Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4-Phenylpyridinium hydrogensquarate

T. Kolev,[a] R. Wortmann,[b] M. Spiteller,[c] W. S. Sheldrick[d]* and M. Heller[d]

[a]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Building 9, 1113 Sofia, Bulgaria, [b]Faculty of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany, [c]Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Straße 6, D-44221 Dortmund, Germany, and [d]Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

Correspondence e-mail:
william.sheldrick@rub.de

Received 22 April 2004
Accepted 29 April 2004
Online 8 May 2004

The 4-phenylpyridinium cation of the title compound, $C_{11}H_{10}N^{+}\cdot C_4HO_4^{-}$, exhibits an interplanar angle of 28.6 (1)° and interacts with a neighbouring hydrogensquarate anion through a single N—H···O hydrogen bond [N···O = 2.697 (2) Å]. Individual anions are linked into centrosymmetric dimers by strong O—H···O hydrogen bonds [H···O = 1.52 Å and O···O = 2.493 (2) Å]. Alternating layers of 4-phenylpyridinium cations and hydrogensquarate anions are stacked along the [001] axis.

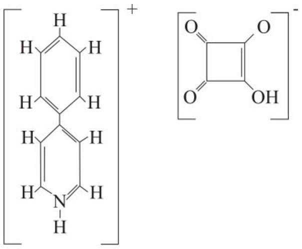
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.100
Data-to-parameter ratio = 11.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The crystal structure of 4-phenylpyridinium hydrogensquarate, (I), was determined as part of our continuing spectroscopic and structural studies on organic compounds with nonlinear optical, photorefractive and electro-optical properties (Chemla & Zyss, 1987; Nalwa *et al.*, 1997; Wolff & Wortmann, 1999. A reversible single-crystal to single-crystal polymorph transition (from the monoclinic to the triclinic crystal system) of the hydrogen-bonded system has been reported for the related 4,4′-bipyridinium salt (Reetz *et al.*, 1994). Furthermore, 4-phenylpyridine has been found to exhibit a remarkable inclusion ability, forming a novel host complex with nickel(II) dibenzoylmethanate (Soldatov *et al.*, 2002). IR and Raman spectra of (I) indicate that the protonated 4-phenylpyridinium N atom participates in an N—H···O hydrogen bond to the hydrogensquarate anion, as confirmed by the crystal structure. In contrast with most reported structures, in which hydrogensquarate anions are linked into infinite chains by O—H···O interactions (Angelova *et al.*, 1996*a*), anion dimerization is observed for (I), as previously found in the case of L-guanidinium hydrogensquarate (Angelova *et al.*, 1996*b*).



(I)

Experimental

A water–ethanol (1:1) solution of 4-phenylpyridine was added to an aqueous solution of an equimolar quantity of squaric acid and set aside to crystallize. The product, (I), was purified by multiple recrystallization from distilled water and crystals suitable for X-ray diffraction were grown by slow evaporation.

DOI: 10.1107/S1600536804010487

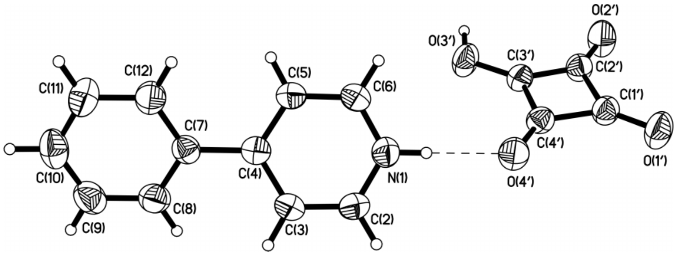


Figure 1
The 4-phenylpyridinium cation and hydrogensquarate anion of (I), with the hydrogen bond shown as a dashed line. Displacement ellipsoids are drawn at the 50% probability level

Crystal data

$C_{11}H_{10}N^+\cdot C_4HO_4^-$
$M_r = 269.25$
Monoclinic, $P2_1/c$
$a = 11.781$ (3) Å
$b = 8.994$ (2) Å
$c = 12.988$ (3) Å
$\beta = 113.91$ (2)°
$V = 1258.0$ (6) Å^3
$Z = 4$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 57 reflections
$\theta = 7.7\text{–}14.6°$
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
$0.46 \times 0.41 \times 0.39$ mm

