Fig. 2. Normal projection of DPIA on (010) showing the packing in the unit cell.

secondary bonds $I(2)\cdots O(4^i)$, $I(1)\cdots O(W1)$, and the H bond $O(2^i)\cdots O(W1) = 2\cdot79$ (1) Å (together with the symmetrically related bonds), form a tetramer around the centre of symmetry at (0,0,0). The tetramer constitutes the true structural unit of the crystal. A network of H bonds, $O(W1)\cdots O(W3)$, $O(W3)\cdots O(W2)$ and $O(W2)\cdots O(W3^{ii})$, links tetramers around centres of symmetry to form columns along **c** (see also Fig. 2, which shows a projection of the structure). A list of short intra- and intermolecular distances has been deposited.

H bond $O(W2)\cdots O(1) = 2\cdot66$ (1) Å. The angle $I(1)-O(1)\cdots I(2) = 101\cdot0$ (3)° is smaller than the corresponding angle $I(2)-O(2)\cdots I(1) = 108\cdot4$ (4)°. To complete the octahedral arrangement of bonds, $I(1)$ requires the O atom of the water molecule $W1$, whilst $I(2)$ requires the centrosymmetrically related acetoxy O atom, $O(4^i)$. The rather short H bonds $O(6)\cdots O(W2) = 2\cdot69$ (1) Å and $O(W2)\cdots O(1) = 2\cdot66$ (1) Å and the two secondary bonds $I(1)\cdots O(2)$ and $I(2)\cdots O(1)$ bridge two formula units to form a dimer. Two such dimers, linked by the

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Triethylammonium Salt of 1,2,3,4-Tetrahydro-6-hydroxy-4-oxo-N-phenyl-2-thio-5-pyrimidinecarboxamide, Ethanol Solvate

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Abstract. $(C_2H_5)_3NH^+.C_{11}H_8N_3O_3S^-.C_2H_5OH$, $M_r = 410\cdot5$, orthorhombic, $P2_12_12_1$, $a = 11\cdot765$ (3), $b = 12\cdot788$ (3), $c = 15\cdot011$ (3) Å, $U = 2258\cdot4$ Å^3, $Z = 4$, $D_x = 1\cdot21$ g cm^{-3}, $F(000) = 880$, $\lambda(Mo\ K\alpha_1) = 0\cdot70926$ Å, $\mu = 1\cdot4$ cm^{-1}, room temperature, $R = 0\cdot059$ for 1931 'observed' reflections. The molecular dimensions are interpreted in favour of canonical forms in which the formal negative charge on the anion is delocalized over two sites. In addition the double bonds of the $-NH-CS-NH$ and $-CO-NH-$ moieties are

also delocalized. The anions, cations, and ethanol of solvation are linked by a network of hydrogen bonds.

Introduction. Antineoplastic activity has rarely been demonstrated in barbituric acid derivatives. Consequently, when 1,2,3,4-tetrahydro-6-hydroxy-4-oxo-*N*-phenyl-2-thio-5-pyrimidinecarboxamide (1) was shown to have powerful antitumour activity against a number of mammalian cancers on experimental animals, including murine L1210 leukaemia, B16 melanoma and M5076 sarcoma (Brewer, Minatelli, Plowman, Paull & Narayanan, 1985), we decided to determine the structure in the solid state to ascertain whether the molecule had any unexpected structural features. Suitable crystals of the triethylammonium salt (2) were obtained by heating (1) with a slight excess of triethylamine in ethanol solution. The resulting crystals also contained ethanol of solvation which is slowly lost on standing in air.
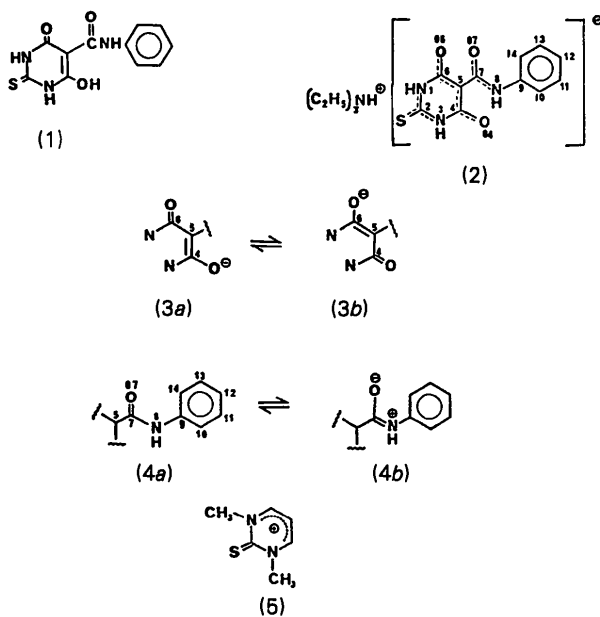
Experimental. A crystal $0.28 \times 0.36 \times 0.40$ mm was selected from a freshly grown sample and quickly coated completely with epoxy cement; this treatment effectively eliminated solvent loss from the crystal. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections (with θ in the range 10–15°) measured on an Enraf–Nonius CAD-4 diffractometer. Space group $P2_12_12_1$, uniquely from the systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. Intensity data were collected by the $\omega/2\theta$ method in two shells, $2 < \theta < 20°$ and $20 < \theta < 27°$. 3 standard reflections; <3% variation. In all, 2796 unique reflections were measured, of which 1931 (69%) had $I > 3\sigma(I)$ and were labelled 'observed' and used in structure solution and

