Crystal structure of *R*-(+)-1-phenylethylammonium hydrogensquarate monohydrate, $C_{12}H_{13}NO_4 \cdot H_2O$

T. Kolev^I, Z. Glavcheva^{II}, M. Schürmann^I, H. Preut*^I, P. Bleckmann^I and V. Radomirska^{II}

^I Universität Dortmund, Fachbereich Chemie, Otto-Hahn-Str. 6, D-44221 Dortmund, Germany

^{II} Bulgarian Academy of Sciences, Institute of Organic Chemistry, 1113 Sofia, Bulgaria

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Abstract

$C_{12}H_{13}NO_5$, monoclinic, $P12_11$ (No. 4), $a = 7.035(1)$ Å, $b = 11.024(2)$ Å, $c = 8.686(2)$ Å, $\beta = 111.89(3)^\circ$, $V = 625.1$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.044$, $R_w(F^2) = 0.116$, $T = 293$ K.

Source of material

The title compound was prepared by adding an ethanol/water (1:1) solution of *R*-(+)-1-phenylethylamine free base to a water solution of squaric acid in a 1:1 molar ratio with continuous stirring at room temperature. After addition the amine the mixture was stirred at ambient temperature for 30 minutes. The product was purified by repeated crystallization from doubly distilled water. Colourless crystals were grown from an aqueous solution at room temperature. The compound was characterized by elemental analysis and spectroscopic methods. The IR spectrum in the solid state (KBr pellet) confirms that *R*-(+)-1-phenylethylammonium hydrogensquarate monohydrate exists as a cation and that the amino group is protonated. The melting point of the title compound is over 550 K with decomposition.

Discussion

The choice of special molecules and the crystal-growth methods are of main importance for obtaining nonlinear optically active single crystals of good quality and large size. A main advantage of the used organic materials is the possibility of altering the molecular structure in order to improve the nonlinear optical (NLO) properties [1].

The structure determination of the title compound was undertaken in order to study the conformational effects on the nonlinear optical properties. The structure of the enantiomeric crystal *S*-(-)-1-phenylethylammonium hydrogen squarate was determined [2]. It was of great interest to compare the hydrogen bonding network of *S*-(-)-1-phenylethylammonium hydrogensquarate anions with the network of the title compound in order to predict its NLO properties.

Table 1. Data collection and handling.

Crystal:	colorless column, size 0.15 x 0.2 x 0.4 mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	0.95 cm ⁻¹
Diffraction, scan mode:	Nonius Mach3, $\omega/2\theta$
$2\theta_{\text{max}}$:	54.86°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	3092, 2869
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2273
$N(\text{param})_{\text{refined}}$:	178
Programs:	PARST95 [3], SHELXS-90 [4], SHELXTL-Plus [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(3)	2a	0.501(7)	0.616(5)	1.027(6)	0.10(1)
H(5A)	2a	0.394(4)	0.545(3)	0.442(4)	0.047(7)
H(5B)	2a	0.420(6)	0.604(5)	1.324(5)	0.09(1)
H(1A)	2a	0.5482	0.2860	1.4306	0.061
H(1B)	2a	0.5711	0.2898	1.2712	0.061
H(1C)	2a	0.5633	0.4020	1.3566	0.061
H(12)	2a	0.9674	0.2228	1.7551	0.097
H(13)	2a	1.0740	0.3112	2.0168	0.137
H(14)	2a	1.0567	0.5136	2.0451	0.138
H(15)	2a	0.9442	0.6359	1.8163	0.136
H(16)	2a	0.8419	0.5524	1.5528	0.092
H(17A)	2a	0.8860	0.3430	1.2413	0.102
H(17B)	2a	1.0778	0.3768	1.3990	0.102
H(17C)	2a	0.8920	0.4666	1.3324	0.102
H(18)	2a	0.8774	0.2371	1.4707	0.067