Data collection

Siemens *P*4 four-circle diffractometer
Profile fitted ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 1995)
$T_{\min} = 0.933$, $T_{\max} = 0.963$
2323 measured reflections
2211 independent reflections
1494 reflections with $I > 2\,s(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 25.0°$
$h = -14 \rightarrow 0$
$k = -10 \rightarrow 0$
$l = -14 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: 20%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.100$
$S = 1.03$
2211 reflections
196 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.1558P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0040 (19)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3′—H3′$\cdots$O2′$^{\rm i}$	1.01 (4)	1.52 (4)	2.493 (2)	161 (3)
N1—H1$\cdots$O4′	0.86	1.84	2.697 (3)	171

Symmetry code: (i) $1-x, 1-y, 1-z$.

H atoms of the 4-phenylpyridinium ion were visible in difference maps and were subsequently treated as riding atoms, with distances C—H = 0.93 Å and N—H = 0.86 Å, and with individual isotropic displacement parameters. The hydrogensquarate atom H3′ participates in a strong O3′—H3′$\cdots$O2′($1-x, 1-y, 1-z$) hydrogen bond and was therefore allowed to refine freely, to afford O3′—H3′ and H3′...O2′ distances of 1.01 (4) and 1.50 (4) Å, respectively .

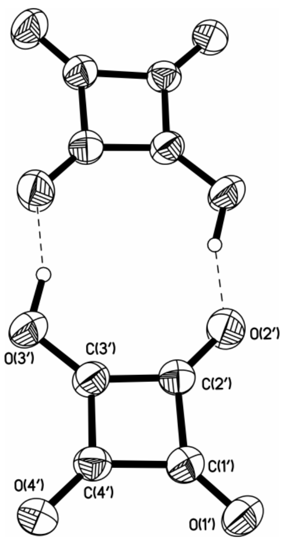


Figure 2
Dimerization of hydrogensquarate anions through strong O3′—H3′$\cdots$O2′$^{\rm i}$ hydrogen bonds (dashed lines). Dispacement ellipsoids are drawn at the 50% probability level. [Symmetry code as in Table 1.]

Data collection: *R*3*m*/*V* (Siemens, 1989); cell refinement: *R*3*m*/*V*; data reduction: *R*3*m*/*V*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

TK, RW and MS thank the DAAD for a grant within the priority programme 'Stability Pact South-Eastern Europe', the Alexander von Humboldt Foundation and the Bulgarian National Fund for Research (grant No. X-1213).

References

Angelova, O., Velikova, V., Radomirska, V. & Kolev. T. (1996*a*). *Acta Cryst.* C**52**, 2218–2220.
Angelova, O., Velikova, V., Radomirska, V. & Kolev. T. (1996*b*). *Acta Cryst.* C**52**, 3252–3256.
Chemla, D. S. & Zyss, J. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, edited by D. S. Chemla and J. Zyss, pp. 23–187. New York: Academic Press.
Nalwa, H. S., Watanabe, T. & Miyata, S. (1997). *Nonlinear Optics of Organic Molecules and Polymers*, edited by H. S. Nalwa & S. Miyata, pp. 89–329. Boca Raton: CRC Press Inc.
Reetz, M., Moeger, S. & Harms, K. (1994). *Angew. Chem.* **106**, 193–195; *Angew. Chem. Int. Ed. Engl.* **33**, 181–183.
Sheldrick, G. M. (1995). *SHELXTL*. Release 5.03 for Siemens *R*3 crystallographic research system. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1989). *R3m/V Crystallographic Systems User's Guide*. Version 3.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soldatov, D., Enright, G. & Ripmeester, J. (2002). *Chem. Mater.* **14**, 348–356.
Wolff, J. & Wortmann, R. (1999). *Adv. Phys. Org. Chem.* **32**, 121–217.