

Crystal structure of the nonlinear optical compound L-arginine fluoride

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L-arginine fluoride is a promising compound that exhibits nonlinear optical properties. It efficiently converts two single photons of the same polarization and frequency ω to one photon of frequency 2ω (type I phase matching). $C_6H_{15}N_4O_2^+ F^-$ is monoclinic, space group $P2_1$, $a = 5.4475(4)$ Å, $b = 8.5133(6)$ Å, $c = 10.2195(7)$ Å, $\beta = 93.475(6)^\circ$. The cation has a zwitterionic form, protonated at both the guanidyl and amino groups. The arginine C γ atom is in a *trans* position to the carboxyl group. A complex three-dimensional hydrogen bond network links the anions and cations together.

KEY WORDS: L-arginine fluoride; second harmonic generator; X-ray structure.

Introduction

Lasers are increasingly used for high-speed recording and storage and for information transmission and processing. Many electrooptical devices rely on the use of nonlinear materials in particular those with the capability of frequency conversion (Second Harmonic Generation—SHG). L-arginine phosphate monohydrate (known as LAP) is a relatively new, efficient nonlinear optical material used principally in SHG applications at the UV region.¹ It combines a large nonlinear optical coefficient, wide transparency range, and chemical inertness.

The synthesis and optical properties of L-arginine fluoride have been first reported by Monaco *et al.*² on a systematic study of a series of 11 L-arginine salts with the aim of finding new compounds with strong nonlinear optical properties, similar to L-arginine phosphate. L-arginine fluoride turned out to be the most promising of the series, with a generated second-order intensity measured on a polycrystalline sample at 1064 nm about six times that of a

quartz standard. Also, measurements of the phase-matching loci on a single crystal have shown that L-arginine fluoride has a very strong type I position, which is angularly insensitive relative to L-arginine phosphate. This property may be exploited for third harmonic generation in certain cascade schemes. In addition, L-arginine fluoride is noncritically phase matched near 950 nm, which might be valuable foreseeing applications requiring blue–green light. Moreover, the free fluoride anion is a very strong Lewis base and is of significant interest in inorganic and organic synthesis. Organic fluoride salts are efficient auxiliary bases and indispensable reagents in organosilicon chemistry.³ L-arginine fluoride is a candidate for a stable, easily accessible “naked” fluoride ion source. Despite these interesting properties, the structural data available for this compound is rather scarce. Monaco *et al.* reported the cell parameters and space group ($P2_1$) but not the crystal structure which we report in this work.

Experimental

L-arginine fluoride was obtained in an attempt to synthesize L-arginine dysprosium fluoride. Dysprosium metal was dissolved in fluoric acid and then added to a water solution of L-arginine in a 1:3 molar

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Table 1. Summary of Crystal Data, Data Collection, and Structure Refinement

Compound	C ₆ H ₁₅ N ₄ O ₂ ⁺ F ⁻
CCDC no.	CCDC-1003/5893
Color/shape	White prism
Crystal dimensions, mm	0.37 × 0.30 × 0.30
Formula weight, g mol ⁻¹	194.22
Temperature, K	293(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 5.4475(4) Å <i>b</i> = 8.5133(6) Å <i>c</i> = 10.2195(7) Å <i>β</i> = 93.475(6)°
Cell volume, Å ³	473.07(6)
<i>Z</i>	2
Density (calculated) g/cm ³	1.363
μ(Mo K _α), mm ⁻¹	0.116
Diffractometer/scan mode	Enraf-Nonius CAD4/ω-2θ
θ range for data collection	3.12° < θ < 28.97°
Range of <i>h</i> , <i>k</i> , <i>l</i>	-5 ≤ <i>h</i> ≤ 7, 0 ≤ <i>k</i> ≤ 11, -13 ≤ <i>l</i> ≤ 13
Decay of standards	<1%
Reflections measured	1472
Independent/observed reflections	1238/1113
Structure solution	SHELXS97
Structure refinement	SHELXL97
No. of refined parameters	163
Goodness of fit on <i>F</i> ²	1.095
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0383, <i>wR</i> 2 = 0.0747
Largest peak and hole (e ⁻ Å ⁻³)	-0.17, 0.29

proportion. After several weeks an inhomogeneous solid was formed and some small white single crystals could be found.

Intensity data were collected at room temperature on a CAD4 automated 4-circle diffractometer using graphite monochromatized Mo K_α radiation. The cell parameters were determined from a least-squares refinement of 25 strong and well-centered reflections in the θ range 7.63–14.0°. The structure was solved by direct methods using SHELXS97.⁴ The structure refinement was performed with SHELXL97,⁵ and PLATON⁶ was used for generating the structure plots and further analysis. The coordinates of all hydrogen atoms were freely refined. Their isotropic temperature factor were constrained to that of the parent atom. A multiplicative factor of 1.5 was used for the NH₃ group whereas for all other hydrogen atoms a multiplicative factor of 1.2 was used. Crystal data and conditions of data collection and refinement are reported in Table 1.