refinement; in the 2–20° shell 92% of the data were 'observed'. $h\,0\rightarrow 15$, $k\,0\rightarrow 16$, $l\,0\rightarrow 19$. The coordinates of the S atom were determined from a Patterson synthesis: early electron-density maps were complicated by the presence of pseudo-mirror symmetry (caused by the S atom having an x coordinate very close to 0.5), but by careful selection of peaks the structures of both anion and cation were revealed, the latter having fairly diffuse density for the C atoms. Full-matrix isotropic refinement (Sheldrick, 1976) reduced R to 0.15 and a subsequent difference map revealed three connected maxima (two of which were quite diffuse) which we took to be the ethanol of solvation. One of the atoms (the best defined, with largest peak-density) was 2.9 Å from an O of the anion, consistent with a hydrogen-bonded distance, and we took this to be the ethanolic oxygen. For computational convenience and because we could discern from the difference map that the ethanol molecule was either markedly anisotropic or slightly disordered in its cavity, in subsequent refinement cycles we included the ethanol molecule as a fixed group with idealized constrained geometry. In the next round of calculations, the cation and anion atoms were allowed anisotropic motion and R was reduced to 0.10. All hydrogen atoms in the cation and anion were then found in a difference map. In the final round of calculations the hydrogen atoms were allowed for in idealized positions (C—H, N—H $= 0.95$ Å) and overall isotropic thermal parameters were refined for the different types of hydrogen atoms. After six rounds of full-matrix least-squares calculations, with the non-hydrogen atoms allowed anisotropic motion, the refinement process converged with $R = 0.059$ and $wR = 0.061$. In the refinement cycles, weights were derived from the counting statistics $w = 1/(\sigma_F^2 + 0.0002F^2)$ and scattering factors were from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). A final difference map had a number of small peaks 0.5–$0.3\,\text{e Å}^{-3}$ around the ethanol of solvation, but no other significant features. The final shift/e.s.d. ratios were all less than 0.1 in the final refinement cycle. Final fractional coordinates* are in Table 1; details of cation and anion dimensions and the hydrogen bonding are in Table 2. Fig. 1 is an *ORTEP* (Johnson, 1976) view of the anion, cation and ethanol solvent molecule; Fig. 2 shows how these moieties pack in the crystal lattice.

Discussion. Our X-ray analysis unequivocally establishes the structure of the title compound to be as shown in (2). The crystals contain discrete well resolved

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$$C_6H_{16}N^+ \cdot C_{11}H_8N_3O_3S^- \cdot C_2H_6O$$

Table 1. *Final fractional coordinates* $(\times 10^4)$ *for the title compound with estimated standard deviations in parentheses*

