Stoe & Cie (1988a). *DIF4. Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988b). *EMPIR. Empirical Absorption Correction Program.* Version 1.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988c). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Van Lommen, G., De Bruyn, M. & Schroven, M. (1990). *J. Pharm. Belg.* **45**, 355-360.

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Structure of 1-(3-Butynyl)pyridinium *p*-Toluenesulfonate

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Abstract

The 1-(3-butynyl)pyridinium *p*-toluenesulfonate salt, $C_9H_{10}N^+.C_7H_7O_3S^-$, contains a C—H···O hydrogen bond between the acetylenic H atom of the cation and a sulfonate O atom of the anion in the solid state [C···O 3.32 (1), H···O 2.49 Å, C—H···O 159°]. The X-ray analysis was complicated by disorder in both the cation and anion. A major (85%) and a minor (15%) component of the 1-(3-butynyl)pyridinium cation are present, both occuping the same volume element in the lattice. The methyl H atoms and sulfonate O atoms of the *p*-toluenesulfonate anion are disordered over two orientations.

Comment

The pyridinium salt, 1-(3-butynyl)pyridinium *p*-toluenesulfonate, (1), was synthesized from the reaction of 3-butynol and *p*-toluenesulfonyl chloride in pyridine. The present structural determination establishes the formulation as $C_5H_5NCH_2CH_2C{\equiv}CH^+.CH_3C_6H_4SO_3^-$ (1), Fig. 1. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that the cation $pyCH_2CH_2C{\equiv}CH^+$ in (1) has not been reported previously. This cation is disordered such that a major (85%) and a minor (15%) orientation occupy the same volume element in the lattice. The methyl H atoms and sulfonate O atoms of the *p*-toluenesulfonate anion are also disordered over two orientations.

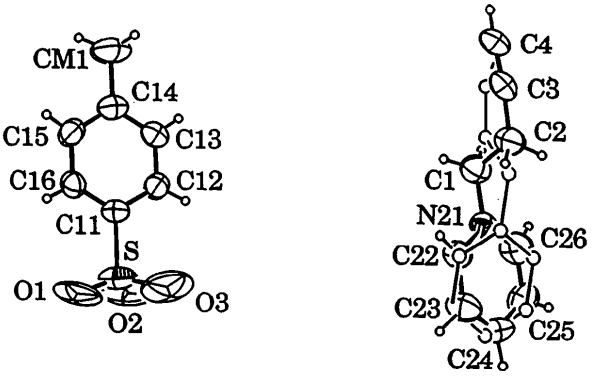

Fig. 1. An *ORTEP* view of the major and minor sites of the alkynyl pyridinium cation with the hydrogen-bonded *p*-toluenesulfonate anion. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, only one of the two possible locations of the methyl H and sulfonate O atoms is shown; the H atoms and the non-H atoms of the minor site are drawn as small spheres of arbitrary size.

Despite the disorder, dimensions of the anion and of the major component of the 1-(3-butynyl)pyridinium cation are as expected, with acetylenic HC(4)≡C(3) 1.167 (6) Å and C(4)≡C(3)—C(2) 173.8 (5)°. The acetylenic H atom H(4) was positioned at the coordinates obtained from a difference map (C—H 0.87 Å, C≡C—H 176°). This acetylenic C≡C—H group is involved in hydrogen bonding with an O atom of the disordered sulfonate group of a neighbouring anion: C(4)···O(1) 3.32 (1), H(4)···O(1) 2.49 Å, C(4)—H(4)···O(1) 159°. Such acetylenic C≡C—H···O hydrogen bonding is well established, *e.g.* in *o*-bromobenzoylacetylene with C···O 3.260 (15) Å (Ferguson & Tyrrell, 1965) and in *o*-chlorobenzoylacetylene with C···O 3.212 (9) Å (Ferguson & Islam, 1966). Coordinates for the minor cation component were obtained from difference maps and idealized. The dihedral angle between the major and minor aromatic ring planes is 23°.

The single bond C(1)—C(2) is 1.506 (7) Å, while C(2)—C(3) is 1.458 (6) Å. The N—C bonds in the pyridinium ring are similar, 1.328 (5) and 1.339 (5) Å; the four C—C bond lengths are in the range 1.337 (7)-1.374 (7) Å, with a mean value of 1.360 (7) Å. The C_{ar}—C_{ar} bond lengths in the *p*-toluenesulfonate anion are normal and in the range 1.360 (5)-1.392 (5) Å with a mean value of 1.378 (5) Å.

