)–C(4)–N(4)	120·6 (4)
C(11)–C(5)–C(6)	120·8 (5)	C(7)–C(6)–C(5)	121·2 (4)
C(9)–C(7)–C(6)	118·0 (4)	C(9)–C(8)–C(4)	117·2 (4)
C(8)–C(9)–C(7)	120·1 (4)	C(10)–C(9)–C(7)	118·1 (4)
C(10)–C(9)–C(8)	121·8 (4)	C(11)–C(10)–C(9)	121·5 (5)
C(10)–C(11)–C(5)	120·2 (5)	C(13)–C(12)–N(5)	118·9 (7)
C(12)–N(5)–C(12)	123·4 (8)	C(14)–C(13)–C(12)	119·2 (7)
C(13)–C(14)–C(13)	120·3 (9)	C(7′)–C(8)–C(9)	120·9 (4)
		C(9)–C(7)–C(8′)	119·1 (4)

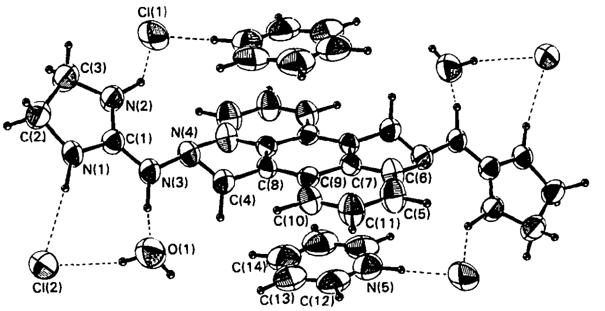

Fig. 1. View showing the stacking interaction between pyridinium and bisantrenium ions and the H bonding to chloride ions. Cl(1) and the pyridinium ring are located along a crystallographic twofold axis. An inversion center is located at the center of the anthracene ring.

References

Citarella, R. V., Wallace, R. E., Murdock, K. C., Angier, R. B. & Durr, F. E. (1980). 20th Intersci. Conf. Antimicrob. Agents Chemother. Abstract 23.

Feigon, J., Denny, W. A., Leupin, W. & Kearns, D. R. (1984). *J. Med. Chem.* **27**, 450–465.

Lown, J. W., Hanstock, C. C., Bradley, R. D. & Scraba, D. G. (1984). *Mol. Pharmacol.* **25**, 178–184.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Powis, G. & Korvach, J. S. (1983). *Cancer Res.* **43**, 925–929.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Spiegel, R. J., Blum, R. H., Levin, M., Pinto, C. A., Wernz, J. C., Speyer, J. L., Hoffman, K. S. & Muggia, F. M. (1982). *Cancer Res.* **42**, 354–358.

Tseng, M. T. & Safa, A. R. (1983). *Cancer Res.* **43**, 5910–5914.

Von Hoff, D. D., Myers, J. W., Kuhn, J., Sandback, J. F., Pocelinko, R., Clark, G. & Coltman, C. A. (1981). *Cancer Res.* **41**, 3118–3121.

Yap, H. Y., Yap, B. S., Bumenschein, G. R., Barnes, B. C., Schell, F. C. & Bodey, G. P. (1983). *Cancer Res.* **43**, 1402–1404.

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Structure of 2,5-Diamino-3*H*-1,3,4-thiadiazolinium Chloride Monohydrate

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Abstract. $C_2H_5N_4S^+.Cl^-.H_2O$, $M_r = 170{\cdot}6$, monoclinic, $P2_1/a$, $a = 14{\cdot}217$ (3), $b = 9{\cdot}526$ (2), $c = 5{\cdot}0497$ (9) Å, $\beta = 98{\cdot}31$ (2)°, $V = 676{\cdot}7$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}67$ (by flotation), $D_x = 1{\cdot}675$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}127$ mm^{-1}, $F(000) = 352$, $T = 293$ K, final $R = 0{\cdot}027$ for 1083 observed unique

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reflections. The cation consists of a 3*H*-thiadiazoline ring and exocyclic $-NH_2$ and $-N^+H_2$ groups. The cation is almost planar. All N—H distances lie in the range 0·80–0·88 Å, and O—H distances are 0·82 and 0·72 Å. Both ions and the water molecule are held together by H bonds.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms*

	x	*y*	*z*	B_{eq}*
S	0·66602 (2)	0·45137 (3)	0·68086 (5)	1·99
N(1)	0·59215 (6)	0·25196 (8)	0·3976 (2)	2·03
N(2)	0·56261 (7)	0·36816 (9)	0·2429 (2)	1·91
N(3)	0·68138 (7)	0·17559 (9)	0·7998 (2)	2·69
N(4)	0·58332 (7)	0·61133 (9)	0·2739 (2)	2·56
C(1)	0·64664 (7)	0·2737 (1)	0·6277 (2)	1·92
C(2)	0·59691 (7)	0·4804 (1)	0·3665 (2)	1·83
Cl	0·33495 (2)	0·17104 (3)	0·22551 (5)	2·53
O	0·44281 (7)	0·02621 (8)	0·7457 (2)	3·25

* Hamilton (1959).

