organic papers

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.009 Å

H-atom completeness 63%

R factor = 0.042

wR factor = 0.134

Data-to-parameter ratio = 8.2

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

(R)-2-[(2-Ethoxy-3,4-dioxocyclobut-1-en-1-yl)-amino]-3-phenylpropanamide hemihydrate

The title compound, $C_{15}H_{16}N_2O_4 \cdot 0.5H_2O$, is the first structurally characterized example of an ester amide of a squaric acid amino acid derivative. There are two conformationally inequivalent organic molecules and a water molecule in the asymmetric unit. Molecules are linked via N—H···O and O—H···O hydrogen bonds to build the non-centrosymmetric crystal structure.

Comment

The present investigation of the title compound, (I), is part of a project dealing with non-linear optical, electro-optical and photorefractive materials (Chemla & Zyss, 1987; Nalwa & Miyata, 1997; Wolff & Wortmann, 1999). Several optically active salts of squaric acid have been synthesized and their crystal structures have been reported, namely (R)-(−)-1-phenylglycinium hydrogensquarate monohydrate (Angelova, Petrova et al., 1996), L-argininium hydrogensquarate (Angelova, Velikova et al., 1996), L-serinium hydrogensquarate (Kolev, Stahl, Preut, Bleckmann & Radomirska, 1998) and L-asparaginium hydrogensquarate (Kolev, Stahl, Preut, Konicek et al., 1998). This study was continued with the synthesis of squaric acid covalent derivatives.

(I)
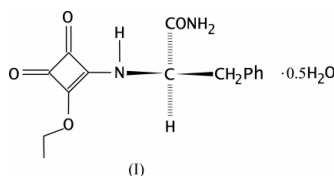
The first reported structure of a squaric acid ester amide is that of 4-[(4-N,N-dimethylaminophenylene)amino]-3-ethoxy-3-cyclobutene-1,2-dione (Kolev et al., 2001), which was synthesized according to the general procedure described by Tietze et al. (1991). We tried to apply this approach to free amino acids. The procedure did not result in the desired products because of the zwitterionic nature of amino acids. The amino acid carboxy group was transformed into an amide group, and then the coupling reagent diethylsquarate reacted with the free amino group of the amino acid amide. As a result, a squaric acid amide ester was obtained in excellent yield. The title compound was synthesized via condensation of L-phenylalaninamide and diethyl squarate in ethanol at room temperature. Further treatment of this ester amide with an amino acid derivative in the same solvent in the presence of triethylamine led to the formation of the corresponding squaric acid diamide, which is of very low solubility in any solvent and has an extremely high melting point. Our efforts
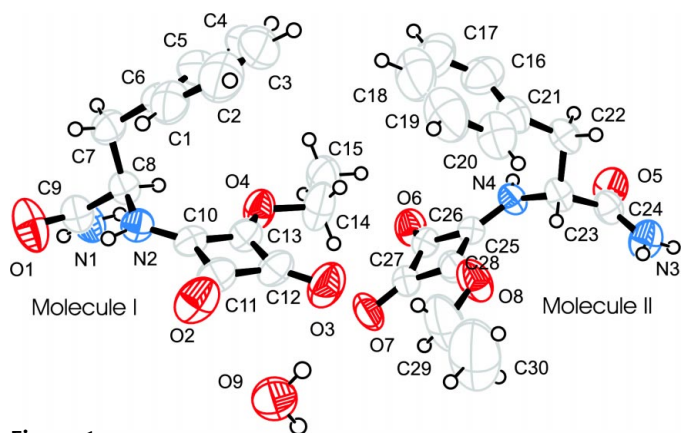
Figure 1
The asymmetric unit of the title compound, with the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

to obtain a single-crystal suitable for X-ray analysis are in progress.