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Experimental

Crystal data

$C_9H_{10}N^+.C_7H_7O_3S^-$
M_r = 303.37
Orthorhombic
$P2_1cn$
a = 7.2214 (5) Å
b = 8.0172 (7) Å
c = 26.2878 (21) Å
V = 1521.9 (2) Å^3
Z = 4
D_x = 1.32 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.5–18.5°
μ = 0.2 mm^{-1}
T = 293 K
Block
0.60 × 0.60 × 0.40 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3309 measured reflections
3309 independent reflections
2500 observed reflections [$I_{net} > 3.0\sigma(I_{net})$]
θ_{max} = 27.0°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 33$
3 standard reflections
frequency: 60 min
intensity variation: 2.0%

Refinement

Refinement on F
R = 0.046
wR = 0.080
S = 1.72
2500 reflections
218 parameters
H atoms refined as riding atoms
$w = 1/[\sigma^2(F) + 0.0015F^2]$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement 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}
S	0.12080	0.25548 (10)	0.37010 (3)	0.0713 (5)
C(11)	0.1035 (5)	0.4263 (3)	0.41299 (10)	0.0468 (14)
C(12)	0.1705 (5)	0.5798 (4)	0.39834 (12)	0.0538 (16)
C(13)	0.1537 (5)	0.7140 (4)	0.43136 (13)	0.0569 (18)
C(14)	0.0702 (5)	0.6985 (4)	0.47747 (14)	0.0586 (18)
C(15)	0.0068 (5)	0.5419 (5)	0.49222 (13)	0.0605 (18)
C(16)	0.0235 (5)	0.4072 (4)	0.45992 (11)	0.0506 (15)
C(M1)	0.0522 (8)	0.8471 (5)	0.51304 (20)	0.093 (3)
O(1)	0.084 (4)	0.1183 (7)	0.3947 (3)	0.173 (15)
O(2)	0.0237 (24)	0.3028 (17)	0.3276 (5)	0.120 (9)
O(3)	0.3241 (19)	0.2677 (19)	0.3540 (8)	0.185 (12)
O(4)	0.142 (3)	0.3046 (16)	0.3228 (4)	0.141 (15)
O(5)	0.2581 (18)	0.1460 (13)	0.3861 (4)	0.102 (6)
O(6)	−0.0675 (21)	0.168 (3)	0.3763 (6)	0.193 (12)
C(1)	0.0361 (7)	0.5192 (5)	0.21916 (19)	0.0669 (24)
C(2)	0.2068 (7)	0.6086 (6)	0.23752 (20)	0.071 (3)
C(3)	0.1528 (8)	0.7485 (4)	0.26969 (19)	0.0672 (24)
C(4)	0.1075 (9)	0.8500 (5)	0.29899 (18)	0.076 (3)
N(21)	0.0903 (6)	0.3801 (4)	0.18421 (12)	0.0541 (16)
C(22)	0.1255 (8)	0.2299 (4)	0.20314 (13)	0.0574 (19)
C(23)	0.1706 (8)	0.1018 (5)	0.17159 (17)	0.0683 (24)
C(24)	0.1829 (7)	0.1289 (7)	0.12007 (20)	0.076 (3)
C(25)	0.1483 (10)	0.2855 (7)	0.10164 (16)	0.081 (3)
C(26)	0.1039 (10)	0.4075 (5)	0.13411 (17)	0.075 (3)
C(1′)	0.21535	0.52336	0.21951	0.05
C(2′)	0.04112	0.62171	0.23050	0.05
C(3′)	0.06265	0.73715	0.26954	0.05
C(4′)	0.11518	0.87422	0.29433	0.05
N(11′)	0.19558	0.37225	0.18631	0.05
C(22′)	0.16101	0.21670	0.20811	0.05
C(23′)	0.14262	0.07616	0.17723	0.05
C(24′)	0.15881	0.09118	0.12455	0.05
C(25′)	0.19339	0.24673	0.10275	0.05
C(26′)	0.21178	0.38726	0.13362	0.05