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S	4846 (1)	3213 (1)	−1686 (1)	4·84 (8)
N(1)	3998 (3)	2230 (3)	−282 (2)	3·2 (2)
C(2)	4909 (4)	2681 (4)	−675 (3)	3·3 (2)
N(3)	5865 (3)	2676 (3)	−178 (3)	3·2 (2)
C(4)	5962 (4)	2247 (4)	667 (3)	2·9 (2)
C(5)	5003 (4)	1721 (4)	1035 (3)	3·1 (2)
C(♦)	3970 (4)	1742 (4)	556 (3)	3·4 (2)
O(4)	6909 (3)	2362 (3)	1039 (2)	3·8 (2)
O(6)	3028 (3)	1381 (3)	780 (3)	4·3 (2)
C(7)	5062 (4)	1178 (4)	1898 (3)	3·6 (2)
O(7)	4242 (4)	697 (4)	2215 (3)	5·5 (2)
N(8)	6074 (4)	1215 (4)	2320 (3)	4·2 (2)
C(9)	6405 (6)	705 (4)	3125 (4)	4·0 (2)
C(10)	7559 (6)	653 (6)	3278 (4)	5·6 (3)
C(11)	7968 (7)	194 (7)	4021 (5)	7·3 (4)
C(12)	7217 (8)	−203 (7)	4679 (6)	7·3 (5)
C(13)	6092 (8)	−123 (6)	4518 (5)	6·4 (4)
C(14)	5669 (6)	328 (5)	3737 (4)	5·3 (3)
N(21)	2337 (4)	718 (4)	6493 (3)	4·7 (2)
C(22)	3357 (6)	678 (5)	5927 (4)	5·4 (3)
C(23)	4014 (8)	1695 (7)	5887 (6)	8·4 (6)
C(24)	2604 (7)	999 (6)	7486 (5)	6·4 (4)
C(25)	3409 (10)	298 (7)	7897 (6)	9·0 (6)
C(26)	1425 (7)	1449 (6)	6127 (6)	7·3 (5)
C(27)	918 (9)	1155 (8)	5333 (8)	11·5 (8)
C(31)	1982 (18)	3547 (19)	3253 (17)	29 (3)
C(32)	2999 (18)	3007 (15)	2930 (11)	20 (2)
O(33)	3306 (11)	2128 (11)	3505 (8)	20 (1)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond lengths* (Å)

S–C(2)	1·666 (5)	C(9)–C(10)	1·378 (8)
N(1)–C(2)	1·352 (6)	C(9)–C(14)	1·352 (8)
N(1)–C(6)	1·405 (7)	C(10)–C(11)	1·350 (10)
C(2)–N(3)	1·349 (6)	C(11)–C(12)	1·419 (10)
N(3)–C(4)	1·387 (6)	C(12)–C(13)	1·349 (12)
C(4)–C(5)	1·426 (6)	C(13)–C(14)	1·397 (9)
C(4)–O(4)	1·254 (6)	N(21)–C(22)	1·471 (8)
C(5)–C(6)	1·412 (6)	N(21)–C(24)	1·565 (8)
C(5)–C(7)	1·471 (7)	N(21)–C(26)	1·503 (9)
C(6)–O(6)	1·247 (6)	C(22)–C(23)	1·514 (10)
C(7)–O(7)	1·239 (6)	C(24)–C(25)	1·442 (12)
C(7)–N(8)	1·350 (7)	C(26)–C(27)	1·443 (13)
N(8)–C(9)	1·426 (7)		

C(2)–N(1)–C(6)	126·8 (4)	O(7)–C(7)–N(8)	121·6 (5)
S–C(2)–N(1)	122·4 (4)	C(7)–N(8)–C(9)	128·5 (5)
S–C(2)–N(3)	122·9 (4)	N(8)–C(9)–C(10)	115·6 (5)
N(1)–C(2)–N(3)	114·7 (4)	N(8)–C(9)–C(14)	124·3 (5)
C(2)–N(3)–C(4)	125·2 (4)	C(10)–C(9)–C(14)	120·0 (6)
N(3)–C(4)–C(5)	118·4 (4)	C(9)–C(10)–C(11)	120·7 (7)
N(3)–C(4)–O(4)	115·7 (4)	C(10)–C(11)–C(12)	120·6 (7)
C(5)–C(4)–O(4)	125·8 (4)	C(11)–C(12)–C(13)	117·4 (7)
C(4)–C(5)–C(6)	118·4 (4)	C(12)–C(13)–C(14)	122·0 (8)
C(4)–C(5)–C(7)	121·8 (4)	C(9)–C(14)–C(13)	119·3 (7)
C(6)–C(5)–C(7)	119·8 (4)	C(22)–N(21)–C(24)	113·2 (5)
N(1)–C(6)–C(5)	116·3 (4)	C(22)–N(21)–C(26)	114·8 (5)
N(1)–C(6)–O(6)	115·3 (4)	C(24)–N(21)–C(26)	107·8 (6)
C(5)–C(6)–O(6)	128·4 (5)	N(21)–C(22)–C(23)	114·2 (6)
C(5)–C(7)–O(7)	122·4 (5)	N(21)–C(24)–C(25)	113·3 (6)
C(5)–C(7)–N(8)	116·0 (4)	N(21)–C(26)–C(27)	114·4 (7)