Table 2. *Bond distances* (Å) *and angles* (°)

(*a*) Non-H-atom values

S—C(1)	1·730 (1)	S—C(2)	1·764 (1)
C(1)—N(1)	1·316 (1)	N(1)—N(2)	1·385 (1)
N(2)—C(2)	1·298 (1)	C(1)—N(3)	1·322 (1)
C(2)—N(4)	1·336 (1)		

C(1)—S—C(2)	87·62 (5)	S—C(1)—N(1)	110·55 (7)
C(1)—N(1)—N(2)	117·66 (8)	N(1)—N(2)—C(2)	108·97 (8)
N(2)—C(2)—S	115·18 (7)	S—C(1)—N(3)	123·62 (7)
N(1)—C(1)—N(3)	125·82 (9)	S—C(2)—N(4)	119·68 (7)
N(2)—C(2)—N(4)	125·14 (9)		

(*b*) Possible hydrogen bonds

	$X\cdots Y$	$X\cdots$H	$\angle X\cdots$H$-Y$
Cl···H(O)2—O	3·161 (1)	2·35 (1)	173 (1)
N(2)···H(N4)2—N(4^{i})	3·096 (1)	2·27 (1)	173 (1)
Cl···H(N3)2—N(3^{ii})	3·311 (1)	2·53 (1)	166 (1)
O···H(N1)—N(1^{ii})	2·773 (1)	1·90 (1)	171 (1)
Cl···H(N3)1—N(3^{iii})	3·188 (1)	2·39 (1)	157 (1)

Symmetry codes: none x, y, z; (i) $1-x, 1-y, -z$; (ii) $1-x, -y, 1-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, -1+z$

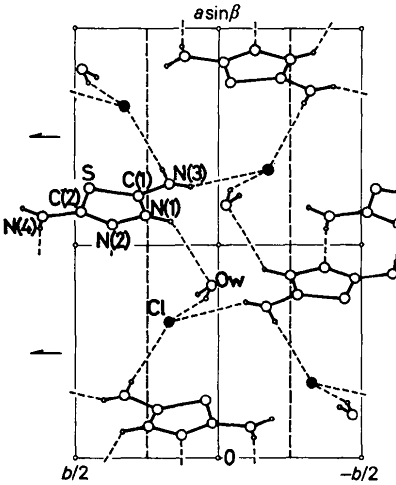

Fig. 1. Crystal structure projected along **c**. Hydrogen bonds are indicated by broken lines.

Introduction. Recently we reported the formation of heterocyclic ring compounds, 1,2,4-thiadiazole and 1,2,4-thiadiazoline derivatives, by reaction between substituted thioureas and $FeCl_3$ (Senda & Maruha, 1985*a*,*b*). Here we report the structure of the compound prepared from dithiobiurea $[H_2NC(=S)NH-]_2$ (dtbu) and $FeCl_2$.

Experimental. An ethanol solution of $FeCl_2.4H_2O$ was added to a suspension of dtbu in ethanol (molar ratio of Fe and dtbu 1:2). The mixture was refluxed at about 330 K for 5 h. A dark-violet iron complex precipitated. Pale-yellow crystals formed from an aqueous solution of the complex were used for X-ray analysis.

Space group $P2_1/a$, systematic absences 0*k*0, *k* odd; *h*0*l*, *h* odd. Crystal: 0·45 × 0·25 × 0·21 mm. Rigaku AFC-4 four-circle diffractometer, graphite-monochromated Mo *Kα*. Cell parameters refined by least-squares method on the basis of 2*θ* values of 25 reflections ($25{\cdot}7 < 2\theta < 39{\cdot}1°$). Intensity measurement performed to $2\theta = 50°$, *θ*–2*θ* scan technique, scan speed 4° min^{-1} (*θ*), *h* 0→16, *k* 0→11, *l* −6→6. Four standard reflections showed no significant variation, $0{\cdot}996 < |F_o|/|F_o|_{\text{initial}} < 1{\cdot}014$. 1320 independent reflections, 237 reflections with $|F_o| < 3\sigma|F_o|$ considered unobserved, 1083 observed unique reflections. Lorentz–polarization correction, no absorption correction. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All of the nine non-H atoms located from *E* map and refined by block-diagonal least-squares method on *F* with anisotropic thermal parameters using *UNICS* program system (Sakurai, 1967). Seven H atoms obtained from ΔF synthesis and included in the refinement isotropically. Final $R = 0{\cdot}027$, $wR = 0{\cdot}019$, $w = 1/(\sigma^2|F_o| - 0{\cdot}0815|F_o| + 0{\cdot}0039|F_o|^2)$, $S = 0{\cdot}66$. $(\Delta/\sigma)_{\max} = 0{\cdot}18$ for non-H atoms and 1·20 for H atoms. Max. and min. height in final ΔF synthesis $\pm 0{\cdot}16$ e Å^{-3}. Scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974) and for H atoms from Stewart, Davidson & Simpson (1965). All calculations performed on a FACOM M-360AP computer.