Results and discussion

Atomic positions of the nonhydrogen atoms and equivalent isotropic displacement parameters are

given in Table 2. Selected bond lengths and angles are summarized in Table 3.

The cation exists as a positively charged zwitterion in which the guanidyl and amino groups are protonated (see Fig. 1). Inspection of the C–O distances in the carboxyl group [1.243(2) Å–1.248(2) Å] show that these are deprotonated.

Table 2. Final Coordinates and Equivalent^a Isotropic Displacement Parameters of the Nonhydrogen Atoms

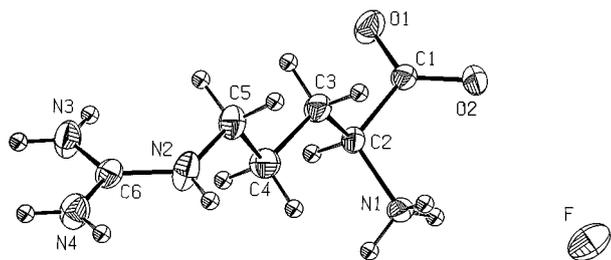
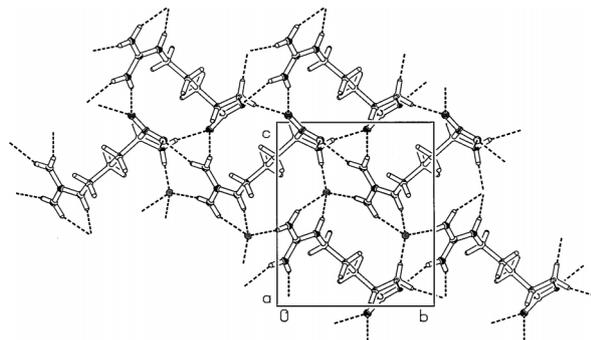
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.2592(2)	0.07394(18)	1.03911(14)	0.0359(3)
O2	0.2495(2)	0.27671(18)	0.90223(15)	0.0345(3)
N1	-0.2428(3)	0.26603(18)	0.86038(14)	0.0223(3)
N2	-0.5828(3)	-0.2505(2)	0.60762(16)	0.0326(4)
N3	-0.6511(3)	-0.4511(2)	0.75463(17)	0.0351(4)
N4	-0.8942(3)	-0.4249(2)	0.56383(18)	0.0341(4)
C1	0.1542(3)	0.1628(2)	0.95697(16)	0.0220(3)
C2	-0.1155(3)	0.1245(2)	0.91643(15)	0.0208(3)
C3	-0.1212(3)	-0.0080(2)	0.81598(18)	0.0258(3)
C4	-0.3767(3)	-0.0617(2)	0.7662(2)	0.0295(4)
C5	-0.3523(4)	-0.1970(2)	0.67104(19)	0.0302(4)
C6	-0.7081(3)	-0.3763(2)	0.64283(17)	0.0252(3)
F	0.1493(3)	0.81700(17)	0.38139(12)	0.0437(3)

^a*U*_{eq} = 1/3 of the trace of the orthogonalized *U* tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Bond distances	
O1—C1	1.243(2)
O2—C1	1.248(2)
N1—C2	1.487(2)
N2—C5	1.451(3)
N2—C6	1.332(2)
N3—C6	1.328(2)
N4—C6	1.323(2)
C1—C2	1.537(2)
C2—C3	1.524(2)
C3—C4	1.523(2)
C4—C5	1.519(3)
Bond angles	
C5—N2—C6	125.15(16)
N2—C5—C4	114.64(16)
N3—C6—N4	120.37(19)
N2—C6—N3	121.42(17)
N2—C6—N4	118.20(18)
O2—C1—C2	117.44(15)
O1—C1—O2	126.07(16)
O1—C1—C2	116.46(15)
N1—C2—C1	110.35(13)
N1—C2—C3	110.48(13)

The side chain of arginine can assume many different conformations on account of its length and flexibility. The conformation of the aminoacid cation is best described by the torsion angles according to the rules of IUPAC-IUB (1970):⁷ ϕ^1 (O1—C1—C2—N1) 158.81(15)°, ϕ^2 (O2—C1—C2—N1) -23.2(2)°, χ^1 (N1—C2—C3—C4) -59.40(19)°, χ^2 (C2—C3—C4—C5) -178.08(16)°, χ^3 (C3—C4—C5—N2) -174.96(16)°, χ^4 (C4—C5—N2—C6) -100.2(2)°, χ^{51} (C5—N2—C6—N3) 11.1(3)°, χ^{52} (C5—N2—C6—N4) -169.55(19)°. The C4 atom is in a staggered *trans* position relative to the carboxyl group, as in L-arginine dihydrate.⁸ This situation differs from that found in L-arginine phosphate where this γ -carbon atom is at the *trans* position to the amino group.^{9,10} In the closely related compound,


Fig. 1. ORTEP plot of the title compound showing the displacement ellipsoids (drawn at the 50% level) and the labelling scheme.