Cation–anion				
N(21)–H···O(6^i)	N···O	2·921	H···O	2·06
N(21)–H···O(7^i)	N···O	2·811	H···O	2·13

Solvate–anion		
O(33)–H···O(7)	O···O	2·883

Intra-anion				
N(8)–H···O(4)	N···O	2·611	H···O	1·80

Inter-anion				
N(1)–H···O(4^{ii})	N···O	2·758	H···O	1·84
N(3)–H···O(6^{iii})	N···O	2·957	H···O	2·02

The superscripts refer to the following transformations which should be applied to the appropriate coordinates given in Table 1: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$.
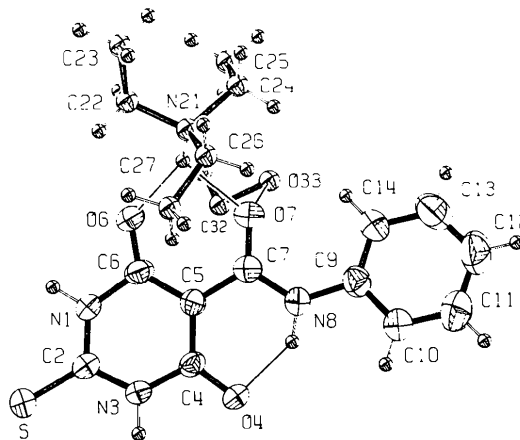
cations, anions and ethanol of solvation linked by an extensive hydrogen-bonded network.

The location of all hydrogen atoms in the anion (Fig. 1) together with the bond-length data [in particular the C—O and C—C distances C(4)—O(4) 1·254 (6), C(6)—O(6) 1·247 (6), C(4)—C(5) 1·426 (6) and C(5)—C(6) 1·412 (6) Å] are consistent with equal contributions of resonance forms such as (3a) and (3b) to the ground-state structure of the anion. The bond lengths involving N(1) and N(3) occur in pairs [N(1)—C(2) 1·352 (6), N(3)—C(2) 1·349 (6), mean 1·351 (6) Å, and N(1)—C(6) 1·405 (7), N(3)—C(4) 1·387 (6), mean 1·396 (6) Å], which are significantly different and are in accord with N(1)—C(2) and N(3)—C(2) having some double-bond character; this would imply some partial positive charge on N(1) and N(3), a corresponding partial negative charge on the exocyclic S atom, and some reduction in the double-bond character of the C=S bond. The C—S bond length [1·666 (5) Å] is longer than that found for C=S in the related 1,2-dihydro-1,3-dimethyl-2-thioxopyrimidinium cation (5) [1·630 (5) Å] where no delocalization of the C=S bond occurs (Ferguson, Kaitner, Lloyd & McNab, 1984); the N(1)—C(6) and N(3)—C(4) bond lengths [mean 1·396 (6) Å] in (2), which we formulate as essentially single C—N bonds, are not significantly different from the N—C single bonds in (5) [1·388 (6) Å].