In the present paper, we describe the synthesis and crystal structure of (L)-2-[(2-ethoxy-3,4-dioxocyclobut-1-en-1-yl)-amino]-3-phenylpropaneamide hemihydrate. This organic molecule is optically active and possesses considerable conformational flexibility. This is probably the reason why there are two conformationally inequivalent organic molecules in the asymmetric unit (Fig. 1), which differ in their torsion angles and in the relative positions of the phenyl and squarate moieties. The principal torsion angles describing the conformation of molecule I are C5—C6—C7—C8 = 88.4 (5)°, C6—C7—C8—N2 = 64.6 (5)° and C7—C8—N2—C10 = 105.0 (4)°. The values of the corresponding angles in molecule II are 70.0 (5)°, 54.1 (5)° and 117.8 (4)°, respectively. The dihedral angle between the phenyl and squarate moieties is 42.0 (1)° in molecule I and 62.3 (2)° in molecule II. The amide groups form various hydrogen bonds. The two organic molecules and a water molecule are linked along the *a* axis by hydrogen bonds of the type N1—H1B···O9—HW2···O6—C—C—O7···H1A—N1, building polymeric zigzag chains (Fig. 2 and Table 1). The chains are connected along the *c* axis by hydrogen bonds, forming complex rings of the type N3—H3B···O3—C—C—O2···H3A—N3. The shortest hydrogen bond is that between the water molecule and the amide O atom of molecule I. The presence of a range of hydrogen-bond lengths is shown by the IR spectrum measured from a KBr pellet. The band at 3184 cm^{-1} is assigned to the shortest bond, O9—HW1···O1. The broad band between 3340 and 3370 cm^{-1} can be attributed to the bonds in which the donor–acceptor distance varies in the range 2.82–2.89 Å. There is a shoulder at about 3470 cm^{-1} that corresponds to the longest hydrogen bonds, N3—H3A···O2 and N1—H1A···O7. This transparent crystalline material could be a representative of a new series of prospective crystalline materials suitable for second-order non-linear optical applications in conventional diode lasers. In contrast to the known ionic non-centrosymmetric materials (Anwar *et al.*, 2000), this compound has the technical advantage of its water insolubility, high melting point and high degree of crystallinity.
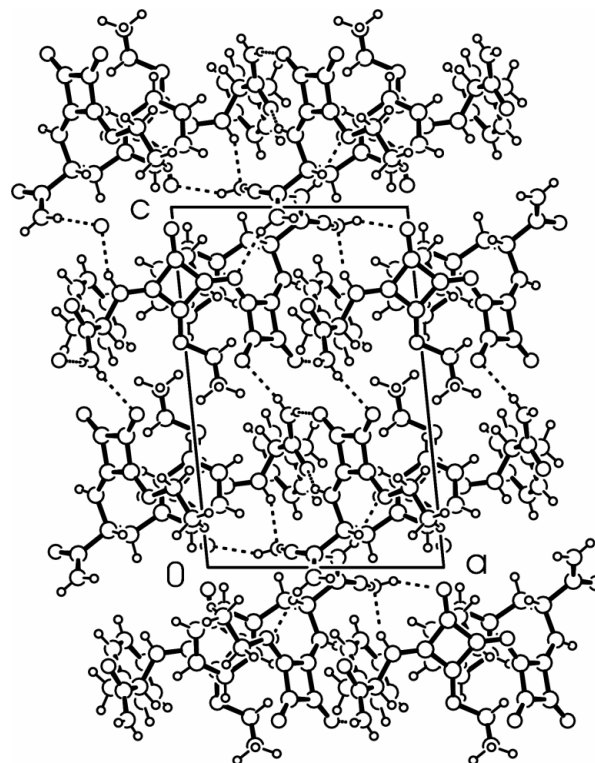

Figure 2
Projection of the structure along the *b* axis. Dashed lines denote hydrogen bonds.

Experimental

The title compound was prepared in a similar fashion to the general procedure reported by Tietze *et al.* (1991). L-Phenylalaninamide (1.53 g, 10 mmol) and diethyl squarate (1.70 g., 10 mmol) were dissolved in ethanol (95%, 45 ml). The reaction mixture was stirred at room temperature until the reaction was complete (24 h), as monitored by thin-layer chromatography. The solvent (20 ml) was removed by evaporation under vacuum, and the product began to crystallize after 2 d. The precipitate was separated by filtration and recrystallized from methanol. The purity of the compound was confirmed by elemental analysis, IR, UV–vis and mass spectrometry. Prismatic colorless single crystals suitable for X-ray analysis were grown from methanol by slow evaporation at room temperature over a period of several weeks.

Crystal data

$C_{15}H_{16}N_2O_4 \cdot 0.5H_2O$	$D_x = 1.247$ Mg m^{-3}
$M_r = 297.3$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 22
$a = 9.244$ (3) Å	reflections
$b = 12.115$ (3) Å	$\theta = 18.0$–$19.1°$
$c = 14.2116$ (19) Å	$\mu = 0.09$ mm^{-1}
$\beta = 95.78$ (2)°	$T = 293$ (2) K
$V = 1583.4$ (7) Å^3	Prism, colorless
$Z = 4$	$0.26 \times 0.26 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 26.0°$
diffractometer	$h = 0 \rightarrow 11$
Non-profiled $\omega/2\theta$ scans	$k = -14 \rightarrow 14$
6597 measured reflections	$l = -17 \rightarrow 17$
3261 independent reflections	3 standard reflections
1854 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.047$	intensity decay: 8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0843P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.0866P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} < 0.001$
3261 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
396 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···O7^i	0.86	2.10	2.922 (5)	160
N1—H1B···O9	0.86	2.05	2.894 (5)	169
N2—H2A···O5^{ii}	0.86	2.10	2.821 (4)	141
N3—H3A···O2^{iii}	0.86	2.17	3.026 (5)	170
N3—H3B···O3^{iv}	0.86	2.10	2.930 (5)	162
N4—H4A···O9^v	0.86	2.05	2.860 (4)	155
O9—HW1···O1^{vi}	0.91 (8)	1.78 (8)	2.698 (6)	177 (6)
O9—HW2···O6^{vii}	0.89 (6)	2.06 (6)	2.869 (6)	149 (5)

Symmetry codes: (i) $1-x, \frac{1}{2}+y, 2-z$; (ii) $1+x, 1+y, z$; (iii) $x-1, y-1, z$; (iv) $-x, y-\frac{1}{2}, 1-z$; (v) $-x, y-\frac{1}{2}, 2-z$; (vi) $1-x, y-\frac{1}{2}, 2-z$; (vii) $-x, \frac{1}{2}+y, 2-z$.

The data set contained no Friedel pairs. In the absence of significant anomalous scattering, the absolute configuration was indeterminate from X-ray diffraction and was assumed from the synthesis. Large displacement parameters for atom C30 indicate possible disorder, but this could not be resolved. H atoms bonded to O atoms were located in a difference map and refined freely [O—H = 0.90 (7) and 0.91 (7) Å]. Other H atoms were positioned geometrically (C—H = 0.93–0.98 Å and N—H = 0.86 Å) and refined as riding, with U_{iso}(H) = $1.2U_{eq}$(carrier atom).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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