Fig. 2. Projection of the crystal structure along the *a* axis showing the hydrogen bond network. F⁻ ions are shown as gray and the oxygen atoms are shown as black balls.

L-arginine fluoride hydrogenfluoride¹¹ there are two independent arginine anions with such conformations that the γ -carbon is in a *gauche* position to both the amino and carboxyl groups in one ion and at the *trans* position to the amino group in the other. It should be noted that because none of the atoms is a sufficiently strong anomalous scatterer at the Mo K α wavelength, the absolute configuration of the arginine cation could not be determined from the X-ray data but the correct enantiomorph was chosen so that the chiral carbon C $^{\alpha}$ has the well known *S* conformation of L-arginine.

Each fluorine ion is an acceptor of four hydrogen bonds from three neighbouring cations with N \cdots F distances in the range 2.5895(19)–2.797(2) Å (see Fig. 2). Thus, saturation for H-bonding capability of the anion is achieved in this structure. The strongest H-bond is that involving the amino group, which is an almost linear bond with an N—H \cdots F angle of 179(2)°. The remaining, weaker, N \cdots F bonds are directed toward the guanidyl groups. The O atoms of the carboxylate group are acceptors of two protons each, one

Table 4. Hydrogen Bond Distances (Å, deg)^a

	Atoms	D—H	H \cdots A	D—H \cdots A	Angle
<i>a</i>	N1—H1A \cdots F*	0.88(3)	1.71(3)	2.5895(19)	179(2)
<i>b</i>	N1—H1B \cdots O1**	0.89(3)	2.00(3)	2.819(2)	151(2)
<i>c</i>	N1—H1C \cdots O2***	0.85(2)	1.99(2)	2.8252(19)	168(3)
<i>d</i>	N2—H2 \cdots F****	0.88(2)	1.89(3)	2.720(2)	156(2)
<i>e</i>	N3—H3A \cdots O2****	0.91(3)	2.03(4)	2.835(2)	147(2)
<i>f</i>	N3—H3B \cdots O1*****	0.85(3)	2.09(3)	2.916(2)	163(3)
<i>g</i>	N4—H4A \cdots F*****	0.83(3)	1.86(3)	2.677(2)	167(3)
<i>h</i>	N4—H4B \cdots F*****	0.89(3)	2.01(3)	2.797(2)	147(2)

^a Symmetry code: *—*x*, -1/2 + *y*, 1 - *z*; **—*x*, 1/2 + *y*, 2 - *z*; ***—1 + *x*, *y*, *z*; ****—1 + *x*, -1 + *y*, *z*; *****—*x*, -1/2 + *y*, 2 - *z*; *****—1 - *x*, -3/2 + *y*, 1 - *z*.

Table 5. Basic First- and Second-Level Graph-Set Descriptors Involving Hydrogen Bonds which are Designated *a–h* following Table 4

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>
<i>a</i>	D	D ₂ ² (5)	D ₂ ² (5)	C ₂ ¹ (9)	D ₂ ² (12)	D ₂ ² (12)	C ₂ ¹ (11)	C ₂ ¹ (11)
<i>b</i>		C(5)	C ₂ ² (11)	D ₂ ² (10)	C ₂ ² (15)	R ₂ ² (15)	D ₂ ² (12)	D ₂ ² (12)
<i>c</i>			C(5)	D ₂ ² (10)	C ₂ ² (15)	C ₂ ² (10)	D ₂ ² (12)	D ₂ ² (12)
<i>d</i>				D	D ₂ ² (7)	D ₂ ² (7)	C ₂ ¹ (6)	R ₂ ¹ (6)
<i>e</i>					C(10)	C ₂ ² (6)	D ₂ ² (7)	D ₂ ² (7)
<i>f</i>						C(10)	D ₂ ² (7)	D ₂ ² (7)
<i>g</i>							D	C ₂ ¹ (4)
<i>h</i>								D

donated by a guanidyl, the other by the amino group of neighbour molecules (Table 4).

In L-arginine dihydrate,⁸ there are two amino hydrogens not involved in hydrogen bonding, but in L-arginine fluoride all H atoms of both the amino and guanidyl groups participate in intermolecular hydrogen bonds, and as a result the H-bond network is quite complex.

In L-arginine fluoride, N–H...F distances are somewhat shorter than in L-arginine fluoride hydrogenfluoride¹¹ where they range from 2.652(3) to 2.897(3) Å. The results of hydrogen-bond graph-set analysis¹² are given in Table 5 for the basic first- and second-level graph sets. Each hydrogen-bond was labelled according to Table 4. The large number of finite graphs in Table 5 is because of the substantial involvement of the F⁻ ion in the hydrogen bonding. Among the second-level graphs, the R₂²(15) and R₂¹(6) ring patterns are the most apparent in the packing diagram together with fourth-level *adgh*-R₄²(13) and *abfg*-R₄²(10) pattern.

Inspection of the structure with PLATON showed that there are no residual voids accessible to solvent molecules.

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