Fig. 1. An *ORTEP* plot (Johnson, 1976) of the Et$_3$NH$^+$.C$_{11}$H$_8$-N$_3$O$_3$S$^-$.EtOH structure showing the numbering scheme. In the anion, the non-hydrogen atoms are shown with ellipsoids drawn at the 50% probability level. For clarity, the atoms of the cation, the ethanol of solvation and the hydrogen atoms are shown as spheres of arbitrary radii. The thin lines show the hydrogen bonding between anion, cation and ethanol molecule.
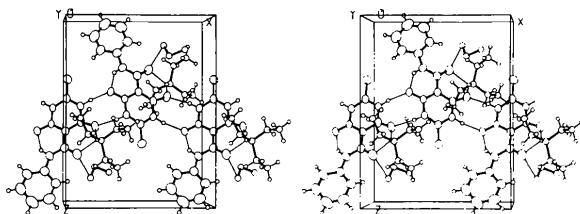
Fig. 2. A stereoview of part of the unit cell showing the inter-anion hydrogen bonding which develops infinite chains in the **a** direction.

In addition, the bond lengths in the C(5),C(7),-O(7),N(8),C(9) region [Fig. 1, Table 2, C(5)—C(7) 1·471 (7), C(7)—N(8) 1·350 (7), C(7)—O(7) 1·239 (6), N(8)—C(9) 1·426 (7) Å] are indicative of contributions from forms such as (4a) and (4b) to the ground-state structure of the anion. The length of the exocyclic C(5)—C(7) bond [1·471 (7) Å] is close to that expected for a C(sp^2)—C(sp^2) single bond, and would imply little conjugation between the resonance forms shown in (3) and (4). The anion is not planar in the solid mainly because of a small rotation [18·4 (6)°] of the phenyl ring about the N(8)—C(9) bond.

The bond lengths in the phenyl ring show a short–long alternation [means 1·350 (8), 1·398 (8) Å] but whether this is a genuine effect or a consequence of the phenyl carbon atoms having maximum U_{ij} values up to twice as large as those of the tightly hydrogen-bonded pyrimidine ring is not clear. The C atoms of the cation have large vibration parameters, as anticipated (maximum U_{ii} 0·219 Å^2), and the C—C bond lengths (1·44–1·51 Å) reflect this marked anisotropy and are not at all well determined. The N atom [N(21)] which is hydrogen-bonded to the anion has close to tetrahedral geometry [C—N—C 107·8–113·2 (5)°].

In the crystals, all N—H groups are involved in hydrogen bonding (see Fig. 2). The cation forms a bifurcated hydrogen bond with anion oxygens O(6) and

O(7). Thus the hydrogen H(N21) on cation nitrogen N(21) is essentially equidistant from O(6) (2·06 Å) and O(7) (2·13 Å) with N(21)···O(6) 2·921 (7) Å and N(21)···O(7) 2·811 (7) Å. O(7) is also involved in an intermolecular O···N—O hydrogen bond with the ethanol of solvation, O(7)···O(ethanol) 2·883 (7) Å. Although the hydrogens of the ethanol molecule were not located, because it is only loosely trapped in the crystal lattice, the O···O distance is indicative of O···H—O hydrogen bonding. The hydrogen H(N8) on N(8) is involved in an intra-ion hydrogen bond to O(4) [N(8)···O(4) 2·611 (7), H(N8)···O(4) 1·80 Å]; this is clearly of importance in maintaining the planarity of the exocyclic O(7)—C(7)—N(8) moiety with the pyrimidine ring. The anions are linked into infinite hydrogen-bonded chains extending along the crystallographic *a* axis by inter-ion N—H···O hydrogen bonds [N(1)—H···O(4), N···O 2·758 (7), H···O 1·84 Å, and N(3)—H···O(6), N···O 2·957 (7), H···O 2·02 Å].

Although the structure shows a number of features which might not be easily predictable, the precise reason for antineoplastic activity is not immediately obvious from the structural data. Further work is in progress on related compounds.

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Structure of 1-(1-Naphthyl)-1*H*-1,2,3-triazole

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Abstract. $C_{12}H_9N_3$, $M_r = 195·22$, orthorhombic, *Pbca*, $a = 9·089$ (1), $b = 15·545$ (1), $c = 13·845$ (1) Å, $V = 1955·9$ (2) Å^3, $Z = 8$, $D_x = 1·326$ g cm^{-3}, λ(Mo $K\alpha$) $= 0·71069$ Å, $\mu = 0·90$ cm^{-1}, $F(000) = 816$, $T = 295$ K, $R = 0·053$ for 785 observed independent reflections. The dihedral angle between the mean plane