The space group for the title compound was determined from the systematic absences ($h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$) to be either $P2_1cn$ (a non-standard setting of the non-centrosymmetric space group $Pna2_1$, No. 33) or $Pmcn$ (a non-standard setting of the centrosymmetric space group $Pnma$, No. 62). The structure was solved and refined satisfactorily in the non-centrosymmetric space group $P2_1cn$. The direction of the chiral axis was determined by comparing the residuals after refinement with the chirality η parameter set to +1 and −1. Least-squares refinement with η fixed at −1.00 gave an R factor and wR factor 0.01 greater than when it was fixed at +1.00. An analysis on the reflections for which the Bijvoet difference is most significant demonstrates that this is the correct model. It became obvious at an intermediate stage of the refinement that there was disorder in both the cation and the anion. The cation was disordered such that there was a minor component (15%) present in the same volume element. The non-H atoms associated with this minor conformer were revealed in difference maps and included in the structure-factor calculations at these positions with a common thermal parameter U = 0.05 Å^2 (the minor pyridine moiety was treated as a planar hexagon; C—C and C—N 1.395 Å). No H atoms were included for this minor orientation. The O atoms of the sulfonate group were disordered over two orientations and the six sites were each refined with half occupancy. Occupancies of disordered sites were estimated from difference syntheses and were not varied in the least-squares refinements. The methyl H atoms were also disordered over two orientations. The H atoms were included at geometrically idealized positions as riding atoms in the structure-factor calculations with appropriate occupancies and C—H 0.95 Å, except for the acetylenic H(4) which was located from difference maps.

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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 71426 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1050]

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Ferguson, G. & Islam, K. M. S. (1966). *J. Chem. Soc. B*, pp. 593-600.
Ferguson, G. & Tyrrell, J. (1965). *J. Chem. Soc. Chem. Commun.* pp. 195-196.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384-387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

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Intermolecular N—H···O=C Hydrogen-Bonding in the Crystal Structure of 6-Amino-1,3-dimethyluracil

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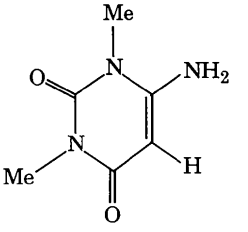
Abstract

The 6-amino-1,3-dimethyluracil molecule [6-amino-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione], $C_6H_9N_3O_2$ (I), lies on a crystallographic mirror plane and participates in an extensive two-dimensional hydrogen-bonding network in the solid state. Each molecule is involved in N—H···O=C hydrogen bonding involving the amino and carbonyl groups, with O···N separations of 2.894 (3) and 2.904 (3) Å.

Comment

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in terms of the preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991). In general, the strongest hydrogen-bond donors pair off with the strongest hydrogen-bond acceptors. Similar pairing processes are repeated until all the hydrogen-bond donors and acceptors have been utilized. Herein we report the formation of a two-dimensional network of intermolecular N—H···O=C hydrogen bonds in the structure of 6-amino-1,3-dimethyluracil (I).



The 6-amino-1,3-dimethyluracil molecule (I) lies on a crystallographic mirror plane and participates in an extensive two-dimensional hydrogen-bonding network in the solid state (see Fig. 1). The bond lengths in this structure are similar to those previously observed in related structures, *e.g.* C=O 1.224 (3) and 1.237 (3) Å; C(sp^3)—N 1.460 (3) and 1.458 (3) Å. Likewise, the bond angles do not deviate from the accepted values and are in the range 115.8 (2) for N(3)—C(4)—C(5) to 125.5 (2)° for O(4)—

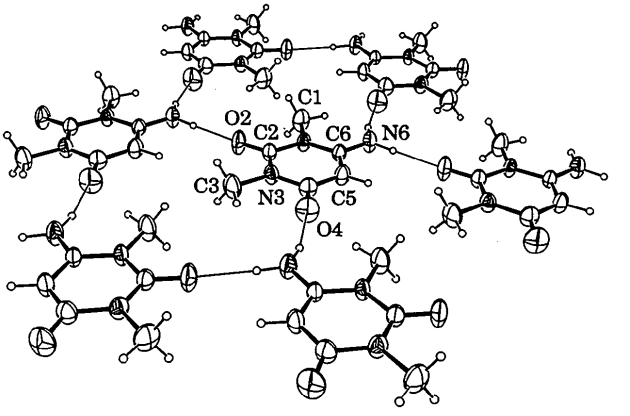


Fig. 1. A view of the two-dimensional hydrogen-bonding environment in the crystal structure of 6-amino-1,3-dimethyluracil (I). The non-H atoms are depicted with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.

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