Discussion. Final atomic coordinates are given in Table 1, and bond distances and angles in Table 2.* The crystal structure is indicated in Fig. 1 together with atom numbering of the crystallographic system.

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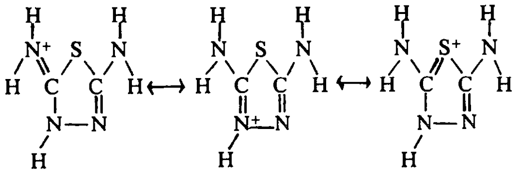
* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, bond distances and angles including H atoms, torsion angles and deviations of atoms from the least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42861 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The five-membered heterocyclic ring is planar: the sum of internal bond angles is 539·98° and maximum deviation from the least-squares plane is 0·008 Å for C(1). The deviation from the plane of the H atom attached to the ring N is 0·03 Å, and for the exocyclic N(3) and N(4) atoms the deviations are −0·011 and −0·023 Å. All N—H distances lie in the range 0·80–0·88 Å, and O—H distances are 0·82 and 0·72 Å. The bonding parameters of the ring are comparable with those reported by Flippen (1972) for a mesoionic thiadiazole derivative. Consideration of the bond lengths shows that in the crystalline state the cation exists mainly in the resonance structures indicated below, with partly double S—C(1), C(1)—N(1) and C(1)—N(3) bonds and a C(2)=N(2) bond.



The cation, the chloride ion and the water molecule are held together with four types of H bonds as seen from Fig. 1. A pair of N(4)—H$\cdots$N(2) H bonds across the center of symmetry results in an H-bonded dimer of the cation. Such dimerization has also been observed in some other 1,3,4-thiadiazole derivatives (Mathew & Palenik, 1974; Kornis, Marks & Chidester, 1980). The H-bond parameters are listed in Table 2. The remaining shortest contacts are Cl$\cdots$N($4^{\rm iv}$) 3·345 (1) [(iv) $1-x$, $1-y$, $1-z$] and Cl$\cdots$O$^{\rm v}$ 3·347 (1) Å [(v) x, y, $-1+z$].

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References

FLIPPEN, J. L. (1972). *Acta Cryst.* B**28**, 2749–2754.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 73, 75. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KORNIS, G., MARKS, P. J. & CHIDESTER, C. G. (1980). *J. Org. Chem.* **45**, 4860–4863.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MATHEW, M. & PALENIK, G. J. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 532–536.
SAKURAI, T. (1967). Editor. *Universal Crystallographic Computation Program System.* The Crystallographic Society of Japan, Tokyo.
SENDA, H. & MARUHA, J. (1985*a*). *Acta Cryst.* C**41**, 1329–1331.
SENDA, H. & MARUHA, J. (1985*b*). *Acta Cryst.* C**41**, 1626–1628.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Acta Cryst. (1986). C**42**, 1089–1091

Lead Indium Bismuth Chalcogenides. III. Structure of $Pb_4In_2Bi_4S_{13}$

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(*Received* 10 *May* 1985; *accepted* 21 *February* 1986)

Abstract. $M_r = 2311{\cdot}15$, orthorhombic, *Pcma* (conventional setting *Pbam* by transforming *b* into −*c* and *c* into *b*), $a = 21{\cdot}344\ (4)$, $b = 4{\cdot}002\ (1)$, $c = 26{\cdot}494\ (5)$ Å, $V = 2263{\cdot}08$ Å^3, $Z = 4$, $D_x = 6{\cdot}783$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 614{\cdot}0$ cm^{-1}, $F(000) = 3864$, room temperature, final $R = 0{\cdot}054$ for 1373 independent observed reflections. The structure consists of In—S tetrahedra and octahedra, mono- and bicapped trigonal prisms of Pb—S, and Bi—S octahedra; all polyhedra are distorted and

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