* Correspondence author

(e-mail: uch002@uxp1h.hrz.uni-dortmund.de)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	2a	0.4277(3)	0.2699(1)	0.6332(2)	0.065(1)	0.0300(7)	0.0348(7)	0.0021(6)	0.0211(7)	−0.0072(6)
O(2)	2a	0.5303(3)	0.2514(1)	1.0304(2)	0.086(1)	0.0221(6)	0.0312(7)	0.0013(7)	0.0169(8)	0.0030(6)
O(3)	2a	0.5350(3)	0.5359(1)	1.0605(2)	0.076(1)	0.0234(6)	0.0305(7)	0.0005(7)	0.0187(7)	−0.0028(6)
O(4)	2a	0.4055(3)	0.5646(1)	0.6625(2)	0.079(1)	0.0275(8)	0.0350(7)	0.0069(6)	0.0277(7)	0.0072(6)
O(5)	2a	0.3829(3)	0.5363(2)	1.3441(2)	0.078(1)	0.0417(9)	0.0386(8)	−0.0026(8)	0.0295(8)	−0.0011(7)
N(1)	2a	0.6061(3)	0.3253(2)	1.3699(2)	0.047(1)	0.0339(8)	0.0385(9)	−0.0062(7)	0.0128(7)	−0.0076(7)
C(1)	2a	0.4515(3)	0.3430(2)	0.7453(2)	0.039(1)	0.0226(8)	0.0318(9)	0.0019(7)	0.0145(7)	0.0007(7)
C(2)	2a	0.5006(3)	0.3349(2)	0.9259(2)	0.044(1)	0.0226(8)	0.0300(9)	0.0014(7)	0.0128(8)	−0.0006(7)
C(3)	2a	0.4992(3)	0.4635(2)	0.9355(2)	0.044(1)	0.0226(8)	0.0286(9)	0.0008(7)	0.0159(8)	0.0011(6)
C(4)	2a	0.4432(3)	0.4783(2)	0.7586(2)	0.042(1)	0.0236(9)	0.0317(9)	0.0031(7)	0.0182(8)	0.0018(7)
C(11)	2a	0.8964(3)	0.3788(2)	1.6269(3)	0.039(1)	0.053(1)	0.037(1)	−0.0094(9)	0.0135(8)	−0.0046(9)
C(12)	2a	0.9634(5)	0.3067(3)	1.7656(4)	0.056(2)	0.085(2)	0.050(1)	−0.012(1)	0.016(1)	0.015(1)
C(13)	2a	1.0257(6)	0.3600(6)	1.9227(4)	0.068(2)	0.166(5)	0.040(1)	−0.017(2)	0.020(1)	0.014(2)
C(14)	2a	1.0167(6)	0.4797(6)	1.9397(4)	0.066(2)	0.164(5)	0.050(2)	−0.040(2)	0.027(2)	−0.045(2)
C(15)	2a	0.9494(6)	0.5524(4)	1.8037(5)	0.091(3)	0.102(3)	0.087(2)	−0.035(2)	0.042(2)	−0.055(2)
C(16)	2a	0.8883(5)	0.5024(3)	1.6457(4)	0.075(2)	0.054(2)	0.054(2)	−0.015(1)	0.023(1)	−0.016(1)
C(17)	2a	0.9314(4)	0.3827(4)	1.3473(3)	0.052(1)	0.108(2)	0.046(1)	−0.009(2)	0.022(1)	−0.010(2)
C(18)	2a	0.8342(3)	0.3223(2)	1.4565(3)	0.045(1)	0.043(1)	0.044(1)	0.0023(9)	0.0136(9)	−0.0076(9)

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References

1. Nalwa, H. S.; Miyata S. (Eds.): *Nonlinear Optics of Organic Molecules and Polymers*, Chapter 4 and 5. Boca Raton; CRS Press 1997.
2. Kolev, T.; Stahl, R.; Preut, H.; Bleckmann, P.; Radomirska, V.: Crystal structure of 1-phenyl-ethyl-ammonium hydrogensquarate monohydrate, C₁₂H₁₅NO₅. *Z. Kristallogr. NCS* **212** (1997) 417-418.
3. Nardelli, M.: A system of Fortran routines for calculating molecular structure parameters from the results of crystal structure analyses. *J. Appl. Crystallogr.* **28** (1995) 659.
4. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46** (1990) 467-473.
5. Sheldrick, G. M.: SHELXTL-Plus. Release 4.1 Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1991.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.